Per Enghag

WILEY-VCH

Encyclopedia of the Elements

Technical Data • History • Processing • Applications

P. Enghag

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Technical Data · History · Processing · Applications

Title Picture: Sulfur crystals, photograph by Svend V. Sölver

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Foreword

The publication of Per Enghag's book *Encyclopedia of the Elements* is a project that the Swedish National Committee has decided to support because the book and its message is important for teachers and pupils in senior high schools and also for students and scientists at the universities.

Apart from its considerable scientific and technical value to researchers and professionals in industry, the book is a well-written encyclopedia about the elements, their occurrence and use by mankind. The book is an exciting and also humorous general view of the element discoveries. It lets us meet the discoverers to see how they worked, thought and believed.

History of science deals with people and how they act towards scientific facts. One cannot enough emphasize the importance of this type of history to create interest for and understanding of scientific models and ideas. This book is a good example.

June 2004, Gothenburg

Bengt Nordén
Chairman of the Nobel Committee for Chemistry
of the Royal Swedish Academy of Sciences

Encyclopedia of the Elements. Per Enghag

ISBN 3-527-30666-8

Table of Contents

Encyclopedia of the Elements. Per Enghag

ISBN 3-527-30666-8

7 Copper *139*

8 Iron *167*

Preface

This book was originally written as a trilogy in Swedish with the title *"The Elements on Earth and their Discovery"*. It was aimed to describe the history of the element discoveries but also the elements origin in the earth crust and their manufacturing as well as their properties and use in modern technology. The trilogy was published by *Industrilitteratur* in Stockholm 1998–2000 and was very well accepted. The books seemed to be suited for all interested in science and modern technology as well as for those interested in history of science. A periodical for teachers in natural sciences characterized the trilogy as a *"gold mine to dig in for all teachers in science but also for teachers in sociology and history"*.

In English the book is more than a translation of the Swedish trilogy. It contains indeed the same moments of discovery history, element occurrence, winning and manufacturing, as well as element properties and use. The environmental viewpoints have however been given more space. This book, unlike the Swedish original, also deals with the transuranium elements. Another difference is that the fact tables at the beginning of every element chapter have been considerably extended to provide encyclopedic character. The structure of the book is presented in Chapter 1, *Introduction*, where general information about the different literature sources is also given.

From the very beginning of the work with this book project, the *Swedish National Committee for Chemistry* supported it, for which I thank especially its chairman at that time, Professor Bengt Nordén. Many thanks are also due to Svend V. Sölver, former lecturer at the Swedish School of Mining and Metallurgy and to Dr. Sven Arvidsson at The Geological Survey of Sweden. They have commented on the manuscript, critically and amicably, and they have given much of mineralogical and geological information of value for the book. Svend V. Sölver has also provided all the mineral photos. Cordial thanks are also directed to Professor Stig Rundqvist of Uppsala University, Sweden, and Professor Fathi Habashi of Laval University, Canada, who have both shown great interest and support for the project. Stig Rundqvist also read the Swedish manuscript and discussed selected parts of it. I am also grateful to Dr. Björn Arén at Örebro University, who read and commented parts of the first manuscript in English.

The Swedish National Committee for Chemistry, the Knutsberg Foundation, Uppsala, and the Carl Trygger Foundation, Stockholm, have given economic support.

Encyclopedia of the Elements. Per Enghag

ISBN 3-527-30666-8

Their contributions and confidence made this book project possible. I warmly thank the Committee and the Foundations.

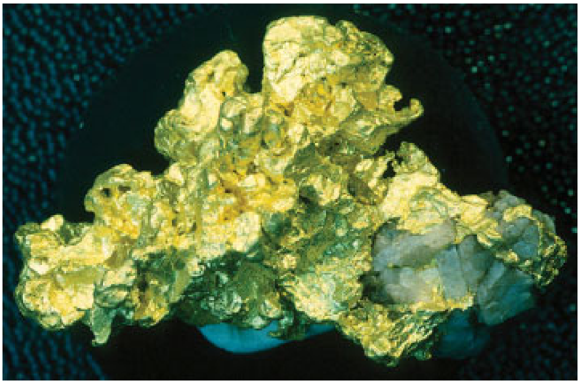
It is the author's expectation that professional chemists, physicists, mineralogists, and metallurgists as well as students on different levels will find the history of the elements, their discovery and properties interesting and exciting. Also that the fact tables at the beginning of every element chapter shall be useful both in industrial and academic research and education. I dare also believe that this book shall be a bridge-builder over the gap between science and technology on one side and culture and humanistic topics on the other side. To persuade technicians and scientists to be interested in cultural and historical questions and – on the other hand – make humanists interested in science as culture and of modern technical applications.

Örebro, June 2004 *Per Enghag*

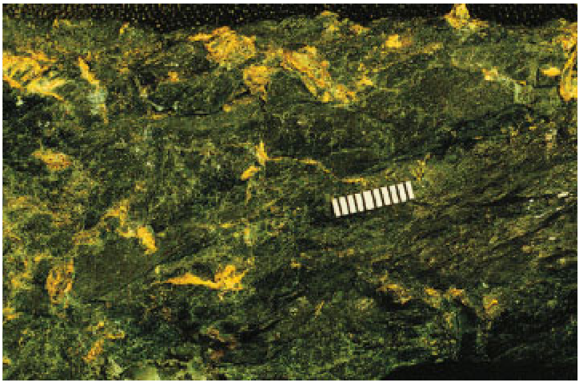
Color Plates

Encyclopedia of the Elements. Per Enghag

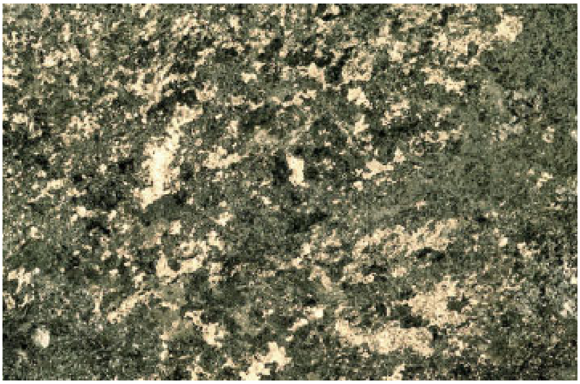
ISBN 3-527-30666-8



M1 Gold Au, aggregate of fine cubic crystals from Ditz Mine, Mariposa County, California, U.S.A.



M2 Gold Au on mylonitic rock, from ETC's gold mine Sheba, Barberton, South Africa. From the collection of Rob H. Hellingwerf.

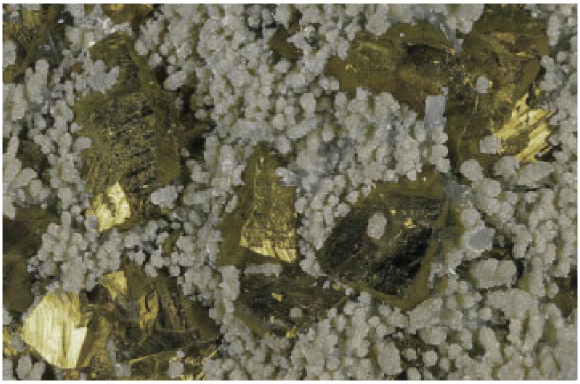


M3 Gold-silver alloy, electrum Au-Ag from the copper mine in Falun. The sample is from the 350 m level.

M4 Silver Ag from North Ltd, Zinkgruvan Mine in central Sweden. The silver has been precipitated on a fracture in a working stope on the 190 m level.

M5 Malachite and azurite. Monoclinic crystals of blue azurite $Cu_3(OH)_2(CO_3)_2$ on green malachite $Cu_2(OH)_2CO_3$. From Bogoslovsk in the Ural Mountains, Russia.

M6 Chalcopyrite $CuFeS_2$. Yellow tetragonal crystals of chalcopyrite between smaller, white crystals of quartz, overgrown with barite (heavy spar, barium sulfate $BaSO_4$). From the mine Baia Mare in Romania.

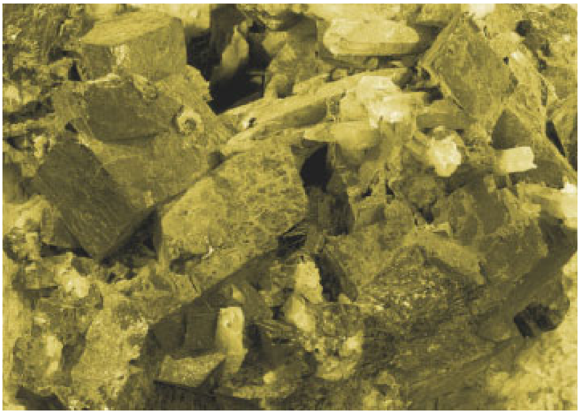


M7 Meteorite iron with Widmanstätten structure, found in Xiquipilco, the Toluca region in Mexico.

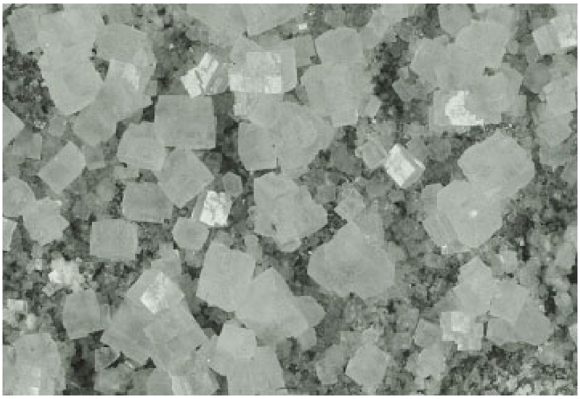
M8 Lake and bog iron ore, mainly consisting of limonite, hydrous iron oxide, FeOOH with varying quantities of water. 1, 2.and 4: Pearl, powder and penny ore from lake bottoms in Småland and Värmland, Sweden; 3: Bog ore from Långban, Sweden .

M9 Magnetite Fe_3O_4 or rather, to separate divalent from trivalent iron, ($FeO \cdot Fe_2O_3$). Octahedral crystals from Norberg in central Sweden.

M10 Hematite, Fe_2O_3, trigonal crystals, black with a blood-red color when crushed to powder (Greek aimatites, blood stone). From the island of Elba, Italy. Collection of Stig Adolfsson.

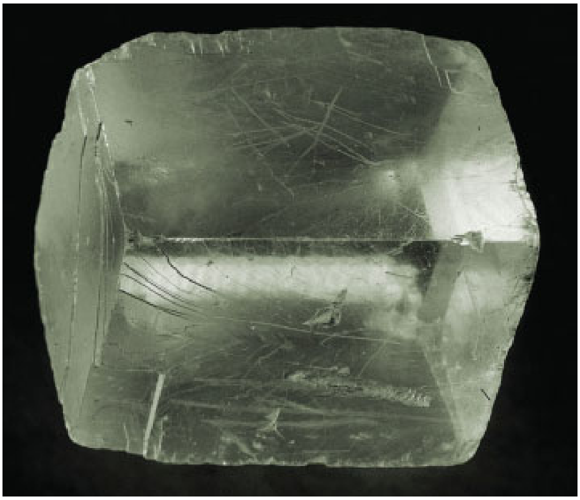


M11 Siderite $FeCO_3$, trigonal (hexagonal rhomboedric) brown crystals and quartz crystals. Named after the Greek word sideros for iron. From the Ivigtut cryolite mine in Greenland.

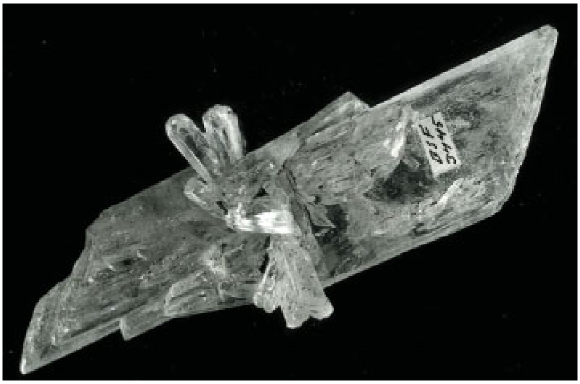


M12 Halite, rock salt NaCl. Cubic crystals from the salt mine in Wieliczka, about 1000 years of age, in southern Poland.

M13 Lepidolite, petalite, pollucite, rubidium microcline. Lithium, cesium, and rubidium containing minerals from Varuträsk in Northern Sweden. Uppermost left: Violet lepidolite. Uppermost right: Petalite. At the bottom left: Pollucite. At the bottom right: Feldspar, containing rubidium.

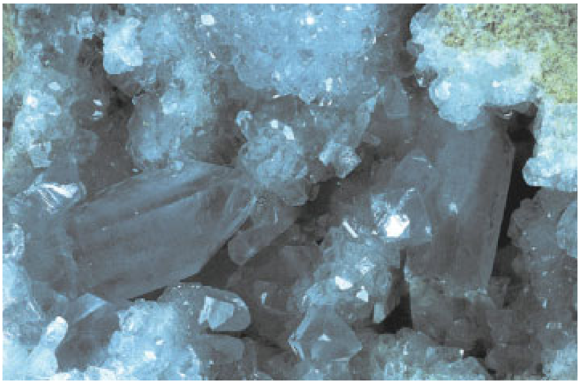


M14 Calcite $CaCO_3$, trigonal (hexagonal rhomboedric) cleavage piece from Eskifjördr in Seydisfjördr, Iceland.



M15 Gypsum $CaSO_4 \cdot 2H_2O$. Monoclinic crystals from Neuenhain in Hessen, Germany.

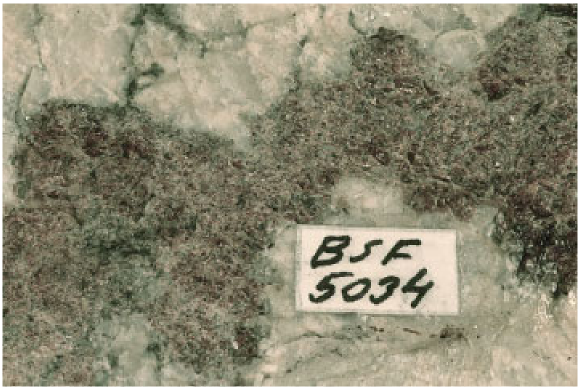
M16 **Beryl** $Al_2Be_3Si_6O_{18}$ from North Carolina in USA (to the left). **Emerald**, which is beryl, green colored by chromium (to the right). The hexagonal form is clearly visible. From Takowaja in the Urals.



M17 **Celestite** (**celestine**) $SrSO_4$. Sky-blue, orthorhombic crystals from Madagascar.

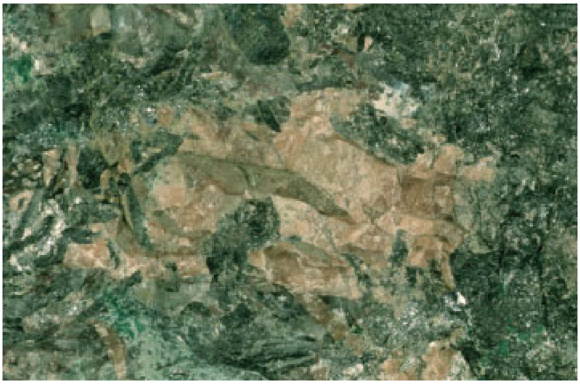
M18 **Gadolinite** $Y_2FeBe_2(O \cdot SiO_4)_2$. Lustrous, black monoclinic crystals in pegmatite from Ytterby, Sweden.

M19 Fergusonite (Y,Er,Ce,Fe)(Nb,Ta,Ti)O_4. Tetragonal crystals in pegmatite from Ytterby, Sweden.



M20 Xenotime YPO_4 from Ytterby, Sweden. Tetragonal. Reddish-brown vein in pegmatite.

M21 Thalenite $Y_2Si_2O_7$. Red monoclinic crystals from a closed down quartz quarry at lake Yngen in Central Sweden.



M22 Bastnaesite $CeFCO_3$ from the Bastnaes field at Riddarhyttan in central Sweden. Brownish-yellow crystals in dark allanite (orthite). From the collections of the Swedish Museum of Natural History.

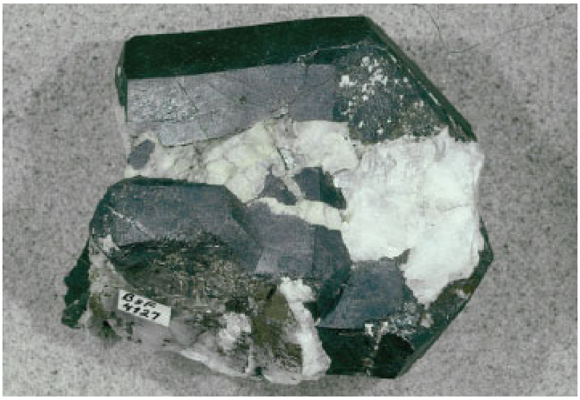
M23 Cerite $(Ca,Mg)_2Ce{+}RE)_8(SiO_4)_7 \cdot 3H_2O$ from Bastnaes at Riddarhyttan. Pale, grayish-brown mineral in dark allanite (orthite). From the collections of the Swedish Museum of Natural History.

M24 Thorite $ThSiO_4$ from Evje in Norway. Tetragonal crystals, partially destroyed by radioactive decay.

M25 Monazite
$(Ce,La,Nd,Th)(PO_4)$, a monoclinic crystal, sole as the name says, from the abandoned quartz quarry in Ytterlida near Svenljunga, central Sweden. From the collection of Bengt Bengtsson.

M26 Kolbeckite
$ScPO_4 \cdot 2H_2O$ on trachyandesite. From Klausen at Gleichenberg, Steiermark in Austria.

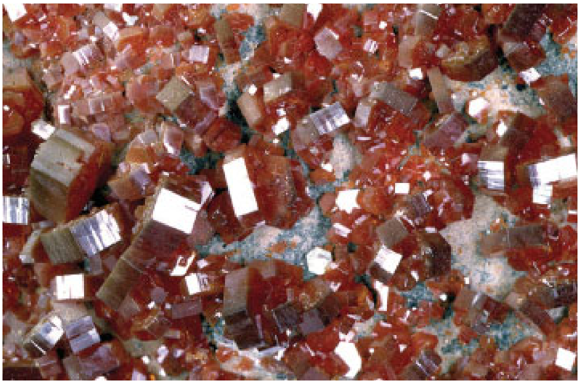
M27 Grossular
$Ca_3(Al,Fe)_2(SiO_4)_3$ from Nordmark, Filipstad in central Sweden. Special garnets containing yttrium (and neodymium) are important laser materials.



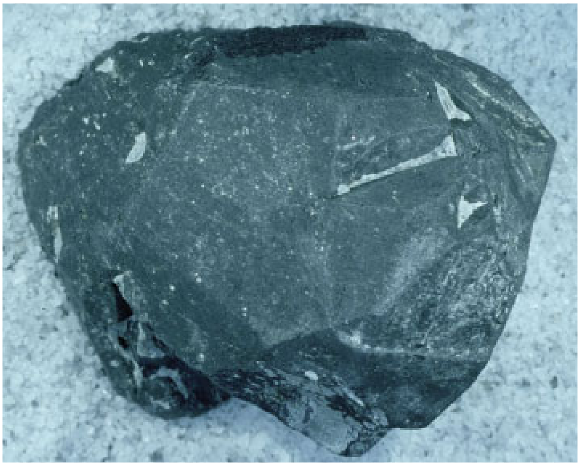
M28 Rutile TiO_2, tetragonal crystals in quartz. From Graves Mountain, Georgia, USA.

M29 Ilmenite $FeTiO_3$. Black trigonal-rhombohedral crystals in pegmatite. From the mine Hultsgruvan in Glava, Värmland, Sweden. Collected by Per H. Lundegårdh.

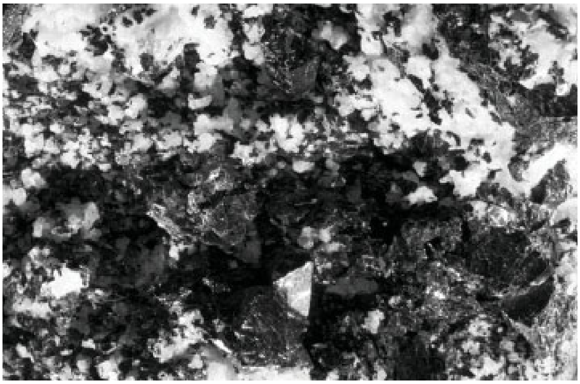
M30 Zircon $ZrSiO_4$, tetragonal crystals. From Brevik in Norway. The prismatic form is visible in combination with the pyramid.



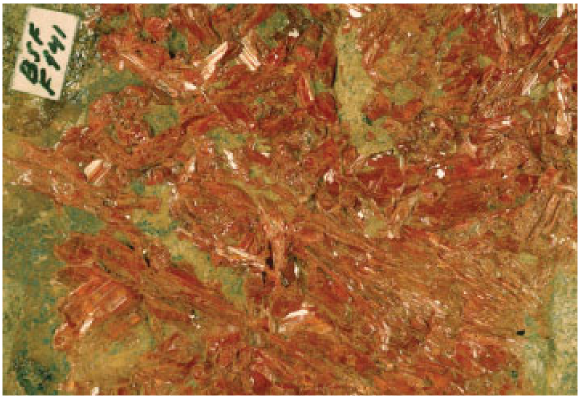
M31 Vanadinite
$Pb_5(VO_4)_3Cl$, aggregate of hexagonal prismatic crystals from Mibladen in Morocco.



M32 Columbite
$(Fe,Mn)(Nb,Ta)_2O_6$, orthorhombic crystal from Katiala in Finland. From the collection of Roland Eriksson.

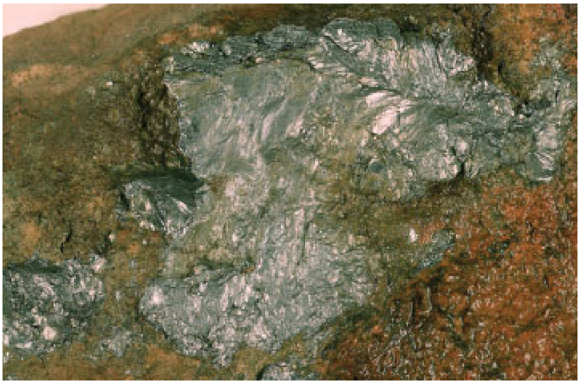


M33 Pyrochlore
$(Na,Ca)_2(Nb,Ti,Ta)_2O_6(OH,F,O)$. Aggregate of cubic octahedral crystals from Visnevye Gory, Ural, Russia. At heating the mineral glows greenish, hence its name. From the collection of Stojan Bratuz.



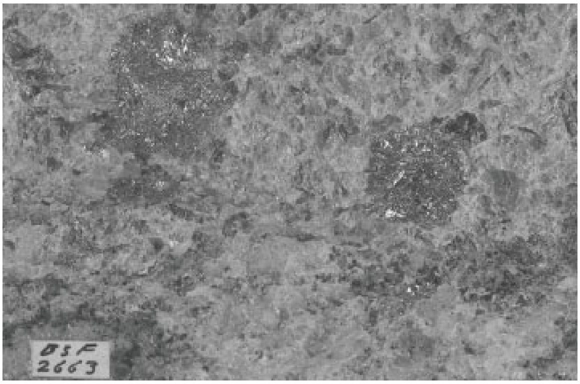
M34 Crocoite red lead ore, $PbCrO_4$ from Nertschinski in Siberia. From Funck's collection.

M35 Chromite $FeCr_2O_4$ in serpentine. This ore from Jarensk-Saranovskaja in Russia is used for ferrochromium manufacturing.



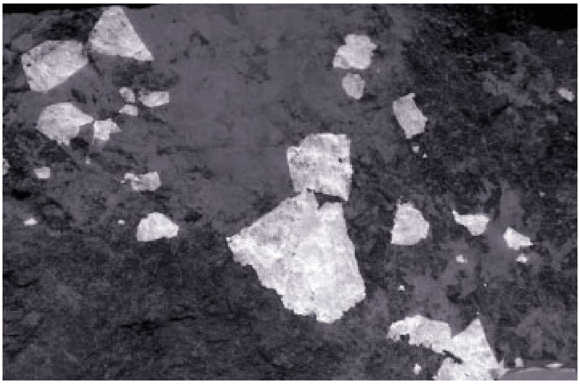
M36 Molybdenite MoS_2 on red, fine-grained granite. From Rödgruvan (the Red Mine), Bispberg in Dalecarlia, Sweden. From A. Johnson & Co's collection.

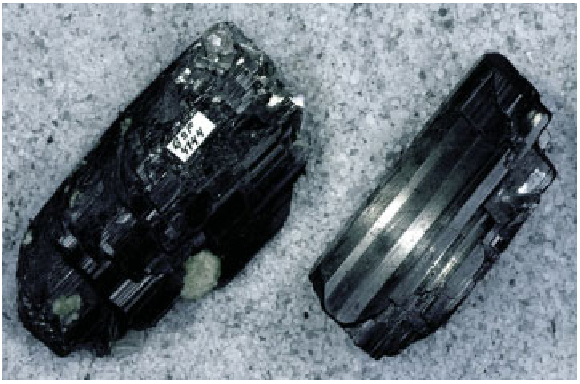
M37 Molybdenite MoS_2 in granite from A/S Knaben in Norway. It may have been an ore of this type in which Walter and Ida Noddack discovered the element rhenium.



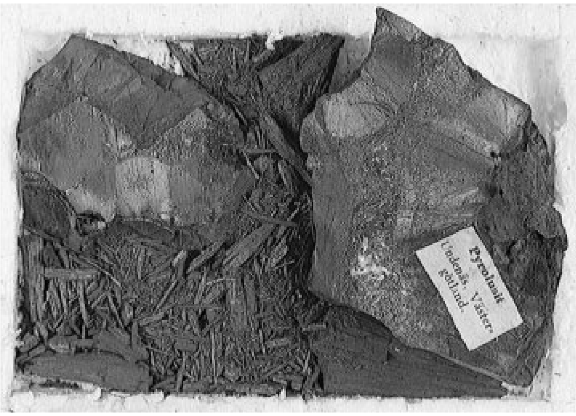
M38 Scheelite $CaWO_4$ with fluorite and hornblende. From Yxsjö Mines in Central Sweden.

M39 Scheelite $CaWO_4$ in UV-radiation. The scheelite fluoresces in the UV-light with a white color, quite different from the surrounding minerals.





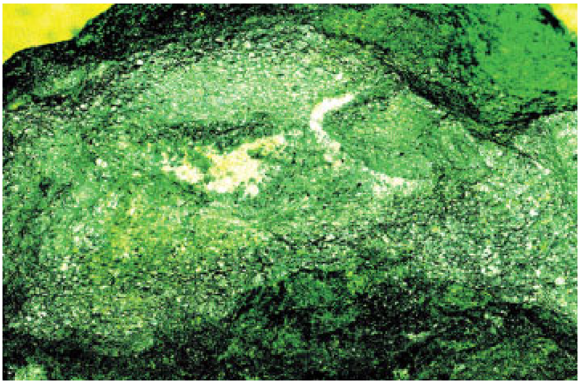
M40 Wolframite $(Fe,Mn)WO_4$, Monoclinic crystals from Mina La Panasqueira, Beira Baixa, Portugal.



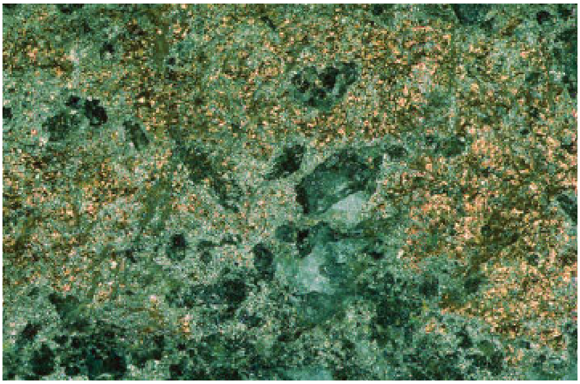
M41 Pyrolusite MnO_2 from the manganese mines in Bölet in southern Sweden. From Anton Sjögren's collection.

M42 Manganese nodules, built up of concentrically arranged layers of manganese and iron oxides. Brought up from the bottom of the ocean south-east of the Hawaiian Islands by Scripps Institute of Oceanography. The specimens given to the School of Mining and Metallurgy in Filipstad, Sweden by Professor Gustaf Arrhenius.

M43 **Cobaltite** CoAsS, crystals in pyrrhotite and chalcopyrite. The cubic crystal forms are visible. From Håkansboda copper-cobalt deposit in central Sweden.

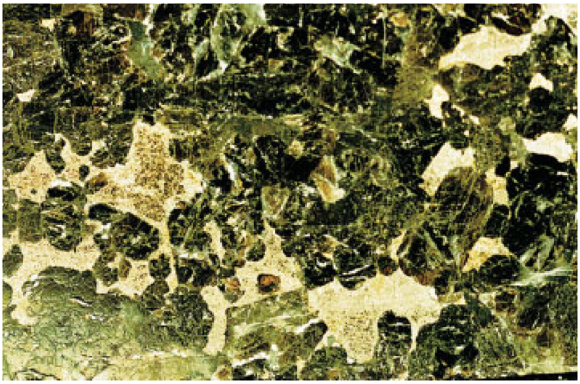


M44 **Gersdorffite** white NiAsS together with the green secondary mineral **annabergite** $Ni_3(AsO_4)_2 \cdot 8H_2O$. From Bengt Reinhold Geijer's collection, the Swedish Museum of Natural History in 1831. See further the text in chapter 31, section nickel deposits.



M45 **Nickeline**, „kupfernickel" NiAs in quartz. From Lainijaur in northern Sweden. Collected by Roland Eriksson.

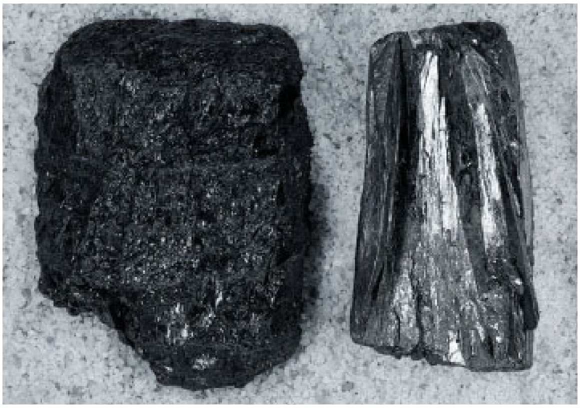
M46 Platinum Pt. Platinum Group Elements (PGE) minerals and gold Au in coarse pyroxene taken from a drill core in the Bushveld Complex in South Africa. Present from Selene Mining (PTY)LTD., procured by Peter Sölver. See further the text in the Geology section in chapter 32.



M47 Sphalerite, zinc blende, (Zn,Fe)S, cubic hextetrahedral crystals together with crystals of quartz and chalcopyrite. From Laxy, Isle of Man, Great Britain.

M48 Cinnabar HgS, trigonal crystals with a twin crystal, from Tongren and Dayan in Guizhou province in China. The name was possibly taken from an old Persian word for dragon blood.

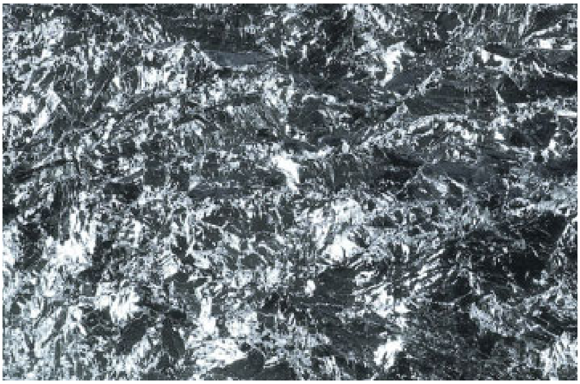
M49 **Corundum** Al_2O_3. Bottom left specimen from Madras in India with the hexagonal crystal form, typical for corundum. Besides a specimen of **ruby**, which is corundum, red colored by chromium. From Froland in Norway and Roland Eriksson's collection.



M50 **Coal and graphite** C. The coal to the left is from the Langenbrahm mine in Westfalen in Germany, the hexagonal crystallizing plate-like graphite from Sri Lanka.

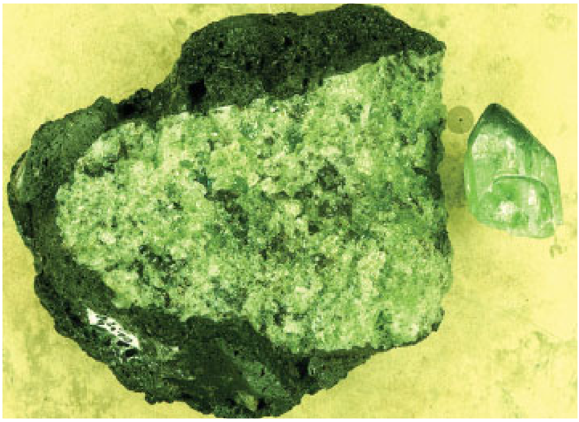
M51 **Diamond** C, four cubic crystals of 0.3 carats, surrounded by eight diamonds for industrial use in rock drill bits, rock saws, tools for abrasive machining of hard materials etc. From Hagby-Asahi AB in Nora, central Sweden.

M52 Quartz, rock crystal SiO_2 from Diamantina in the province of Minas Gerais in Brazil.

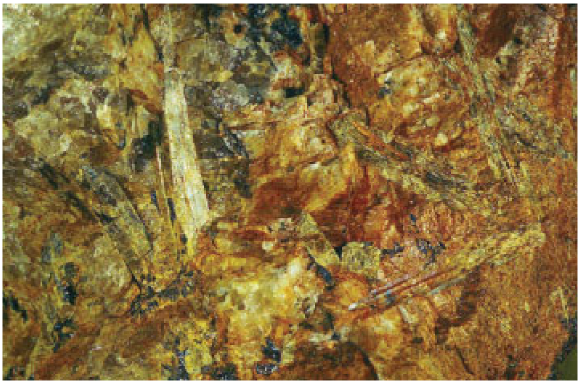


M53 Silicon metal, manufactured from pure quartz by reduction with carbon in electric arc furnace. Elkem Thamshavn Verk A/S, Orkanger, Norway.

M54 Nesosilicate Orthorhombic crystals of the nesosilicate **topaz** $Al_2F_2SiO_4$ from Brazil.

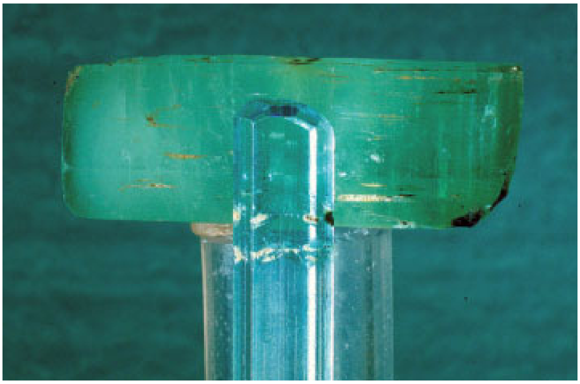


M55 Nesosilicate
Volcanic black basalt with the green nesosilicate **olivine** $(Mg,Fe)_2SiO_4$ from Lanzarote, the Canary Islands. Besides a crystal of the nesosilicate **forsterite** Mg_2SiO_4 from Pakistan.



M56 Sorosilicate, disilicate
monoclinic, prismatic crystals of the sorosilicate **thortveitite** $Sc_2Si_2O_7$ in pegmatite. From Routevaare, Jokkmokk in northern Sweden. From the collection of Fredrik Grensman.

M57 A mineral with sorosilicate character
monoclinic crystals of blackish-green **epidote**.
It is a complicated mineral with the formula $Ca_2(Fe,Al)Al_2(O,OH,SiO_4,Si_2O_7)$. It has the character of a sorosilicate. In the picture also white calcite, calcium carbonate, is shown.

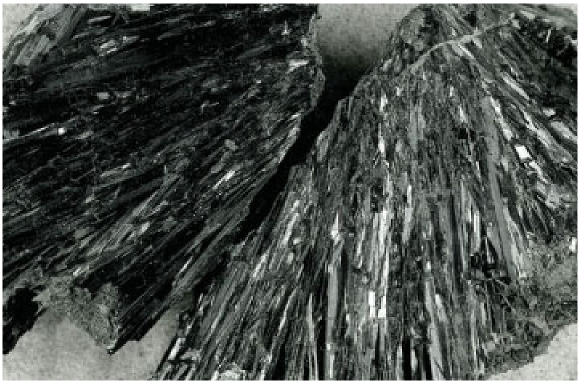


M58 Cyclosilicate with ring structure
Beryl $Al_2Be_3(Si_6O_{18})$ from Haddam, Connecticut, USA and Adunschelon in Transbaikalia, Siberia.The Swedish Museum of Natural History.

M59 Cyclosilicate with ring structure
In the **tourmaline** group of trigonal prismatic minerals the anionic group $(BO_3)Si_6O_{18}$ is coupled to varying cations: Na, Li, Ca, Mg, Fe, Mn, Al, resulting in varying colors of species with special names. From top left to bottom right: 1. Tourmaline in lepidolite from Pala in California. 2. Schorl from Yinnietharra in Western Australia. 3. Rubellite from Himalaya Mine, San Diego, in California. 4. Verdelite. 5. Two colored tormalines from Brazil. 6. Indigolite from Utö in Stockholm archipelago.

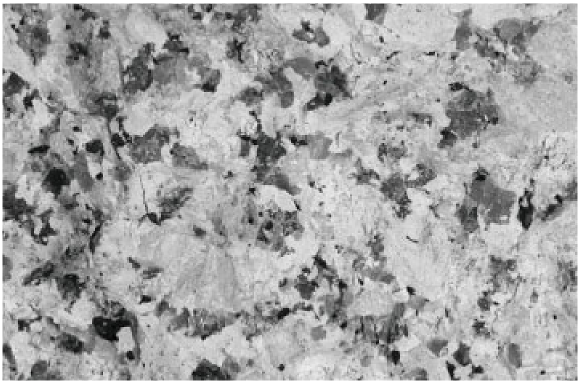
M60 Inosilicate with chain structure
Hedenbergite $CaFe(SiO_3)_2$, monoclinic black crystals, a pyroxene. From the iron ore mine in Nordmark, Filipstad in central Sweden.

M61 Inosilicate with band structure, Hornblende $NaCa_2(Mg,Fe)_4Al_3Si_6O_{22} \cdot (OH)_2$. The formula is general. In the actual specimen fluorine is also present. From the iron ore mine in Nordmark, Filipstad in central Sweden.



M62 Inosilicate with band structure
Asbestos of amphibole type, actinolite $Ca_2(Mg,Fe)_5(OH \cdot Si_4O_{11})_2$. From the iron ore mine in Nordmark, Filipstad in central Sweden.

M63 Phyllosilicate with double layers, Muscovite $KAl_2(OH,F)_2AlSi_3O_{10}$ from Shelby, Cleveland, North Carolina, USA.



M64 Phyllosilicate with double layers
At weathering of granite from Gunheath Pit in Cornwall **kaolinized granite** has been obtained, containing the sheet silicate **kaolinite** with the composition $Al_4(OH)_8Si_4O_{10}$ and quartz.

M65 Phyllosilicate with double layers, Vermiculite
$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot nH_2O$. Heating to about 300 °C causes the mineral to exfoliate and expand due to the steam formation from water between the layers. Vermiculite is used in light concrete and as insulating material.

M66 Tectosilicate Orthoclase $KAlSi_3O_8$, monoclinic prismatic twin crystals from Gängerhäusel near Karlsbad in Bohemia.

M67 Tectosilicate
Microcline $KAlSi_3O_8$. Four crystals of which two are green, a distinctive feature of **amazonite**, a variety of microcline.

M68 Germanite
$Cu_{13}Fe_2Ge_2S_{16}$, cubic, with gallite $CuGaS_2$, tetragonal. A massive aggregate from the Tsumeb Mine in Namibia.

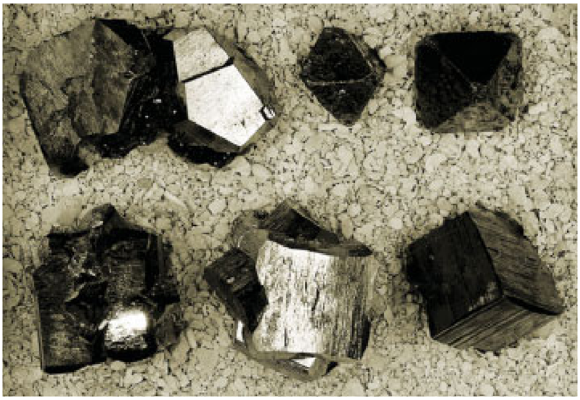
M69 Cassiterite SnO_2. Tetragonal crystals and quartz. From Schlaggenwald in Bohemia, the Czech Republic.

M70 Galena, lead glance PbS, cubic crystals. From Continental Mine, Picher, in Oklahoma, USA.

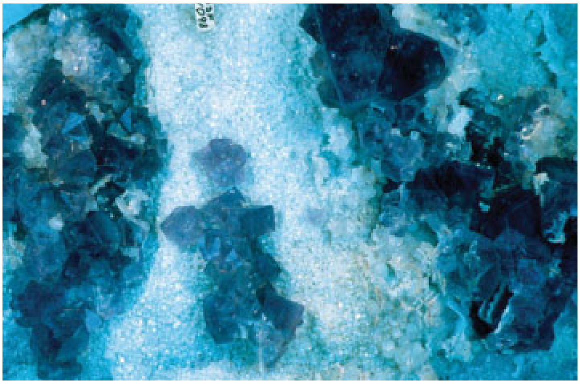
M71 Realgar and **orpiment**. Monoclinic crystals of realgar AsS, and the golden yellow orpiment As_2S_3. From the Getchell Mine, Humboldt County, Nevada, USA.

M72 Stibnite, antimony glance, Sb_2S_3, orthorhombic crystals, black shining, like a spear (Latin *stibnium*), and crystals of quartz. Collected by Kay Sund in the 200 meters level in the Baia Mare mine in Romania.

M73 **Sulfur** S. Orthorhombic yellow crystals from Cinciana on Sicily.



M74 **Pyrite** FeS_2, cubic diploidal (disdodecahedral) crystals from Logrono in Spain and Kleva in Central Sweden. The striation on the cube form, meeting at right angles at the edges, is very characteristic.



M75 **Fluorite** CaF_2, cubic crystals from Weardale, Durham County, England.

M76 **Uraninite** UO_2 to the left. A cubic twin crystal from Stackebo in the Province of Älvsborg in southern Sweden. **Pitchblende** UO_2 to the right, from Joachimsthal in Erzgebirge, Germany

1
Introduction

1.1
What is an Element?

The concept of an element was established in connection with the renewal of chemistry at the end of the 18th century. In 19th-century textbooks of chemistry, elements were defined as "*simple bodies, which cannot be divided into other different elements by available means*". This definition is still valid if "available means" are simple chemical or electrochemical reactions. Thus, water is not an element because it can be split into the elements hydrogen and oxygen. Further dividing is not possible "by simple means".

Present-day chemists describe elements as matter composed of atoms. Each atom is built up of a nucleus surrounded by electrons in one or more orbits or waves. In the nucleus there are a number of protons with positive charge and neutrons without charge. The number of protons is the atomic number. *What is an element in the light of these facts?* The answer is that *an element is a piece of matter built up of atoms, every one with the same atomic number.* (Atoms of one element can, however, contain different numbers of neutrons and thus have different atomic masses. These different atoms are isotopes of the specific element).

1.2
Elements known from Time Immemorial

Nine elements have been known since the dawn of history and we know very little about their discovery. Seven metals, gold, silver, mercury, copper, iron, tin and lead, are mentioned in ancient literature and descriptions. The two non-metals known were carbon and sulfur. The Old Testament in the Bible gives information about ancient minerals, metals and other materials. Of the seven metals listed above, all except mercury are described there.

The development of tools for handicrafts and agriculture, and the utilization of copper, bronze (copper/tin), iron and steel (iron/carbon) became the basis of increased welfare. The same alloys were also used for weapons as means for political power. The elements were thus important for peace and war.

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From a social history point of view it is very interesting to follow how knowledge about silver and gold was developed in Egypt, Greece and Rome and further in Europe in the middle ages. In connection with the platinum metals we are astonished by an advanced indigenous metallurgy in South America in pre-Spanish times. Gold in the printed circuit card of the mobile telephone and platinum metals in the car engine catalytic converter are examples of modern technical applications of the precious metals.

1.3
Searching, Finding and Using

Parallel to the development of the element concept there arose a systematic search for undiscovered elements. Which are they? What properties do they have? What names are suitable for them? The history of discovery is a story about how people worked to find the elements and how the discoveries were verified or rejected. It is the story of brilliant success and of enormous efforts on the wrong track – efforts that came to nothing. We meet learned, often bitter, controversies but also generosity and team spirit.

We meet many striking and eccentric personalities. Their work and view of life have been elucidated. The descriptions in this book therefore are both *personal history, social history* and *history of science*.

In a book about elements (not limited to their discovery) it is desirable also to give descriptions of modern applications. Great attention is therefore devoted to the uses of the elements in modern technology and in everyday applications. Many of the actual elements, e.g. iron, copper, tin, zinc, aluminum, have had and still have a great and positive influence on human efforts to improve living standards. Some elements, e.g. lead, cadmium and mercury, have also caused problems for the environment.

For some elements no practical use could be observed after the discovery but there are many examples where such situations have changed. When the metal tungsten was detected and isolated, the discoverers said that they could not see any use at all for the new metal. They hoped, however, that the element would not remain totally worthless in the future. That was an understatement. Today, tungsten is one of the most important metals for tools in mining and metal-working industries and it is the glowing wire in light bulbs, giving illumination to millions of homes all over the world.

Another example is the discovery of the rare earth metals (REM), seventeen in number. It started at the turn of the century 1800 in two small Swedish villages, Ytterby in the archipelago of Stockholm and Bastnœs in the province of Vestmanland. For a long time these metals, with their curious names, *dysprosium, samarium, ytterbium …*, were of only academic interest. Today the rare earth metals attract worldwide technical interest for many advanced applications, e.g. batteries, magnets, lasers, fiber optics, RE-doped semiconductors, magneto-optical disks, superconductors and so on.

Elements are not only metals. Of very great importance, not least for life on our planet, are carbon, oxygen, phosphorus and sulfur. The noble gases, discovered more than one hundred years ago, were first looked upon as curiosities but soon acquired considerable technical importance e.g. for neon lights and as a protective gas in welding.

We are fascinated by the achievements of Henri Becquerel and Marie Curie in their investigation of the naturally radioactive elements, uranium, radium, etc. These elements also have an everyday interest for us, with the debates about nuclear power and the problem of radon accumulation in homes.

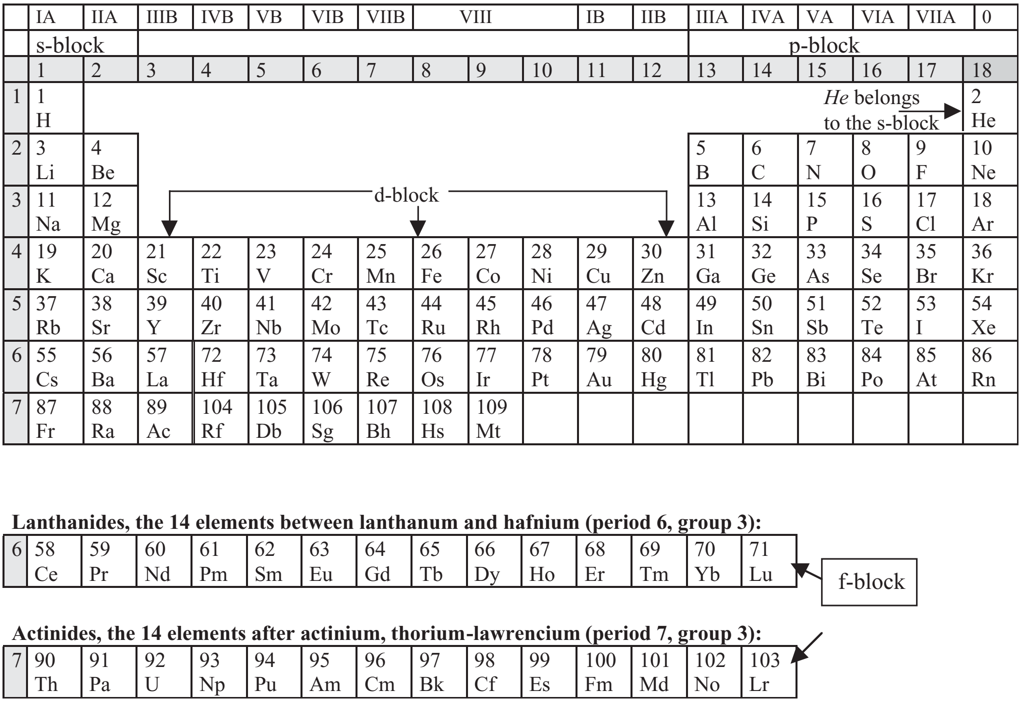
1.4
Systematic Searches

In the period 1860–1870 it was found that the properties of elements were repeated in a distinct manner. In 1869, Lothar Meyer in Germany and the Russian chemist Dmitrij Mendelejev independently formulated systems for the elements. The latter's was the more sophisticated and became the basis of the modern *periodic table of the elements*. This allowed the properties of an unknown element to be predicted with a high degree of certainty and became very important in the search for and discovery of such elements.

The approach of this book adopts the type of periodic table recommended by the International Union of Pure and Applied Chemistry (IUPAC). The vertical columns, *groups* with related elements, are numbered 1–18. This avoids the earlier designations IA –VIIA, IB–VIIB and VIII, which are more difficult to grasp (see Figure 1.1).

Each horizontal row contains a *period* of elements. The first six periods contain 2, 8, 8, 18, 18 and 32 elements respectively, and each ends with a noble gas. In period 6 the fourteen elements between lanthanum and hafnium have been collected in a special row, separated from the main system, but still they belong to group 3 and period 6. These fourteen elements, called the *lanthanides,* have very similar properties. Because of that it has been difficult to discover, identify and separate them.

The last horizontal row in the table, period 7, is incomplete. In group 3 of this period the element actinium, Ac, and the following *actinides* are collected in the same manner as the *lanthanides*.



	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	s-block												p-block					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

Lanthanides, the 14 elements between lanthanum and hafnium (period 6, group 3):

6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

Actinides, the 14 elements after actinium, thorium-lawrencium (period 7, group 3):

7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 1.1 The periodic table of the elements

1.5
About this Book

1.5.1
A Bridge between Science/Technology and Culture/History

There is a gap between science and technology on one side and culture and humanistic topics on the other. Very much is said today about the importance of bridging this gap, of persuading technicians and scientists to be interested in cultural questions and – equally – making non-scientists interested both in science as culture and in modern technology. This book aims build a bridge across the divide. All matter, minerals in the the earth's crust, the huge body of water in the oceans, the atmosphere, the material in a plastic cup, the high-temperature alloys in an aircraft engine, are all built up of the same elements. In fact they also constitute the material basis for the complicated structures of life.

1.5.2
The Motive for a new Book

The history of the discovery of the elements has strictly speaking already been written. The book *Discovery of the Elements* by Mary Elvira Weeks (see below in the section *Sources)* is a masterpiece of science history. There are, however, different motives for a new book on the same theme. In this book more space is given to information about and descriptions of:

- the occurrence of different elements in the earth's crust, in oceans and in the atmosphere
- modern techniques for manufacturing metals, alloys and compounds
- the uses of the elements in a modern society
- the tools for element identification, especially spectral analysis, X-ray analysis and mass spectrometry
- the roles of the elements in life.

1.5.3
The Book's Layout

1.5.3.1 Chapters of General Character

In this book some chapters are of general character:

- About Matter (Chapter 2)
- The Elements – Origin, Occurrence, Discovery And Names (Chapter 3)
- Geochemistry (Chapter 4)
- Blowpipe and Spectroscope – Important Tools for Discovering Elements (Chapter 10)

1.5.3.2 Element Chapters

Most of the chapters are specific to different elements. After four introductory chapters the "oldest" elements *gold, silver, copper and iron* are given one chapter each. Then the main line of description begins, group by group, starting with *hydrogen*. This line is interrupted after hydrogen with a chapter on spectral analysis, important for understanding the discoveries of the alkali metals and many elements treated later in the book. Some element chapters contain, for different reasons, more than one element. *Sodium* and *potassium* have been treated together in Chapter 11. That makes it possible to review the group of alkali metals before the treatment of the other group 1 metals. For similar reasons *magnesium* and *calcium* are treated together in Chapter 14.

The three elements *arsenic, antimony and bismuth* are dealt with in one chapter (46). This allows many interesting connections to alchemy to be made. Some other elements have been brought together in one chapter owing to their mutual similarity. This holds for

- *rubidium* and *cesium* (Chapter 13)
- *rare earth metals* REM (Chapter 17)
- *platinum metals* (Chapter 31)
- *gallium, indium, and thallium* (Chapter 38)
- *selenium and tellurium* (Chapter 49)
- *halogens* (Chapter 50)
- *noble gases* (Chapter 51)
- *the radioactive elements* (Chapter 52)

For each element the chapter contains information on:

- Important properties of the element
- Its discovery
- Deposits and production of ores in our time
- Extraction and fabrication of the element
- Modern uses of the element and its important chemicals and alloys
- The biological chemistry of the element and environmental problems.

1.6
Useful Definitions and Facts

1.6.1
Some Geological Terms

The discovery of the elements and the manufacture of products from mineral sources bring us in close contact with some geological and mining phenomena. Some of these are defined and explained in Table 1.1.

Table 1.1 Some useful facts and definitions

Subject	Definition, explanation and comments
Mineral	A naturally occurring inorganic, crystalline homogenous substance with defined chemical formula and crystal symmetry. For example, the titanium mineral ilmenite has the formula $FeTiO_3$ and a trigonal rhombohedral form. The chemical formula was earlier written $FeO \cdot TiO_2$. In this book the formula type $FeTiO_3$ is throughout used. In many minerals one element can be substituted by another with similar chemical properties and this is reflected in the formula. In the mineral tantalite Fe and Mn and also Ta and Nb are interchangeable with each other. The tantalite formula is $(Fe,Mn)(Ta,Nb)_2O_6$.
Geochemical prospecting	Analysis of soils or plants is useful in prospecting for metals. Underlying deposits of minerals have some influence on the chemical composition of plants and of the soil in which they grow.
Rock	A naturally formed aggregate or mass of one or (usually) more minerals.

Table 1.1 Continued

Subject	**Definition, explanation and comments**
Magma	Naturally occurring mobile molten rock material, generated within the earth.
Magmatic rocks	Igneous rock masses originating in their present form from cooling and differentiation of molten magmas.
Metamorphic rocks	Formed by transformation in the earth's crust of magmatic or sedimentary rocks. The transformation has occurred under the influence of high pressure and high temperature but below the melting point.
Sedimentary rocks	Rocks formed by accumulation of sediment in water or from air. Aqueous or eolian deposits respectively (Aeolus is the god of the winds).
Ore	A natural aggregate of minerals from which extraction of a metal is economically viable. Integral parts of the ore are the mineral or minerals that make the ore valuable but also the gangue, e.g. feldspar or quartz, in which the ore minerals are embedded.
Dressed ore	Concentrate of valuable minerals, obtained by ore dressing.
Ore dressing	The ore is crushed and ground so the ore minerals are made free from the gangue grains
Ore dressing by density differences	1) Manual separation of heavy valuable minerals from the lighter gangue. An example is washing for gold with a pan. 2) Industrially heavy and light minerals are separated on a shaking table equipped with low laths. The mineral particles are carried in water onto the inclined table. Under the influence of a rapid backward and forward movement parallel to the direction of the laths, the heavier particles move to one edge and are collected there 3) The heavy media separation process. The grains of the crushed ore are stirred into a suspension whose density is higher than the density of the gangue grains but lower than the density of the mineral. The gangue floats up and the valuable mineral is "pressed down". The suspension is made of water with ferrosilicon or magnetite dispersed in it.
Ore dressing based on magnetic properties	The crushed ore on a horizontal band conveyor passes a magnetic drum. Non-magnetic gangue minerals fall vertically, but magnetic minerals such as magnetite, Fe_3O_4, follow the drum longer and fall into a separate container.
Ore dressing by flotation	Chemicals, often containing sulfur, are added to the crushed ore dispersed in water. The chemicals are adsorbed on the surface of the valuable mineral grains and make them hydrophobic. When air is blown into the suspension the air bubbles stick to the hydrophobic mineral-grain surfaces and they float to the surface. The gangue grains stay on the bottom of the container.

1.6.2
Resources and Reserves

A resource is something in reserve, ready for use if needed. This simple definition has, in a more systematic way, been adapted for mineral resources. The following definitions, formulated by the US Geological Survey, USGS, are used in this book[1]

Resource is a concentration of naturally occurring material in the earth's crust in such a form and amount that economic extraction is currently or potentially feasible. Resources whose location, grade, quality and quantity are known or estimated from geological evidence are *identified resources.* Resources whose existence is only postulated are *undiscovered resources.*

That part of an identified resource that meets specified minimum criteria, related to current mining and production practices, is called the *reserve base*. It may encompass those parts of the resources that have a reasonable potential for becoming economically available within planning horizons.

Reserves are that part of the reserve base that may be economically extracted or produced at the time of determination. Reserves include only recoverable materials. Such terms as "extractable reserves" and "recoverable reserves" are thus redundant and are not part of the USGS classification system.

1.7
General Literature Sources

1.7.1
The History behind the Discoveries of Elements

Mary Weeks's *Discovery of the Elements,* revised by Henry M. Leicester [1.1], has been a valuable source of historical information. The historical sections in *Gmelins Handbuch der anorganischen Chemie*, 8th ed. (Deutsche Chemische Gesellschaft) have also been used. Regarding the many Swedish element discoveries, access to the Royal Library in Stockholm and *Transactions of the Royal Swedish Academy of Science*, (Kungl. Veteskapsakademiens Handlingar) has been of special value. General information has also been obtained from Microsoft Multimedia *Encyclopedia Encarta 95* and *Swedish National Encyclopedia*. Multimedia 2000.

James L. and Virginia L. Marshall of the University of North Texas, USA give a different treatment of the elements and their discovery. They have visited different places in which discoveries of the elements were made. In a series of descriptions, "Rediscovery of the elements" they give an historical and scientific background of great importance. Two examples are mentioned in refs [1.7] and [17.15] (in Chapter 17). In a CD [1.8] James L. Marshall takes us on a *Walking Tour of the Elements.*

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[1] US Geological Survey Circular 831, 1980.

1.7.2
Raw Materials and Production

Information about minerals, names and compositions has been obtained from different sources. One important source is *Glossary of Geology* [1.4]. Actual descriptions of deposit types and mine production quantities are given by USGS and detailed references are provided in every chapter. Information about production techniques has been collected from *Ullmann's Encyclopedia of Industrial Chemistry* [1.5] and other sources. Other literature cited is noted as references at the end of every chapter.

1.8
Quantitative Element Descriptions

1.8.1
Units, Conversion Factors and Fundamental Constants in the SI System

The International System of Units (SI) is the modern metric system of measurement. The abbreviation SI is derived from the French *Le Système International d' Unités*. The 11th General Conference on Weights and Measures (CGPM, *Conférence Générale des Poids et Mesures*) established the system in 1960. The seven basic units in the SI system are shown in Table 1.2, the recommended prefixes in Table 1.3 and derived units of general character are shown in Table 1.4. Some constants of importance for this book are collected in Table 1.5. These tables are collected at the end of this chapter (see pp. 14 ff.).

1.8.2
Fact Tables

The element's occurrence and general characterization is expressed in *fact tables* at the beginning of every element chapter. Values are given for chemical, physical, thermodynamic and nuclear properties. These values have been collected from many sources and are generally taken from refs [1.2] and [1.9]–[1.20].

1.8.2.1 The Element

In the first table the element's symbol, atomic number and atomic weight are given. Further, the ground state electron configuration is presented in the usual way as, for instance, for the elements phosphorus $[Ne]3s^23p^3$ and gadolinium $[Xe]4f^75d^16s^2$. The configuration consists of a noble gas core from the previous period in the periodic table and the number (as exponents) of additional electrons in s-, p-, d- and f-orbitals. The element's crystal structure (atomic arrangement) is given as unit cell type and cell dimensions in angstroms. The dominant structure types are cubic (body centered *bcc* or face centered *fcc*) and hexagonal close packed *hcp*. The appearance of these structures is shown in Figure 2.3.

1.8.2.2 Discovery and Occurrence

Values for the abundance of the element in the earth's crust and in sea are reported in many publications and different values are quoted for the same element. This book uses values from *CRC Handbook of Chemistry and Physics* [1.2]. These values are collected in Tables 1.6a and l.6b, and the elements are ranked in order of abundance in the earth's crust. Oxygen, silicon, aluminum, iron and calcium are the most abundant elements and are ranked 1–5. Two elements with the same abundance, as for instance gallium and nitrogen, have both been given the ranking 34–35. For technetium, promethium, francium and astatine no abundance values are available and all four are ranked 89–92.

The tables also report values for the element's residence time in the ocean, based on information from ref. [1.3]. The residence time is the average time an atom of a particular element spends in the ocean. Finally, the table also shows the abundance of the element in the human body.

1.8.2.3 Chemical Characterization

The third table summarizes the element's properties. The *oxidation states* of the element are exemplified, with information mainly based on ref. [1.12]. The *ionization energies,* I_1, I_2, I_3 ..., reported in the table are the energies an atom or ion must absorb in order to lose an electron. The more easily the electrons are lost, and the lower the value of I_1, the more pronounced is the metallic character of the element. Ionization energies are determined by bombarding gaseous atoms or ions with beams of electrons (cathode rays). Of course the energy (I_2) for removal of a second electron is greater than I_1 for removal of the first electron.

In contrast to ionization energy, the *electron affinity* (EA) expresses the energy change when a gaseous atom gains an electron. The reaction $F(g) + e^- \rightarrow F^-(g)$ is for instance exothermic and EA = –328 kJ mol^{-1}. According to another definition, however, EA is the energy change when an anion loses an electron, as in the reaction $F^-(g) \rightarrow F(g) + e^-$. In this case EA for fluorine is positive. In these *fact tables* the former definition is used.

According to an international agreement the *standard electrode potential* E^0 refers to a reduction process in which the element takes part. The electrode potential values in the *fact tables* are written in terms of the corresponding reaction of the type

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$
or
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

When no metallic substance is indicated the potential is measured on an inert electrode, such as platinum or iridium. Strong oxidizing agents, such as fluorine or chlorine, have high electrode potentials (positive) while strong reducing agents, such as sodium, have low values (negative). Note that the reduction character of a process presupposes electrons in the left-hand side of the reaction equation. The meaning of the word *standard* in standard electrode potential is that ionic species are present in aqueous solution at unit activity (approximately with the concentration 1 mol per liter), while gases are at a pressure of 1 bar (approximately 1 atm). Some electrochemical units are summarized in Table 1.8.

The *electronegativity* (EN) describes the ability of an atom to compete for electrons with other atoms to which it is bonded [1.6]. The *fact tables* in this book contain Pauling's EN-values. They range from about 0.7 to 4.0. The lower an element's EN is, the more metallic its character is. Non-metallic elements have high EN-values. In the periodic table the EN-values decrease from top to bottom in a group and increase from left to right in a period. The difference (ΔEN) gives some information about the amount of polar character in a covalent bond. For NaCl the ΔEN-value is 2.23 and its ionic character is 74%. The corresponding values for HCl are 0.96 and ca. 20%. Identical atoms as H form gas molecules H_2 with 0% ionic character. For the metallic bond between identical metal atoms this ΔEN interpretation is not valid.

The *atomic radius* reported in the table is difficult to define, as there is no precise outer boundary of an atom. Its value is obtained from determinations of the atomic distances in a metal by X-ray diffraction methods. The *covalent radius* is one-half of the distance between the nuclei of two identical atoms joined by a single covalent bond. The ionic radius is calculated from the distance between the nuclei of atoms joined by a ionic bond. The atomic radius of a metal in a metallic structure is usually much greater than the ionic radius of an ion of the same element in a salt crystal.

Displacements of the electrons in molecules occur in contacts of types other than metallic, covalent or ionic bonding. They give rise to so-called van der Waals forces, which increase as the polarizability of the molecule increases. The corresponding action radii are called van der Waals radii. These values are much larger than the covalent radii.

Many textbooks and tables quote atomic, covalent and van de Waals radii. The values reported in the *fact tables* are mainly taken from the database *WebElements^{TM}* [1.14], which consistently takes the influence of the coordination number on ionic radii into consideration.

1.8.2.4 **Some Physical Properties**

Density values are given both with the SI unit kg m^{-3} and in g/cm^3 (or g/l for gases). Melting and boiling points are reported in both K and °C. Thermal conductivity in W m^{-1} K^{-1} and resistivity in nΩ m are given for different temperatures. Units for general physical properties and conversion factors are summarized and commented on in Table 1.8, which also explains how the magnetic characterization of the elements is obtained.

One type of physical constant expresses the element's elasticity, which is connected to the bonding and the number of orbitals taking part in the formation of the solid element. *Young's modulus* or the *modulus of elasticity, E,* is defined as the ratio of an applied stress to the elongation. The *shear modulus* or *rigidity modulus, G,* is defined as the ratio of shear stress to the amount of shear or torsion that the shear causes on the loading plane. The *bulk modulus* or *compression modulus, K,* is related to the compressibility of the substance. It is defined as the negative ratio of change in pressure to the fractional change in volume. *Compressibility* is $\beta = 1/K$.

A fourth elastic material constant is *Poisson's ratio*, ν. In an axial loading of a metal sample the specimen is strained and becomes longer. At the same time a lateral strain occurs and the sample becomes a little thinner. *Poisson's ratio* is the ratio of the lateral strain to the uniaxial strain. Its value is typical for an element and is in general close to 1/3.

For E, G, K and ν the following relations exist:

$$K = \frac{E}{3(1-2\nu)} \qquad G = \frac{E}{2(1+\nu)}$$

E- and G-values have been compiled and used for calculation of ν- and K-values with the formulas above.

The solubility in water at different temperatures is also reported for gaseous elements.

1.8.2.5 **Thermodynamic Properties**

The fifth *fact tables* report some thermodynamic properties, many of them from ref. [1.10]. Some background information, as well as units and conversion factors are summarized and commented on in Table 1.9. As an assessment of the reducibility of different oxides at different temperatures, *oxygen potential* values are reported. These are values for the standard Gibbs free energy ΔG^0 of oxide formation. In these *fact tables* all values are counted per mol of oxygen molecules. For example, the ΔG^0-value for the formation of Al_2O_3 at 1000 K is reported (in many tables) as –1361 kJ/mol. In these *fact tables* the equation (with 1 mol O_2) *and* the corresponding value are written, e.g.

$$4/3\text{Al} + O_2 \rightarrow 2/3\text{Al}_2O_3.\ \Delta G^0 = -907 \text{ kJ per mol } O_2$$

This system makes the combination of processes very simple. The values have been compiled from several sources, including [1.2], [1.9], [1.10], [1.18] and [1.19]. The oxygen potential values are further discussed in figure 1.2.

1.8.2.6 **Nuclear and X-ray Properties**

The *isotope composition* of the elements is mainly obtained from the Berkeley database [1.15]. For elements in general only naturally occurring isotopes, stable and radioactive, have been reported in detail. For the radioactive elements, without stable isotopes, the most long-lived isotopes have been described.

NMR spectroscopy has been developed into a very important analytical tool [1.21]. It can be used for examining an unknown substance. For example, the element manganese has a sensitive nucleus with a very wide chemical shift range, and NMR spectroscopy can be used to investigate its chemical and oxidation state in a compound. However, in this case only oxidation states –I, 0, I and VII are by high-resolution NMR spectroscopy.

NMR information in the *fact tables* is cited from Mark J. Winter's database *WebElements*^{TM} (University of Sheffield).

Emission and absorption information is summarized in the following notes.

1. In 1913 the ability to identify elements changed abruptly when Henry Moseley discovered that the wavelength (energy) emitted as X-rays from an element depends on the nuclear charge of the atom (the atomic number). The Kα lines shifted to higher energy with increased atomic number.

   In the *fact tables*, *characteristic X-radiation* data are shown for the actual element and the elements immediately preceding and following it in the periodic table. The comparison shows how effective an element's X-radiation (energy, wavelength or frequency) is as a "fingerprint" for its identity (compare the Moseley diagram in Chapter 10, Figure 10.12).
2. A characteristic property of an element is its tendency to absorb incoming X-radiation with intensity I_o. The transmitted intensity I is a function of the element density ρ (g/cm^3), the thickness d of the material and an *absorption coefficient* μ (cm^2/g). The relationship is $I = I_o e^{-\mu\rho d}$. For a given material, μ is not a constant but a function of the energy (wavelength, frequency) of the incoming radiation. The product μρ is the *linear absorption coefficient* (cm^{-1}). The μ-values reported in the *fact tables* have been calculated using the database XCOM from the National Institute of Standards and Technology, NIST, Gaithersburg MD, USA [1.16].
3. The "*thermal neutron capture cross section*" expresses the element's *ability to absorb neutrons*. This tendency is measured in barns. Elements with high barn values (compare cadmium and boron) are used in control rods for the operation of nuclear reactors. Values reported are cited from [1.2], [1.11] and [1.17].

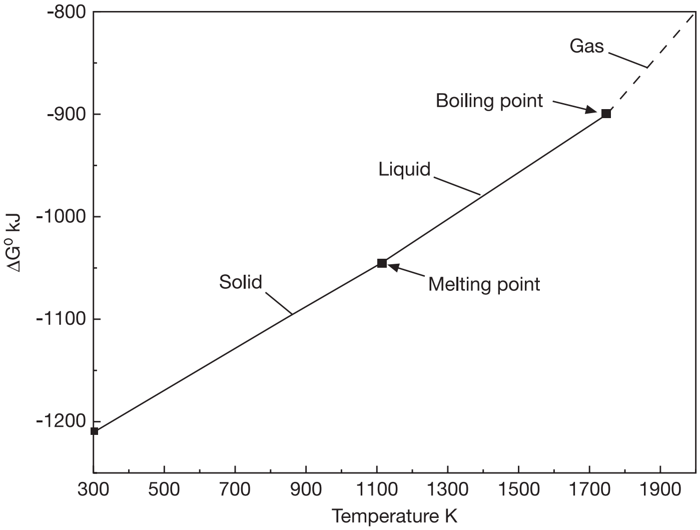

Figure 1.2 The reaction 2Me + O_2 → 2MeO. Gibbs free energy $\Delta G°$ as a function of temperature. The relation is an almost straight line as long as Me is a solid, another straight line for the liquid and a third for the gas states. The slopes for the different parts are different. A small difference between solid and liquid, a bigger between liquid and gas. Interpolation between values in the fact tables No. 5 is most safe if made between two values both on the same type of straight line, solid or liquid. Values on the gas line are uncertain.

Table 1.2 The seven basic SI units

Quantity	Symbol	Unit name	Unit symbol	Comments
Amount of substance	n	mole	mol	The mole is the amount of substance that contains as many elementary units as there are atoms in 0.012 kg of the carbon isotope ^{12}C.
Electrical current	I	ampere	A	The ampere is that current which produces a force of $2 \cdot 10^{-7}$ newton per meter between two parallel wires, which are 1 meter apart in a vacuum.
Length	l	meter	m	The meter is the distance that light travels in a vacuum, in 1/299 792 458 of a second.
Luminous intensity	I_v	candela	cd	The candela is the luminous intensity of a source that emits monochromatic radiation of frequency $540 \cdot 10^{12}$ hertz and that has a radiant intensity in a given direction of 1/683 watt per steradian.
Mass	m	kilogram	kg	The kilogram is the basic unit of mass. It is the mass of an international prototype in the form of a platinum-iridium cylinder kept at Sèvres in France. A new definition, based on fundamental or atomic constants is being considered.
Thermodynamic temperature	T	kelvin	K	The kelvin is the basic unit of temperature. It is 1/273.15 of the thermodynamic temperature of the triple point of water.
Time	t	second	s	The duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium isotope ^{133}Cs

Table 1.3 Recommended prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{-1}	deci-	d	10	deca-	da
10^{-2}	centi-	c	10^{2}	hecto-	h
10^{-3}	milli-	m	10^{3}	kilo-	k
10^{-6}	micro-	µ	10^{6}	mega-	M
10^{-9}	nano-	n	10^{9}	giga-	G
10^{-12}	pico-	p	10^{12}	tera-	T
10^{-15}	femto-	f	10^{15}	peta-	P
10^{-18}	atto-	a	10^{18}	exa-	E

Table 1.4 Units of general character

Quantity	Symbol	Unit	Comments	Conversion
Temperature	t	°C	The temperature difference between the reference temperatures of the freezing and boiling points of water is divided in to 100 degrees.	$t = T - 273.15$
Length	l	µm nm pm Å	1 µm (0.001 mm) is also called 1 micron. Nanometer (nm) and picometer (pm) are used as alternatives to the ångström (Å) to express atomic and ionic radii as well as the dimensions of unit cells and atomic distances in crystallography.	1 µm = 10^{-6} m 1 nm = 10^{-9} m 1 pm = 10^{-12} m 1 Å = 0.1 nm = 10^{-10} m
Pressure	P	Pa bar torr atm	1 Pa (pascal) = 1 N/m^{2} 1 bar = 10^{5} Pa =100 kPa = 0.9869 atm 1 torr 133.32 Pa = 1/760 atm 1 atm = 760 mmHg	1 MPa = 10^{6} Pa = 1 N/mm^{2}

Table 1.5 Fundamental constants

Constant	Symbol	Value
Avogadro constant	N_A or L	$6.022 \cdot 10^{23}$ mol^{-1}
Faraday constant	F	$9.6485 \cdot 10^{4}$ C mol^{-1}
Molar gas constant	R	8.3145 J K^{-1} mol^{-1}
Bohr magneton	μ_B	$9.274015 \cdot 10^{-24}$ J T^{-1}
Nuclear magneton	μ_N	$5.05079 \cdot 10^{-27}$ J T^{-1}
Standard atmosphere	atm	101,325 Pa
Zero of Celsius scale		273.15 K

Table 1.6a Abundance of the elements in the earth's crust, in the oceans and in the human body

Z	Element	The earth's crust		The oceans			The human body
		Ranking[a]	Content ppm[b]	Content ppm[b]	Residence time		Mean content ppm[e]
					log τ[c]	τ, years[d]	
1	Hydrogen	10	1400	$10.8 \cdot 10^4$	–	–	$10 \cdot 10^4$
2	Helium	72	0.008	$7 \cdot 10^{-6}$	–	–	–
3	Lithium	32–33	20	0.18	6.3	$2 \cdot 10^6$	0.03
4	Beryllium	48	2.8	$5.6 \cdot 10^{-6}$	2.0	100	0.004
5	Boron	37	10	4.44	7.0	$10 \cdot 10^6$	0.7
6	Carbon	17	200	28	–	–	$2.3 \cdot 10^5$
7	Nitrogen	34–35	19	0.5	6.3	$2 \cdot 10^6$	$2.6. \cdot 10^4$
8	Oxygen	1	$4.61 \cdot 10^5$	$8.57 \cdot 10^5$	–	–	$6.1 \cdot 10^5$
9	Fluorine	13	585	1.3	5.7	$0.5 \cdot 10^6$	37
10	Neon	73–74	0.005	$1.2 \cdot 10^{-4}$	–	–	–
11	Sodium	6	$2.36 \cdot 10^4$	$1.08 \cdot 10^4$	7.7	$50 \cdot 10^6$	1400
12	Magnesium	7	$2.33 \cdot 10^4$	1290	7.0	$10 \cdot 10^6$	270
13	Aluminum	3	$8.23 \cdot 10^4$	0.002	2.0	100	0.9
14	Silicon	2	$2.82 \cdot 10^5$	2.2	3.8	$6.3 \cdot 10^3$	260
15	Phosphorus	11	1050	0.06	4.0	$10 \cdot 10^3$	$1.1 \cdot 10^4$
16	Sulfur	16	350	905	6.9	$8 \cdot 10^6$	2000
17	Chlorine	19	145	$1.94 \cdot 10^4$	7.9	$79 \cdot 10^6$	1200
18	Argon	43–44	3.5	0.45	–	–	–
19	Potassium	8	$2.09 \cdot 10^4$	399	6.8	$6.3 \cdot 10^6$	2000
20	Calcium	5	$4.15 \cdot 10^4$	412	5.9	$0.8 \cdot 10^6$	$1.4 \cdot 10^4$
21	Scandium	31	22	$6 \cdot 10^{-7}$	4.6	$40 \cdot 10^3$	–
22	Titanium	9	5650	0.001	4.0	$10 \cdot 10^3$	–
23	Vanadium	20	120	0.0025	5.0	$100 \cdot 10^3$	0.03
24	Chromium	21	102	$3 \cdot 10^{-4}$	3.0	$1 \cdot 10^3$	0.03
25	Manganese	12	950	$2 \cdot 10^{-4}$	4.0	$10 \cdot 10^3$	0.2
26	Iron	4	$5.63 \cdot 10^4$	0.002	2.0	100	60
27	Cobalt	30	25	$2 \cdot 10^{-5}$	4.5	$32 \cdot 10^3$	0.02
28	Nickel	23	84	$5.6 \cdot 10^{-4}$	4.0	$10 \cdot 10^3$	0.1
29	Copper	26	60	$2.5 \cdot 10^{-4}$	4.0	$10 \cdot 10^3$	1
30	Zinc	24	70	0.0049	4.0	$10 \cdot 10^3$	33
31	Gallium	34–35	19	$3 \cdot 10^{-5}$	4.0	$10 \cdot 10^3$	–
32	Germanium	55	1.5	$5 \cdot 10^{-5}$	–	–	–
33	Arsenic	54	1.8	0.0037	5.0	$100 \cdot 10^3$	0.05
34	Selenium	69	0.05	$2 \cdot 10^{-4}$	4.0	$10 \cdot 10^3$	0.05
35	Bromine	50	2.4	67.3	8.0	$100 \cdot 10^6$	2.9
36	Krypton	82	$1 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	–	–	–
37	Rubidium	22	90	0.12	6.4	$2.5 \cdot 10^6$	4.6
38	Strontium	15	370	7.9	6.6	$4 \cdot 10^6$	4.6
39	Yttrium	29	33	$1.3 \cdot 10^{-5}$	–	–	–
40	Zirconium	18	165	$3 \cdot 10^{-5}$	–	–	0.05
41	Niobium	32–33	20	$1 \cdot 10^{-5}$	–	–	–
42	Molybdenum	58–59	1.2	0.01	5.0	$100 \cdot 10^3$	0.1
43	Technetium	89–92	–	–	–	–	–
44	Ruthenium	77–80	0.001	$7 \cdot 10^{-7}$	–	–	–
45	Rhodium	77–80	0.001	–	–	–	–
46	Palladium	70	0.015	–	–	–	–

a) Calculated from the values, reported in ref. [1.2].

b) Values from ref. [1.2].

c) Log values from ref. [1.3].

d) Calculated from log values in ref. [1.3].

e) Values from ref. [1.13] and [1.14].

Table 1.6b Abundance of the elements in the earth's crust, in the oceans and in the human body

Z	Element	The earth's crust		The oceans			The human body
		Ranking[a]	Content ppm[b]	Content ppm[b]	Residence time		Mean content ppm[e]
					log τ[c]	τ, years[d]	
47	Silver	68	0.075	$4 \cdot 10^{-5}$	5.0	$100 \cdot 10^{3}$	–
48	Cadmium	66	0.15	$1.1 \cdot 10^{-4}$	4.7	$50 \cdot 10^{3}$	0.7
49	Indium	64	0.25	0.02	–	–	–
50	Tin	51	2.3	$4 \cdot 10^{-6}$	–	–	0.2
51	Antimony	65	0.2	$2.4 \cdot 10^{-4}$	4.0	$10 \cdot 10^{3}$	–
52	Tellurium	77–80	0.001	–	–	–	–
53	Iodine	63	0.45	0.06	6.0	$1 \cdot 10^{6}$	0.2
54	Xenon	83	$3 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	–	–	–
55	Cesium	46–47	3	$3 \cdot 10^{-4}$	5.8	$0.63 \cdot 10^{6}$	0.02
56	Barium	14	425	0.013	4.5	$30 \cdot 10^{3}$	0.3
57	Lanthanum	28	39	$3.4 \cdot 10^{-6}$	–	–	–
58	Cerium	25	66.5	$1.2 \cdot 10^{-6}$	4.7	$50 \cdot 10^{3}$	–
59	Praseodymium	39	9.2	$6.4 \cdot 10^{-7}$	–	–	–
60	Neodymium	27	41.5	$2.8 \cdot 10^{-6}$	–	–	–
61	Promethium	89–92	–	–	–	–	–
62	Samarium	40	7.05	$4.5 \cdot 10^{-7}$	–	–	–
63	Europium	52–53	2	$1.3 \cdot 10^{-7}$	–	–	–
64	Gadolinium	41	6.2	$7 \cdot 10^{-7}$	–	–	–
65	Terbium	58–59	1.2	$1.4 \cdot 10^{-7}$	–	–	–
66	Dysprosium	42	5.2	$9.1 \cdot 10^{-7}$	–	–	–
67	Holmium	56	1.3	$2.2 \cdot 10^{-7}$	–	–	–
68	Erbium	43–44	3.5	$8.7 \cdot 10^{-7}$	–	–	–
69	Thulium	62	0.52	$1.7 \cdot 10^{-7}$	–	–	–
70	Ytterbium	45	3.2	$8.2 \cdot 10^{-7}$	–	–	–
71	Lutetium	61	0.8	$1.5 \cdot 10^{-7}$	–	–	–
72	Hafnium	46–47	3.0	$7 \cdot 10^{-6}$	–	–	–
73	Tantalum	52–53	2	$2 \cdot 10^{-6}$	–	–	–
74	Tungsten	57	1.25	$1 \cdot 10^{-4}$	–	–	–
75	Rhenium	81	$7 \cdot 10^{-4}$	$4 \cdot 10^{-6}$	–	–	–
76	Osmium	76	0.0015	–	–	–	–
77	Iridium	77–80	0.001	–	–	–	–
78	Platinum	73–74	0.005	–	–	–	–
79	Gold	75	0.004	$4 \cdot 10^{-6}$	5.0	$100 \cdot 10^{3}$	0.1
80	Mercury	67	0.085	$3 \cdot 10^{-5}$	5.0	$100 \cdot 10^{3}$	–
81	Thallium	60	0.85	$1.9 \cdot 10^{-5}$	–	–	–
82	Lead	36	14	$3 \cdot 10^{-5}$	2.6	400	1.7
83	Bismuth	71	0.0085	$2 \cdot 10^{-5}$	–	–	–
84	Polonium	87	$2 \cdot 10^{-10}$	$1.5 \cdot 10^{-14}$	–	–	–
85	Astatine	89–92	–	–	–	–	–
86	Radon	88	$4 \cdot 10^{-13}$	$6 \cdot 10^{-16}$	–	–	–
87	Francium	89–92	–	–	–	–	–
88	Radium	85	$9 \cdot 10^{-7}$	$8.9 \cdot 10^{-11}$	6.6	$4 \cdot 10^{6}$	0.001
89	Actinium	86	$5.5 \cdot 10^{-10}$	–	–	–	–
90	Thorium	38	9.6	$1 \cdot 10^{-6}$	2.0	100	–
91	Protactinium	84	$1.4 \cdot 10^{-6}$	$5 \cdot 10^{-11}$	–	–	–
92	Uranium	49	2.7	$3.2 \cdot 10^{-3}$	6.4	$2.5 \cdot 10^{6}$	0.001

a) Calculated from the values, reported in ref. [1.2].
b) Values from ref. [1.2].
c) Log values from ref. [1.3].
d) Calculated from log values in ref. [1.3].
e) Values from ref. [1.13] and [1.14].

Table 1.7 Units for electrochemical properties

Quantity	Symbol	Unit	Comments	Conversion
Electromotive force (emf)	E	V	Also called cell voltage, the potential difference between two half-cells, one at which oxidation occurs (anode) and one with reduction (cathode)	
Standard electrode potential	E^0	V	Measures the tendency for a *reduction process* to occur at an electrode. Ionic species are present with activity 1 (approximately 1 M) and gases with pressure 1 bar (approximately 1 atm)	
Electric conductivity	κ (kappa)	S/m	Siemens/m (S/m) is the reciprocal of the resistivity Ω m	$1\ \mathrm{Sm}^{-1} = 1\ \Omega^{-1}\ \mathrm{m}^{-1}$

Table 1.8 Units for physical properties

Quantity	Symbol	Unit	Comments	Conversion
Density[1]	ρ (rho)	kg m^{-3}	A more common density unit is g/cm^3	1 kgm^{-3}= 1000 g/cm^3
Electric conductivity	κ (kappa)	S/m	Siemens/m (S/m) is the inverse of the resistivity Ωm	1 $Sm^{-1} = 1\ \Omega^{-1}m^{-1}$
Resistivity	ρ (rho)	Ω m	The inverse of the conductivity. Often expressed as (10^{-8} Ω m) or as nΩ m	1 (10^{-8} Ω m)=10 nΩ m
Magnetic susceptibility	χ_{vol} χ_{mass} (chi)	$m^3\ kg^{-1}$ for χ_{mass}	χ_{mass} is obtained by dividing χ_{vol} (dimensionless) by density ρ in kg m^{-3} For paramagnetic substances $\chi > 0$ For diamagnetic substances $\chi < 0$	$\chi_{mass} = \chi_{vol} / \rho$
Specific heat capacity or commonly specific heat	c_p c_v	J kg^{-1} K^{-1}	c_p at constant pressure c_v at constant volume	Compare molar heat capacities C_p and C_v in table 1.9
Molar volume	V	cm^3	For an ideal gas at 0 °C and 1 atm pressure the molar volume is 22 414 cm^3.	
Thermal conductivity	γ (gamma)	Wm^{-1} K^{-1} $calsec^{-1}$ cm^{-1} deg^{-1}	The unit $calsec^{-1}$ cm^{-1} deg^{-1} is the old cgs-unit	1 $calsec^{-1}$ cm^{-1} deg^{-1} = 418.4 Wm^{-1} K^{-1}

[1] Density values are given at a pressure of 0.1 MPa (1 bar) and at a temperature of 25 °C (298 K) for solids, 20 °C (293 K) for liquids and 0 °C (273 K) for gases (if not other values are specified in the tables).

Table 1.9 Units for thermodynamic properties

Quantity	Symbol	Unit	Comments	Conversion
Molar heat capacity	C_p C_v	J K^{-1} mol^{-1} cal deg^{-1} mol^{-1}	According to the Dulong-Petit law, C_v for solids is $3R$. This is however a high-temperature limit value, approached by different elements at different temperatures. C_v is a function of temperature T and vibrational frequency ν of the solid. At room temperature C_v for lead is about $3R$ but for diamond (with very high frequency) only $2.4R$. For solids $C_p \approx C_v + 0.8$ J K^{-1}. For monoatomic gases (noble gases) C_p is $2.5R$ and C_v $1.5\ R$ $C_p/C_v = 5/3 = 1.667$.	1 J K^{-1} mol^{-1} = 0.2390 cal deg^{-1}
Enthalpy	H	J cal	The enthalpy change ΔH for a process is the heat flow at constant temperature and pressure. If reactants and products are in their standard states the change is expressed as the *standard enthalpy change* ΔH^0.	1 cal = 4.184 J
Entropy	S	J K^{-1} cal deg^{-1}	Entropy is related to the way in which energy is distributed in a system. Entropy increases when a solid melts, when a liquid evaporates and when a solute dissolves.	1 J K^{-1} = 0.2390 cal deg^{-1}
Gibbs free energy	G	J cal	$\Delta G = \Delta H - T\Delta S$. For a spontaneous process $\Delta G < 0$. At equilibrium $\Delta G = 0$. If reactants and products are in their standard states the change is expressed as ΔG^0.	1 cal = 4.184 J

Table 1.10 Units for nuclear properties

Quantity	Symbol	Unit	Comments	Conversion
Effective cross-section	σ (sigma)	barn m^2 cm^2	A projectile particle (proton, neutron, etc.) that traverses a layer of matter causes a reaction in the target nuclei. The effective cross-section is the stopping area, in which the nuclei opposes the incident particles. σ is often of the order of 10^{-24} cm^2. Physicists have called this unit a *barn*.	1 barn = 10^{-24} cm^2 10^{-28} m^2
Nuclear spin	I	0 1/2 1 3/2 etc.	Nuclei with even Z and even N have nuclear spin $I = 0$. A nucleus of odd mass number A will have a half-integer spin and a nucleus of even A will have integer spin. Nuclides with an odd neutron number show large integer spins.	
Nuclear magnetic moment	μ (mu)	μ_N	A *nuclear magnetic moment* is associated with each nuclear spin. This magnetic moment produces magnetic interactions with its environment. The nuclear magnetic moment is expressed in the unit μ_N, *nuclear magneton* (parallel to the Bohr magneton μ_B for the electron spin).	

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2
About Matter

2.1
Knowledge started in Handicraft

In striving for better living conditions people have always looked for useful materials and worked them by hand. At different times different materials have been used, as shown by the names Stone Age, Bronze Age and Iron Age for different periods.
A knowledge of materials was developed in different types of handicraft, e.g. preparing knives and other tools from flint; manufacturing metals in furnaces;

- casting melts into moulds for making jewelry, tools and weapons; forming clay for pottery and firing china
- making glass
- glazing china and glass
- extracting cures for illness from medicinal plants
- distilling for making perfumes

About 3500 BC the potters in Mesopotamia had kilns giving temperatures of 1100 °C, which made firing of pottery and china possible. The use of fire also created a foundation for chemical thinking and techniques. With charcoal, metals could be reduced from different ores. New findings have located the origins of the important alloy bronze (copper + tin), which gave its name to the first "metal age" in history, in Thailand earlier than 3000 BC. The Old Testament reveals a considerable knowledge of materials. At the prospect of the building of Solomon's temple 1000 BC we read:

> So David gave orders to assemble the aliens living in Israel, and from among them he appointed stonecutters to prepare dressed stone for building the house of God. He provided a large amount of iron to make nails for the doors of the gateways and for the fittings, and more bronze than could be weighed. He also provided more cedar logs than could be counted, for the Sidonians and Tyrians had brought large numbers of them to David. (Chronicles 1:22)

Encyclopedia of the Elements. Per Enghag

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2.2
Early thinking about Materials

People working with their hands have undoubtedly sometimes asked the question: *What is matter in reality?* In Greek culture some philosophers occupied themselves with thinking about matter. How is matter built up? In the 5th century BC different opinions were formulated.

2.2.1
Four basic Stuffs

Empedokles (ca. 490–430 BC), drawing on earlier suggestions, stated that matter is built of four basic stuffs: earth, water, air and fire. These fundamental elements were looked upon as personified natural powers. Zeus certainly represented the fire and light of the sky, while other gods and goddesses in Greek mythology stood for the other basic elements. Empedokles taught that the elements, under the influence of Love, could be united into an organized whole but that through the action of hostile Strife they were forced apart.

2.2.2
The Atomism or corpuscular Philosophy

Leukippos, living during the last part of the 5th century BC was the teacher of Demokritos (460–370 BC). They had a different opinion of matter and taught that the fundamental constituents of matter are the atoms. There is an infinite number of them and they are small and invisible. They exist in the unbounded void, being entirely separate from each other, and move through the void in random directions. When they collide with other atoms, suitable in shape and size, they become interlocked. In this way composite bodies are formed. The original atomistic theory was of course just a philosophy, and no more scientific than Empedokles' ideas, in spite of its similarities with the science of our time. As a theory of matter it did not become really important until the scientific revival in the seventeenth century.

Bernard Pullman [2.1], however, writes about these early thinkers and their creating power:

> Born twenty-five hundred years ago on the shore of the heavenly sea the atomic hypothesis is the most important and enduring legacy bequeathed by antiquity. For all its scientific implications, it was at first primarily a philosophical idea – just one link in the chain of reflections on the part of Greek thinkers in search of things essential and universal. On this abstract level it remained almost until the nineteenth century. As such its scientific epoch is relatively recent, while its philosophical heritage is ancient; ancient and prestigious, one might add, because of its association with the most illustrious names in this great intellectual epic of mankind. ... It is an overwhelming feeling to realize that we owe this extraordinary adventure of the human spirit to the creative imagination of a handful of Greek thinkers from the distant

> past. Even though the atom of modern science bears only a vague resemblance to the kind of atom envisioned by these early thinkers, the concept they handed down to future generations proved to be one of the most important gifts ever bestowed by man or heaven.

From the Roman poet and philosopher Lucretius, who lived from ca. 95 to 55 BC, a complete statement of the original atomism has reached us from antiquity. In the long poem *De Rerum Natura* [2.2] he argues that the fact that the atoms (primordial particles in the poem) cannot be seen does not imply that they are not present. With a good pedagogic feeling he asks his readers to look at the sunbeams entering a dark, dusty room – asks them to observe the atoms!

> An image, illustrating what I tell you, is constantly at hand and taking place before our very eyes. Do but observe: Whenever beams make their way in and pour the sunlight through the dark rooms of a house, you will see many tiny bodies mingling in many ways within those beams of light, all through the empty space, and as it were in never-ending conflict waging war, combating and contending, troop with troop without pause, kept in motion by perpetual meetings and separations; so that this may help you to imagine what it means that the primordial particles of things are always tossing about in the great void ...

2.2.3
An early Choice

Aristotle (384–322 BC) considered the two doctrinal systems He could not accept atomism, with the primordial particles moving in a void. He believed that in nature a fear of the void, an horror vacui, exists. Instead, all matter is continuous. He accepted Empedokles' teaching about the four elements for earthly things. The matter of the heavens must, however, be different. Above the four terrestrial elements there exists a fifth, distinct, type of matter. This was *quinta essentia*, the quintessence. Everything made of it was unchangeable. This opinion, asserted by Aristotle, had great influence for two thousand years. Some of his ideas were taken over by the church and became orthodox doctrines within scholasticism. This tradition-bound discipline – mainly theology and philosophy – was taught at schools and universities. In these milieus experimental studies did not have a high status. Nor was essential new knowledge about the structure of matter obtained. Instead, antique ideas were considered and embroidered.

2.3
Alchemy – Good and Bad

2.3.1
Not only Gold-making

What is alchemy and why was ancient Egypt its birthplace? The city of Alexandria in Egypt, on the shore of the Mediterranean Sea, was founded in 332 BC by Alexander the Great. It was mainly Greeks, Jews and Egyptians who lived in Alexandria permanently, but many foreigners from Rome and the eastern countries came for shorter or longer visits. Soon after its foundation the population numbered 300 000 free citizens, excluding very many slaves. At the beginning of the 2nd century BC Alexandria became a center of Hellenistic culture and a melting pot for ideas from all over the world. The techniques of Egyptian craftsmen were effective and made a great impression on people from other countries. These techniques encompassed the manufacture of metals and alloys, glass, ceramics, perfumes, dyes and drugs. The skilled Egyptian craftsmen also came into contact with a New World. They had certainly felt the lack of an intellectual root and a general theory and they put the question: What is matter in a deeper meaning? In Hellenistic Alexandria they met many people eager to discuss these types of questions and many were prepared to give answers, founded on their own background of oriental mysticism or Greek philosophy. In this culture the Egyptians' knowledge of chemical processes turned towards alchemy. The word alchemy comes from *Kimiya* (chemistry) and the Arabic definite article *al*. One of many origins for alchemical theory was a concept from Aristotle. His doctrine that all things tend to reach perfection was applied to the science of metals, a field of special interest to the alchemists. Because metals such as silver, copper, iron, etc. were "less perfect" than gold, it was reasonable that gold could be prepared from less noble metals. Just as nature was supposed to do this deep in the earth, so with sufficient skill and diligence it should be possible for a craftsman to do the same thing in the laboratory. The skill could be received by studying alchemy. The aim was to reproduce in the laboratory the operations that Nature achieves on minerals in the "womb of the earth". The womb of the earth had to be replaced by a glass globe, heated in a bath with water or sand. In alchemy Empedokles' idea that matter is built of four basic stuffs, earth, water, air and fire was accepted but some "principles" or characters were added. Mercury and sulfur were regarded as essential constituents of all metals. Their sulfurous character appeared as the colors of the ores from which they could be extracted. The metals showed their "mercuric" character when heated and melted. Alchemical theory and practice was presumably not studied in the famous Museion of Alexandria but in closed, perhaps secret, societies. From Egypt the knowledge spread to Syria and Persia in the 6th century AD. At the end of the Arabic wars of conquest, in about 750, the Greek alchemical books were translated into Arabic. In the 9th century alchemy became very important in Baghdad, which had developed into a center of learning for the Arabic countries. Arabic alchemists were at this time able to manufacture hydrochloric acid, nitric acid, sulfuric acid and aqua regia.

2.3.2
Two Papyri – One Message from Ancient Alchemy

Information about chemical knowledge and practice in the ancient world is given by authors such as Pliny, Dioscorides and others. Their writings are indirect sources and have no details. However, by a fortunate chance two original sources, two Greek papyri written at the end of the 3rd century AD, have been available. These two documents form part of a collection of Greek papyri gathered at Thebes at the beginning of the 19th century by Johann d'Anastasy, vice-consul for Sweden in Alexandria. The main part of this collection was sold in 1828 to the government of The Netherlands. Latin translations of those parts of the collection containing information about alchemy were made public in 1885 and known as the Leyden Papyrus X. One part of the original collection was also donated as a special gift to the Swedish Academy of Antiquities in Stockholm. In 1913 professor Otto Lagercrantz, a philologist in Uppsala, published the Greek text with a translation into German [2.3]. This Stockholm Papyrus is, like the Leyden analogue, a collection of recipes with only few theoretical considerations. The papyri contain methods for purifying metals, making alloys, coloring alloy surfaces, making dyes, writing in letters of gold and silver and dyeing of cloth in purple. Many recipes deal with improving the appearance of precious stones and also with making imitations. Many recipes deal with "asem" or "asemon", alloys intended to imitate gold or silver, mostly the latter. Some examples of recipes:

- Purification of tin that is put into the Alloy of Asem
- Falsification of gold
- Manufacture of copper similar to gold
- Preparation of emerald
- Manufacture of a pearl
- Writing in Letters of Gold
- Cold dyeing of Purple Which Is Done in the True Way

These two papyri, Leyden X and Stockholm, are by far the earliest original sources of ancient chemical knowledge. Translations into English of the two historic documents have been made, [2.4] and [2.5].

2.3.3
Alchemy comes to Europe

From the 12th century onwards Arabic alchemical writings were translated into Latin, mainly in Spain and Sicily, so that alchemy became known and energetically studied in Europe. In the Middle Ages alchemy was almost the only natural research that was practiced in Europe. Prominent representatives, and also critics, for the new divine art were Albertus Magnus in Germany (1193–1280) and Roger Bacon (ca. 1214–1294) in England. Albertus Magnus was a Dominican scholar and alchemist, who translated Aristotle into Latin. He also (probably) discovered the element arsenic. Bacon studied in Oxford and Paris and, after his return to England, entered the order of the Franciscans. He was a man of his time with his interest and belief in alchemy and astrology but was also ahead of his time in many respects. He believed that there were two main routes to a knowledge of nature: the study of mathematics and experimentation. He followed this advice himself and became a very learned man, called Doctor Admirabilis by his contemporaries. He wrote an encyclopedia of all sciences, Opus Majus, with revolutionary ideas and heretical views about the learning of science. For that he was prosecuted and condemned to ten years' imprisonment.

2.3.4
The bad and good Reputation of Alchemy

Alchemy for many of us just involves a dubious desire for gold-making and a search for the philosopher's stone, indefinitely prolonging human life. In the Middle Ages in Europe, at the end of the 15th century, alchemy attracted quacks who gave it an evil reputation, and we are inclined to agree with Toulmin and Goodfield [2.6] when they suggest that "The unforgivable sin of alchemy, as of scholastic philosophy, was that it lasted too long, so that nowadays men recall only the figure of fun it became in its senility. History can be very unjust; and the verdict, which it passes on ideas which outlive their time is frequently merciless." Undoubtedly, however, alchemy became the precursor of modern science, especially chemistry, because of its technical side. A lot of experimental work – metal manufacture, alloying, distillation, filtering, pharmaceutical preparation – widened the group of people who came into contact with chemistry and metallurgy. J. Read, in his excellent overview of alchemy [2.7], quotes from the great 19th-century German chemist and experimentalist Justus von Liebig that "Alchemy was never at any time different from chemistry. It is utterly unjust to confound it, as is generally done, with the gold making of the sixteenth and seventeenth centuries. Alchemy was a science and included all those processes in which chemistry was technically applied." In the 18th century, however, alchemy became more and more questioned and serious scientists began to call themselves chemists instead of alchemists. Alchemy continues to attract interest for its heralding of a coming scientific chemistry and is nowadays described as a more sophisticated discipline than was often portrayed earlier. In addition, alchemy has created subtle levels of arcane symbolism in existential philosophy, as described by Jung [2.8].

2.4
Paracelsus – A Phenomenon in Alchemy and Medical Chemistry

Paracelsus, the Swiss doctor Theophrastus Phillippus Aureolus Bombastus von Hohenheim (1493–1541) was a celebrated physician and reformer of therapeutics. His pseudonym Paracelsus had perhaps the meaning superior to Celsus[1].

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[1] Celsus was a Roman author in the 1st century AD, who edited an encyclopedia covering the whole knowledge of its time in the fields of agriculture, military science, rhetoric and medicine. The book on surgery became an important source of knowledge about medicine in the Hellenistic age.

As an alchemist, Paracelsus believed in the "three principles" of Arabian alchemy, namely:

mercury, which stood for fluidity, heaviness and metallic character;
sulfur, which was the principle of inflammability;
salt, which was characterized by the principles of solidity and relative chemical inertness.

He was, however, an alchemist with no interest in making gold. On the contrary, he stated that "it is physical and psychic health, not gold, that is important". His work marks the beginning of the emergence of the science of chemistry from alchemy. He tried to apply scientific principles on medicine and became a precursor of modern-day pharmacology.

Paracelsus' father was a physician working in different mining towns. From him Paracelsus learned practical medicine. In different industrial villages he became conscious of those types of diseases that could affect people working with mining and metallurgy. From different teachers, including his father, he also learnt alchemy. At the age of fourteen he started a long period of wandering, and visited many universities. Learned people there, and also men in practice, gave him medical, alchemical and mineralogical knowledge. As an adult he worked as a surgeon in many of the armies so common in Europe at that time. In Ferrara in Italy he seems to have taken a university degree as a war surgeon. In 1527 Paracelsus was appointed city physician in Basle, Switzerland, a position connected with the privilege of lecturing at the University. From this time he became a celebrated physician, but it was considered shocking when he gave his university courses in the German language, not in Latin! He was also detested when he attacked the druggists, accusing them of supplying drugs out of greed and not for the health of the patients. When, furthermore, he started a vigorous, public and polemical opposition to the medicine of Galen and Avicenna he became a very controversial figure.

> The prevalent medical opinion originated from two Greeks, Hippocrates (about 400 BC) and Galen (AD 129–199), the greatest physicians of antiquity. In the spirit of the Renaissance the texts of these authorities were in the 16th century translated directly from the Greek. The writings of Celsus were also important as they represented medical terminology in an elegant Latin. Another significant authority was Avicenna, an Arabic/ Persian philosopher and physician living around AD 1000. In his Canon medicinae he had collected the medical knowledge of his time, which he tried to make consistent with Galen's teachings.

The doctrines of these authorities were sharply criticized by Paracelsus. Instead he encouraged students and colleagues to read "the book of nature". Making real observations and learning by traveling, not just reading the classics or the Scriptures, became guiding principles for Paracelsus. He himself taught that the human body was a "factory" for chemical processes. A divine force separated toxic substances from food. In this way a balance was maintained in the body, a balance between the three principles mercury, sulfur and salt. A correct balance implied health while disease was just a disturbed balance. The body defends itself by chemical reactions after taking in suitable remedies. These medicines were often collected from the mineral kingdom. This approach became the key to Paracelsus' great importance for medical chemistry. To set the curative force free from a substance in nature it was necessary to use extractions, distillations and other separation procedures. Many alchemists now changed their gold-making activities and directed their energies towards making medicines. Many doctors and pharmacists too started to experiment, following Paracelsus' new guiding principles. Although Paracelsus in reality lived in a magic and medieval world of ideas, he opened new ways for medicine and chemistry because of his confidence in empiricism and direct investigations of the properties of natural substances. A new branch of chemistry, iatrochemistry, was established in this way. This new branch became so important that the time 1530–1700 is called the iatro-chemical period in chemical history. In fact it did not contribute very much to the development of either chemistry and medicine or public health, as many of the new medicines contained lead, mercury and antimony. Iatro-chemistry became, however, a discipline accepted at the universities in a way that alchemy had never been. When Robert Boyle (see below) in his book *The Sceptical Chymist* (1661) claimed that the three alchemical principles sulfur, mercury and salt were inconsistent with experimental facts, the reputation of iatro-chemistry vanished and in the 18th century it was superseded by a new chemistry. It must, however, be said that Paracelsus has a prominent position in the history of medicine and chemistry. His revolt against trusting only in ancient thinking gave the medical discipline a more scientific course. In chemistry he opened new ways by his confidence in experiments and direct studies of the properties of different substances.

2.5
Two pragmatic Pioneers in the 16th Century

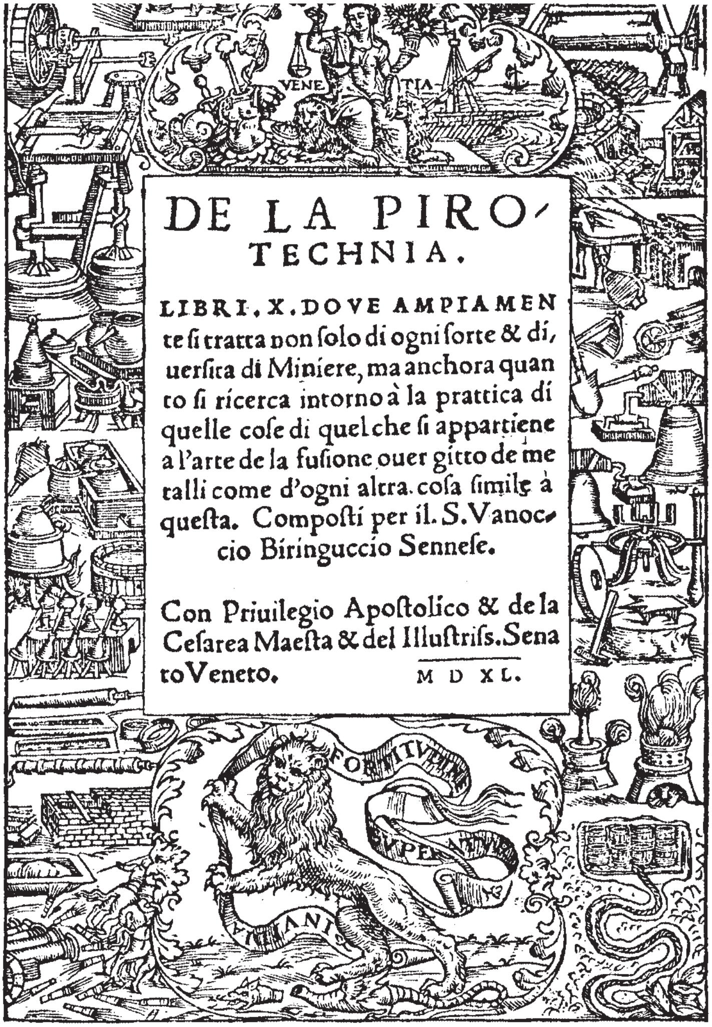
At the turn of the century around 1500, on the threshold of the Renaissance, the humanists began to express their fascination with antiquity and began a stimulating criticism of scholasticism. This awoke the Reformation. It was the time of Erasmus of Rotterdam, Copernicus, Luther, Leonardo da Vinci and others, who are connected with the changing of medieval thought and the birth of the modern world.

At this time, alchemy had been overlaid with mystical theory but with very little in the way of useful theoretical concepts. There was also a lack of clear, comprehensible descriptions of chemical reactions and of the behavior of metals and non-metals. At the beginning of the 1st century of the Modern Age two men changed the situation, Vannoccio Biringuccio, born in 1480 and Georgius Agricola, born in 1494.

2.5.1
Vannoccio Biringuccio – Observer – Experimentalist – Writer

> The Italian metallurgist Vannoccio Biringuccio was born in Siena, a university town in Tuscany. The local authorities belonged to the Petrucci family. During his life and in every conflict Vannoccio showed unswerving loyalty to Pandolfo Petrucci and his sons Borghese and Fabio. The protection and patronage of the Petrucci family made it possible for Vannoccio to study chemistry and metallurgy during his early years and to substantially increase his knowledge by traveling widely through Italy and into Germany. At the age of 27 Vannoccio was sent by Pandolfo to direct the iron mines near Boccheggiano. In 1512 Pandolfo died but support for Vannoccio continued. In 1513 the new ruler, Borghese, appointed him to a post in the Armory of Siena. The prize for success could, however, be high. In 1515 a popular uprising forced Borghese and his followers, including Vannoccio, to flee from Siena. Vannoccio took this as an opportunity and traveled further round Italy, visiting Rome and Sicily. After the intervention of Pope Clement VII the Petrucci family was reinstated and Vannoccio could return to Siena. In 1524 he was granted a monopoly of the production of saltpeter in his hometown and its surrounding area. Two years later a new revolution occurred against the Petrucci and they were expelled forever. The practical Vannoccio took the opportunity to make a second study trip to Germany. When peace was made in Siena in 1530 he returned again and entered the service of the Republique. In 1538 he became the head of the papal foundry in Rome and director of the papal munitions. He died in Rome, probably in 1538 or early 1539.

During his very active life Vannoccio Biringuccio made records of processes he had seen at work. Like a modern scientist he stated that “it is necessary to find the true method by repeating the process again and again, always varying the procedure and then stopping at the best”. He emphasized that furnaces are important as well as balances for the weighing of furnace charges – likewise pen and paper for noting and computing. Biringuccio’s “collected works” *De la Pirotechnia* was edited as ten books in one volume in Venice in 1540, shortly after his death. The title page of this first edition is shown in Figure 2.1. In 1942 a translation into English was edited [2.9]. The second edition from 1959 of the translation is the source for information given in this chapter. The practical character of Biringuccio’s work is evident from the headings of different books and chapters. The contents of *Pirotechnia*, Table 2.1, – including minerals, assaying of ores, separation of gold from silver, casting and fireworks for warfare and festivals – show a book with a surprisingly modern appearance.



DE LA PIRO-
TECHNIA.
LIBRI. X. DOVE AMPIAMEN
te ſi tratta non ſolo di ogni ſorte & di,
uerſita di Miniere, ma anchora quan
to ſi ricerca intorno à la prattica di
quelle coſe di quel che ſi appartiene
a l'arte de la fuſione ouer gitto de me
talli come d'ogni altra coſa ſimile à
queſta. Compoſti per il. S. Vanoc
cio Biringuccio Senneſe.

Con Priuilegio Apoſtolico & de la
Ceſarea Maeſta & del Illuſtriſs. Sena
to Veneto. M D XL.

Figure 2.1 Title page of the first edition of *De la Pirotechnia*. Published in Venice, 1540.

Table 2.1 Headings of the ten books in *Pirotechnia* and examples of chapter titles within each book (see ref. [2.9])

Book No	Title	Examples of chapters within each book
1	Every Kind of Mineral in General	The ore of gold, silver, copper, lead, tin, iron. The practice of making steel, brass
2	The Semiminerals	Quicksilver, sulfur, antimony, vitriol, rock alum and its ore. Glass and other semiminerals

Table 2.1 continued

Book No	Title	Examples of chapters within each book
3	Assaying and Preparing Ores for Smelting	The method of assaying the ore of all metals in general and in particular those containing silver and gold. The method of making cupeling hearths for refining silver in quantity. The properties of charcoal and the different kinds of it
4	The Separation of Gold from Silver	The proper method and procedure in parting gold perfectly from silver in quantity, by means of acid. The method of parting gold from silver by means of sulfur or antimony
5	The Alloys that are Formed Between Metals	The alloys of gold. The alloy of silver with copper. The alloy of copper. The alloys of lead and of tin; their purity and fineness
6	The Art of Casting in General and Particular	The quality of the clay for making molds for bronze founding. The difference in guns and their sizes. How the cores are made for gun molds. Methods of making the moulds for bells of all sizes, and their dimensions
7	Methods of Melting Metals	The methods of melting in ladles and crucibles with charcoal and bellows. The methods for arranging various for moving the bellows for urging melting fires
8	The Small Art of Casting	The various methods of molding reliefs. Note on some materials that have the property of making metals melt easily and run into every corner of the mold
9	The Procedure of Various Works of Fire	The art of alchemy in general. The art of distilling oils and waters and on sublimations. Necessary discourse and advice on working a mint. The manner of drawing out gold, silver, copper and brass by beating and making wire
10	On Certain Artificial Combustible Materials and the Procedures Followed in Making Fireworks to be Used in Warfare and for Festivals	Saltpeter and the procedure of making it. The powder that is used in firing guns. Subterranean mines. The methods of making fire tubes. The manner of making metal balls that burst. The methods of making tongues of fire. The methods of preparing fire pots. The method of making various compositions of artificial fires. Methods of constructing girandoles. Concerning the fire that consumes without leaving ashes, that is more powerful than any other fire, and whose smith is the great son of Venus

2.5.2
Georgius Agricola – A Renewer Of Mining And Metallurgical Technique

> Georgius Agricola (1494–1555) was born in Saxony and studied medicine in Leipzig and in Italy. His real name was Georg Bauer (Bauer is German for farmer). It was later Latinized by his teachers. In 1526 he was chosen town physician in Joachimsthal (Jachymov in the Czech Republic). This town is situated on the eastern slope of the Erzgebirge, with many famous mining towns and villages such as Freiberg, Schneeberg, Geyer and Annaberg within 50 miles. At that time this was one of the most important districts for mining and metallurgy in Central Europe. Agricola became very interested in these things and he spent all the time not required for his medical duties in visiting mines and furnaces. He resigned the position of town physician about 1530 and devoted two or three years to traveling, studying mining and metallurgy. In 1533 he was appointed physician in the big city of Chemnitz in Saxony, a position he held until his death in 1555.

In the middle of the 1530s he began to write the book *De Re Metallica*, not to be published until the year after his death. In this book – more an encyclopedia of twelve books – he describes pragmatically, like a modern technician or scientist, methods for treatment of ores and for production of metals and alloys. He appears as a sober-minded scientist and one of the first to base his theories on observations rather than on metaphysical speculations. It is true that he also worked with problems in alchemy but he did not share its excesses. He stated that "if it were possible to create precious metals they would have by today filled whole towns with gold and silver". The systematic Agricola showed a deep knowledge of minerals, ores and metals, a knowledge that was not used for transforming non-noble metals to noble. Instead he laid the foundation for a new mineralogy, mining technology and metallurgy and became a guide to a new aim and direction for materials science. The brilliant and detailed figures in the book reveal a wonderful medieval world of industrial technique, tools and machinery. This is exemplified in Figure 43.1, page 955. The Latin text of Agricola's book was an obstacle to a more general use. In 1912 *De Re Metallica* was translated into English by Herbert Clarke Hoover (later to be President of the USA) and his wife Lou Henry [2.10]. This translation has been used for the information given in this section.

2.6
New Winds in the 17th Century

Metallurgists and alchemists passed on real chemical knowledge to the 17th century and practical chemistry continued to develop. Theoretical knowledge, however, was static and still based on Aristotle. But new winds blew. The Renaissance – a rebirth of the art and science of classical antiquity – became a rebirth also for the theory of matter. Aristotle had preferred Empedokles' four-element system to Demokritos' atomism. The church followed Aristotle. Renaissance people wished to evaluate the original ancient ideas for themselves without the filtering by church and scholasticism. Among the 17th-century scientists a great interest in Demokritos' atomism awakened. In 1647, the German Joachim Jungius criticized the doctrine of the four elements and the three alchemistic principles. He was probably one of the very first to express the opinion that a substance that cannot be divided into other substances is an element.

Many of the natural philosophers involved in the scientific revival of this century saw themselves as atomists and successors of Demokritos and Lucretius. They referred to their system of ideas as *the corpuscular philosophy*. In Italy and England there were supporters for the corpuscular system as early as the beginning of the 17th century. These corpuscular philosophers and newborn atomists declared that knowledge is received by objective observations and verifiable laboratory experiments. Experimental techniques supporting new hypotheses and theories were available in astronomy but not yet in chemistry. So corpuscular philosophy was just philosophical. However, real physical experiments with gases, especially air, were carried through as a beginning of the long road to a new theory for matter.

> One of the most distinguished European advocates for atomism, new and old at the same time, was Robert Boyle in England (1627–91). He was born in Lismore, Ireland, and educated at Eton and in Geneva and Florence. With the assistance of his colleague and instrument maker Robert Hooke he made celebrated experiments in which he measured how the volume of a given quantity of air varied when the pressure was changed. He found the relation between pressure and volume, known by students of physics in all generations as *Boyle's Law*.

In chemistry Boyle introduced new ideas. In the book *The Sceptical Chymist* (1661) he denied that there are some special substances present in all matter. He thus meant that both Aristotle's four elements and the three principles – mercury, sulfur, salt – of alchemy were inconsistent with experimental facts. Boyle imagined that matter is built up of invisible corpuscles that can be joined together in groups or clusters, constituting distinct substances. He thus, to a certain extent, anticipated the molecular concept. Boyle opened the way for chemistry to develop from a practical art with streaks of mystery to a science based on experimental results. Boyle was one of the founders of the Royal Society in London in 1663 and was in a leading position of this important scientific organization until his death in 1691. A nearly insoluble question had followed atomism during its long history. *Matter is built up of atoms, but how do they stick together?* With hooks as Lucretius expressed it? Toulmin and Goodfield [2.11] describe how Isaac Newton in his book *Opticks* laid down the guiding principles for the future atomism and matter theory around the end of the 17th century.

> The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be some have invented hooks. Atoms, which is begging the Question; and others tell us that Bodies are glued together … that is by an occult Quality, or rather by nothing; and others that they stick together by conspiring motions, that is by relative rest among themselves.

Newton had already demonstrated that physical forces such as gravitation could act across great distances. Might there be similar short-range forces acting only at interatomic distances?

> Have not the small Particles of Bodies certain Powers, Virtues or Forces, by which they act at a distance ... upon one another for producing a great part of the Phaenomena of Nature? For it is well known that Bodies act upon another by the Attractions of Gravity, Magnetism, and Electricity; and these Instances show the Tenor and Course of Nature and make it not improbable but that there may be more attractive Powers than these ...

The idea of interatomic forces had great attractions for Newton. It made it possible to unify into a single system the theory of the heavens and the theory of tiny atoms. The question about the nature of the effect at a distance he left open. It is, as is well known, a major problem in modern physics.

2.7
Phlogiston

At the turn of the century 1700 alchemy was *passé* as a serious science and so was Empedokles' system with four basic elements, water, air, fire and earth as the building blocks of matter. The scientific and very successful chemistry of the 18th century had, however, a last metaphysical component, *the phlogiston hypothesis*. It can perhaps be looked on as a new version of Empedokles' and Aristotle's theory about fire. Phlogiston was a hypothetical substance representing flammability. It was postulated by the German chemists Johann Becher and Georg Stahl to explain the phenomenon of combustion. According to the theory, combustion is a process in which phlogiston is lost. Substances like coal, hydrogen and sulphur were believed to be composed almost entirely of phlogiston. A problem for the theory was that a metal such as copper increased in weight during combustion. Because of that it was assumed that phlogiston is a substance with a negative weight. The phlogiston view of matter became very widespread and gained a strong position during the century, even among very skilled chemists. In the 1770s, oxygen was discovered by the phlogistonists Scheele and Priestley, and the French chemist Antoine Lavoisier realized that it is oxygen that combines with other substances in combustion. This was *the chemical revolution*. The phlogiston hypothesis could be disproved.

2.8
Still in the 18th Century – the Chemical Revolution

2.8.1
Discoveries of new Elements

Although chemical theory was old fashioned during the early 18th century both laboratories and analytical chemistry were developing. Many governments were utilitarian and liked to find new sources for valuable minerals in the own country. These efforts resulted in the discovery of many new elements, as shown in Table 2.2.

Table 2.2 Elements discovered in the 18th century

Element	Discovered	Element	Discovered
Cobalt	1735	Tellurium	1783
Nickel	1751	Tungsten	1783
Magnesium	1755	Zirconium	1789
Hydrogen	1766	Uranium	1789
Nitrogen	1772	Titanium	1791
Oxygen	1774	Yttrium	1794
Chlorine	1774	Beryllium	1797
Manganese	1774	Chromium	1797
Molybdenum	1781		

2.8.2
Lavoisier and the Chemical Revolution

> Antoine Laurent Lavoisier (1743–94) played a crucial role in the reconstruction of chemistry at the end of the 18th century. He was born in Paris and studied law, chemistry and geology at the Collège Mazarin. He held a number of public offices. As a lawyer he was engaged as a *Fermier-général*, a tax collector; as a chemist he became supervisor for the manufacture of saltpeter, gunpowder and other explosives in the government arsenal. In the latter position he could build and equip his own laboratory. This grew into a scientific center with contacts on both sides of the Atlantic. In the French revolution 1789 his sympathies were on the side of reforms and it was possible for him to keep his position at the arsenal and the laboratory. When the revolution moved to its terror phase his position as *Fermier-général* became the focus for attention and he was sent to the guillotine and executed on 8th of May 1794. The following day the mathematician Lagrange said, "It took them only a second to cut this head, but one hundred years are perhaps not enough to bring forth a new one of this greatness."

Lavoisier was probably the first to make really quantitative experiments. He was able to show that the quantity of matter is the same before and after a chemical reaction, even if the matter has changed its state. As already mentioned Lavoisier demonstrated that burning is a process that occurs by combination of a substance with oxygen. This new finding was expressed in the book *Sur la combustion general* (On combustion, 1777). He also investigated water and named its components hydrogen and oxygen. After this he abandoned his belief in phlogiston and showed in *Réflexions sur le phlogistique* (1786) that chemical reactions can be described more simply *without* the phlogiston hypothesis than *with* it. For a chemical world that had stuck in the mud of phlogiston this was bright news of the greatest consequence for scientists in the near future.

Together with *Claude Lois Berthollet* and others he worked out a system of names for chemical substances. He described the new nomenclature in *Méthode de nomenclature chimique* (*Method of Chemical Nomenclature*, 1787). In 1789 he clarified the difference between chemical compounds and elements. He defined the element as a simple substance that could not be further divided by chemical analysis. This was described in *Traité élémentaire de chimie* (*Treatise on Chemical Elements*). It was characteristic of Lavoisier to be practical in his definitions. It would have been tempting to describe matter as composed of simple and indivisible atoms. But he declared: "We know nothing at all about them. To base the classification of chemical substances on hypotheses about their atoms would be utterly premature. One must proceed more modestly, and accept as simple any substance which scientists had found no way of subdividing in the laboratory." Applying this criterion, Lavoisier compiled a first list of elements, 33 in all, including caloric and light. The newly discovered gases were however all classified as compounds and not as elements.

2.9
A Breakthrough for Atomism

At the beginning of the 19th century atomic theory had ripened to a breakthrough. The Frenchman *Joseph Louis Proust* (1754–1826) was active as professor of chemistry in Madrid for ten years around the end of the 18th century. Proust's *law of definite proportions* was published in 1794. It states that all samples of a compound have the same composition. Its elements are all present in distinct proportions by weight, regardless of how the compound is prepared. After a long struggle with L. Berthollet the law was fully accepted in 1811, when the Swedish chemist *Jöns Jacob Berzelius* gave Proust credit for it. In 1799 Proust also established, as the first scientist, a clear distinction between the concepts of chemical compounds, mixtures and solutions. Proust's results contributed greatly to the development of modern atomic theory.

We can feel how Proust's law gave *John Dalton* (1766–1844) the "*aha reaction*", which enabled him to present his famous atomic theory, formulated in *A New System of Chemical Philosophy* (1808; in 1803 he had given a short, preliminary presentation of the theory). Dalton's atomic theory can be expressed in three points:

- In one element all atoms are identical. One atom type is unchangeable and typical for the actual element.
- In varying elements the atoms are different.

- Each element has a characteristic atomic weight.
- Chemical compounds are formed when atoms of one element are combined with atoms of another element.

John Dalton, who formulated the atomic theory, was the son of a weaver in the county of Cumberland in England. He received education first from his father and then at a Quaker school in his native town. From the age of twelve he taught in Quaker schools while he simultaneously studied mathematics and physics. In 1793 he became a teacher of these subjects at New College in Manchester. From 1800 he earned his living by private tuition and later on (as an established scientist) by giving lectures at different universities and institutions. He was made a Fellow of the Royal Society in 1822 and was awarded the Society's gold medal in 1826. In 1830 Dalton became one of the eight foreign associates of the French Academy of Sciences.

Berzelius' careful atomic weight determinations, with a first table in 1815, gave strong support to the atomic theory, even if Berzelius himself only accepted Dalton's theory [2.12] with some hesitation. Dalton, however, made the incorrect assumption that a compound between two elements was formed by the combination of one atom of each. At this time Gay-Lussac was studying the chemical reactions of gases, and found that the ratios of volumes of the reacting gases could be expressed as ratios of small integers. These experimental results were not in agreement with Dalton's hypothesis. In 1811 the Italian scientist *Amadeo Avogadro* (1776–1856) introduced the extremely important concept of molecules in an article in *Journal de physique*. He clearly emphasized the distinction between the molecule and the atom. The "atoms" of nitrogen are in reality "molecules" containing two nitrogen atoms. Two molecules of hydrogen can combine with one molecule of oxygen to produce two molecules of water. Avogadro also suggested that equal volumes of all gases at the same temperature and pressure contain the same number of molecules, which is now known as Avogadro's Principle. Avogadro's ideas were, however, ignored until reintroduced by the Italian chemist *Stanislao Cannizzaro*, (1826–1910), who successfully lobbied for the acceptance of Avogadro's hypothesis at the Karlsruhe Conference of 1860. This conference had been called to resolve current problems in chemistry and was attended by 140 well-known chemists from different countries. Cannizzaro showed that Avogadro's Principle could be used to determine not only molar masses but also, indirectly, atomic masses. After this conference Lothar Mayer wrote. "It was as though the scales fell from my eyes. Doubt vanished and was replaced by a feeling of peaceful clarity."

Dalton's and Avogadro's theories became cornerstones of modern science. They also gave simple explanations of the constant compositions of chemical compounds and to Proust's law of definite proportions.

2.10
Accelerating Knowledge of the Atom

From Demokritos' vague idea of the tiny particles he called atoms to Dalton's formulation of the atomic theory it had taken 22 centuries. And still the knowledge was vague and without experimental proof, although some indications were available through the physics and chemistry of gases. Dalton had, however, given a pattern, a system, in which further development could take place. And from now on, progress accelerated and immense development occurred, creating an entirely new knowledge based on sophisticated experimental techniques and astute analysis by the human brain. About a century after Dalton's formulation in *A New System of Chemical Philosophy* it was possible to determine the atomic arrangement in a crystal and to measure the interatomic distances and radii of the atoms (by X-ray diffractometry). And less than two centuries after Dalton it was possible to observe individual atoms with advanced microscopes.

2.10.1
Atomic Weights

Careful weighing of specific volumes of different gases permits direct comparison of the weights of individual gas molecules. When oxygen is taken as a standard and its atom is given an atomic weight 16.000 atomic mass units (amu) argon is found to have the atomic weight 39.948 amu. It is customary to use the expression "atomic weight" (used throughout this book) although "atomic mass" would be more accurate. Anyhow, atomic weights are measured in the unit amu. From about 1810 Berzelius made very careful determinations of atomic weights, using analytical methods he had himself developed. He calculated the atomic weights relative to oxygen but then it was necessary to know the formulas for the compounds he analyzed. From 1813 he knew that water is H_2O. For other elements he had to guess the atomic composition of the compounds he investigated. In 1818 he presented a table of atomic weights for 45 of the 49 then known elements. The weights were carefully determined but in some cases wrong by a multiple of 1.5, 2.0 or 4.0 owing to a wrong assumed formula for the compound. After 1819 he got some guidance from Dulong and Petit's law about the heat capacities of metal atoms. In 1826 he could publish a new list with atomic weights in good agreement with today's values, although the values for the alkali metals were still doubled. This was corrected in the 1860s. Until the first part of the 20th century, *natural* oxygen (taken as 16 amu) was used as the standard for atomic weight determinations. Chemists used it even after the heavier isotopes ^{17}O and ^{18}O were discovered in 1929. Physicists wished to use just ^{16}O as a standard so two series of atomic weights developed, one chemical and one physical. The difference was very small but nevertheless disturbing. The dispute got a Solomonic solution when, early in the 1960s, the International Union of Chemistry and Physics decided on a new single standard, ^{12}C. This replaced the two earlier standards and was accepted by both chemists and physicists. The new table is in close agreement with the old one based on natural oxygen.

2.10.2
The Structure of the Atom

In 1897, *J. J. Thomson* had shown that cathode rays consist of extremely small particles, negatively charged. They were given the name “electrons”. They formed part of the first “modern” atom model. In 1911, the British physicist *Ernest Rutherford* (1871–1937) discovered that the atom is not a solid piece of matter but mostly empty space. The mass is concentrated in the center, in an infinitesimally small “nucleus”. He also proposed that electrons travel in orbits around the nucleus. His own student and co-worker *Niels Bohr* (born in Copenhagen in 1885) criticized Rutherford’s model. In papers published in 1913 he expressed what has since then been known as Bohr’s atomic model. Making use of the quantum theory and Planck’s constant he postulated that electrons could only be situated in certain orbits or quantum levels. The atom emits electromagnetic radiation when an electron jumps from one quantum level to one of lower energy.

2.10.3
The Element is not Elementary

The Greek word for atom means *indivisible*. In Dalton’s theory there were as many different elementary particles, atoms, as there are elements. An atom is unchangeable and typical for the actual element. Today we know, which Dalton could not know, that the atoms are themselves complex, made up of electrons and atomic nuclei. All nuclei are composed of “protons” (named by Rutherford) and “neutrons” (discovered in 1932 by James Chadwick). Both particles have the atomic weight 1; the proton has the electrical charge +1, the neutron is neutral. The number of protons in the nucleus is equal to the number of electrons in the quantum levels. Every proton and neutron is composed of three “quarks”. Perhaps we have to admit today that the elements of matter in our modern system are in fact fewer than the four of Aristotle. Matter is built of electrons and quarks.

2.11
The Solid State

The interfacial angles in precious stones like rubies and emeralds were an early subject of great interest. Solid-state chemistry and physics began as *crystallography* when the relationships between the plane faces became a subject of scientific measurement. In 1669 Niels Stensen, professor of anatomy in Copenhagen and Vicar Apostolic of the North, compared the interfacial angles in specimens of quartz crystals. (The interfacial angle is defined as the angle between lines drawn normal to the two faces. He found that these angles were always equal in different specimens. This constancy of interfacial angles has been called the *first law of crystallography*. At the University of Munich a group of physicists had the twin interests of crystallography and X-ray radiation. In 1912, under the guidance of *Max von Laue* they passed an X-ray beam ("white" radiation with a continuous spectrum) through a crystal of copper sulfate and obtained a diffraction pattern that could give information about the atomic arrangement in the crystal. The new science of *X-ray crystallography* began. In England, *William Bragg* and his son Lawrence noted the news from Munich with great interest. They developed a new technique, using monochromatic X-radiation.

A crystal in which the unknown distance d between the atomic layers is to be investigated (Figure 2.2). When an X-ray beam passes into the crystal some rays will be reflected at the surface, some at the second layer of atoms, some at the third and so on. The angle of incidence, θ, can be varied by rotating the crystal. In the outgoing wave front the rays reflected from underlying planes have traveled longer distances than the ray reflected at the surface. If the distance difference AB + BC between the first two reflections is just one wavelength, $\lambda = 2\,d\,\sin\theta$, the two rays are in phase giving a reinforcement and a maximum in the intensity of the reflected beam. As reflections also occur from a few underlying planes, the condition for reinforcement is $n\,\lambda = 2\,d\,\sin\theta$ with $n = 1, 2, 3 \ldots$. A simpler X-ray technique is the powder or *Debye–Scherrer method.* Instead of using a single crystal a number of finely divided crystals with random orientation are tested.

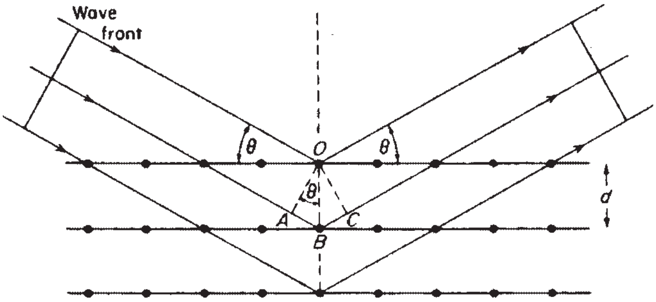
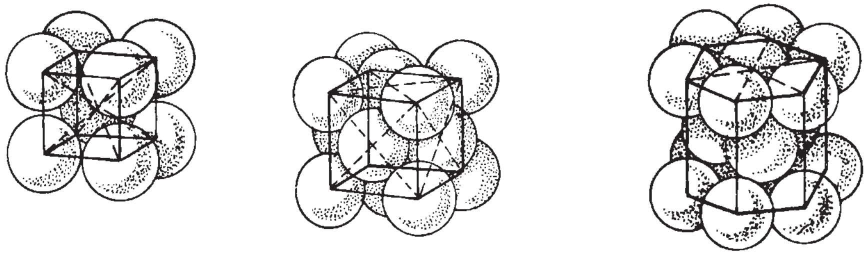


Figure 2.2 The Bragg method for investigating atomic arrangements in crystal structures.

By means of X-ray diffractometry, the atomic arrangements in metals have been determined. Most of the metals crystallize in one of three typical metallic structures with unit cells body-centered cubic, bcc, face-centered cubic, fcc, and hexagonal close packed, hcp (Figure 2.3).

Knowledge of these metal structures is very important for an understanding of plastic deformation of metals and alloys.



bcc fcc hcp

Examples

Metal bcc	Edge length	Metal fcc	Edge length	Metal fcc	Edge length
Iron*)	2.87 Å	Copper	3.62 Å	Titanium**)	

*) Room temperature **) Hexagonal length 2.95 Å; vertical length 4.68 Å

Figure 2.3 Three important crystal structures in metals.

2.12
To Look into Matter

2.12.1
Electron Microscopy – a Review

In the development of knowledge of matter the invention of the *electron microscope* has been of utmost importance. From the theoretical point of view it was *Louis de Broglie* who in 1924 cleared the way for this new type of microscope when he showed that a moving electron can be described both as a particle motion and a wave propagation. If electrons are accelerated in a potential field of 100 kV the wavelength is only 0.04 Å (0.004 nm). The wavelengths for visible light are in the range of 3900–7000 Å (390–700 nm). As the minimum size of detail that can be observed in an optical system is determined by the wavelength of the radiation used, a quite new world opens up if it is possible to use electron beams instead of visible light in microscopy. As the radius of the copper atom is 1.3 Å (0.13 nm) it should in principle be possible to "see" copper atoms.

As often in the history of science the development started practically. The German engineer *Ernst Ruska* (1906–88) worked with cathode rays and oscilloscopes and, at the age of 25, built the first electron microscope in 1931. He also managed the manufacture of the first commercial electron microscope at the end of the 1930s. Almost 50 years later he received the Nobel Prize for physics. During his active time he was professor of electron-optics at the University of Technology in Berlin and worked at Siemens AG. He also became director of the Fritz Haber Institute for Electron Microscopy.

In “ordinary” electron microscopes, TEM and SEM, the electrons pass through the specimen (TEM) or hit the specimen surface. In the latter case secondary electrons are set free and give information about the surface topography (SEM).

Some electron microscopes utilize electrons from a needle with a very sharp tip, brought so close to the specimen surface that a quantum mechanical interaction arises between the electron cloud of the surface and the electron cloud of the atoms in the tip. This technique opened a fantastic way to really see individual atoms. This microscope, *the field ion microscope*, was presented in 1956 by the German *Erwin Müller*, who could for the first time observe individual atoms in a tungsten tip. A widening of the technique, and in fact a new technique, came with the *vacuum-tunneling microscope* in 1978, developed by *Gerd Binnig* in Frankfurt and *Heinrich Rohrer* in Zürich. They shared the Nobel Prize in 1986 with *Ernst Ruska*. A further development of the field ion microscope is the *3-D atom probe*, exemplified below.

2.12.2
Transmission Electron Microscopy (TEM) in Practice

The picture in Figure 2.4 was obtained in the transmission electron microscope, in which an electron beam penetrates a very thin object. Preparation for TEM is made with electrochemical or ion physical methods to get samples thin enough. The elec-

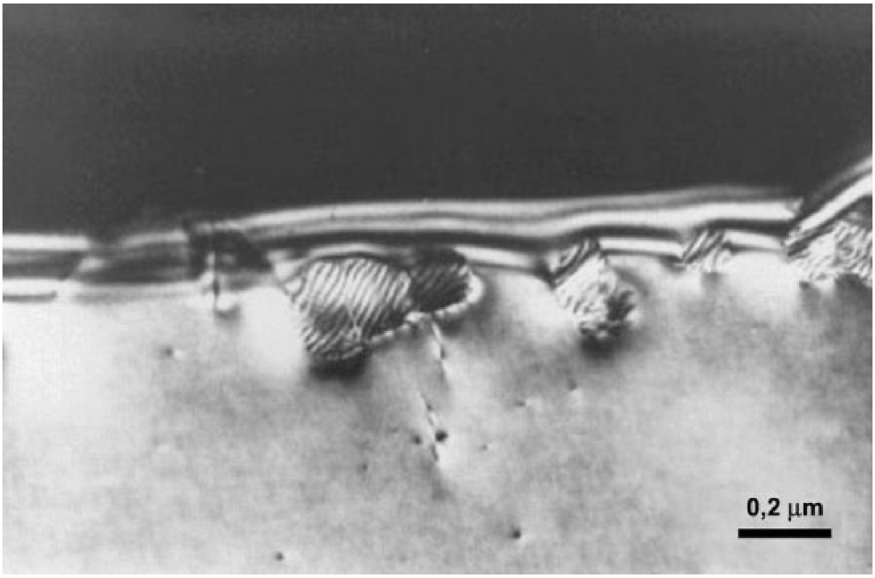


Figure 2.4 Carbides of the type $(Cr,Fe)_{23}C_6$ in a steel “Alloy 800” with 20% Cr, 30% Ni, 0.02% C and small amounts of Ti and Al. The stripes on the carbide particles are Moiré fringes (interference between atomic layers in austenite and carbide) with a distance of about 130 Å (0.013 µm). In the steel the Cr/Fe ratio is 0.4:1, in the carbide 3:1. Thus chromium from the grain surface regions in the steel has been bound into the carbides. (The picture was taken using a Philips 300 TEM microscope and is reprinted with the permission of Dr J. O. Nilsson, AB Sandvik Steel, Sweden.)

trons for imaging are generated from a heated tungsten wire or lanthanum boride LaB_6. They are accelerated over a potential drop of 100–1000 kV. A magnetic condenser lens concentrates the electrons on the specimen. Owing to the high energy input, secondary electrons from the interior of the object are strongly scattered, carrying information about the material structure. As air also absorbs radiation and scatters electrons the microscope must be evacuated to 0.01 Pa (10^{-4} mm Hg).

After passage through the specimen the electron beam broadens and projects a magnified picture of the inner structure of the object. The image can be observed on a fluorescent screen or, alternatively, the transmitted electrons can be used to expose a photographic film, which after development gives a picture of the structure.

2.12.3
Scanning Electron Microscopy (SEM) in Practice

SEM equipment uses an electron gun similar to that already mentioned for TEM. It operates, however, at a much lower voltage, (1–20 kV). The electron beam travels downward through magnetic lenses and the electrons hit the specimen in a very fine point. This time it is not a question of penetration. Instead secondary electrons are set free from the specimen surface. A detector that sends signals to an amplifier counts these electrons. The focused beam scans the specimen surface, row by row, and secondary electrons, knocked out from every point, build up the final image. The magnification can be varied, e.g. in the range 20–100 000 × without refocusing. The resolution is 50 nm or better. Typically, SEM has a very large depth of focus, which endows SEM photos with a three-dimensional and "life-like" appearance. Biological specimens have to be prepared so they conduct electricity, so a very thin gold layer is sputtered on the surface. Two examples of SEM-photos are shown in Figures 2.5 and 2.6.

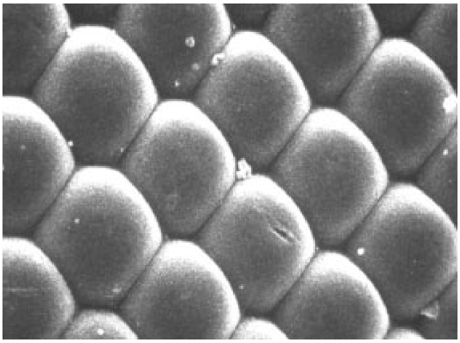


Figure 2.5 The surface of the eye of a fly. SEM photo with original magnification 1000 X.

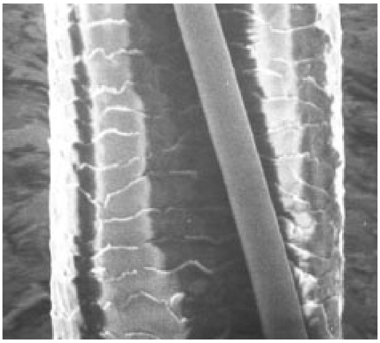


Figure 2.6 A thin resistance wire (0.01 mm) lying obliquely over a hair (0.065 mm).

2.12.4
A new Look at the Atomic World with Tunneling Microscope and Atomic Probe

From the atoms in a metal the electron cloud extends a very small distance above the surface. If a needle with a very sharp tip (so sharp that only 1–2 metal atoms are present on the very tip) is brought close to such a surface a quantum mechanical interaction arises between the electron cloud of the surface atoms and the electron cloud of the tip atoms. When a small voltage is applied, a current (the "tunneling current") flows. Electrons can flow across the forbidden gap owing to this tunneling effect. If the separation distance between tip and surface is a few atomic diameters the tunneling current rapidly increases as the distance between tip and surface decreases. The decrease in distance indicates how close the tip is to individual atoms in the surface. In practice the needle is scanned across the surface laterally while its distance from the surface is adjusted to keep a constant tunneling current. Then the surface topography is obtained from the recorded trajectory of the tip. The result is an atomic resolution [2.13]. The *scanning tunneling microscope* is widely used to obtain images

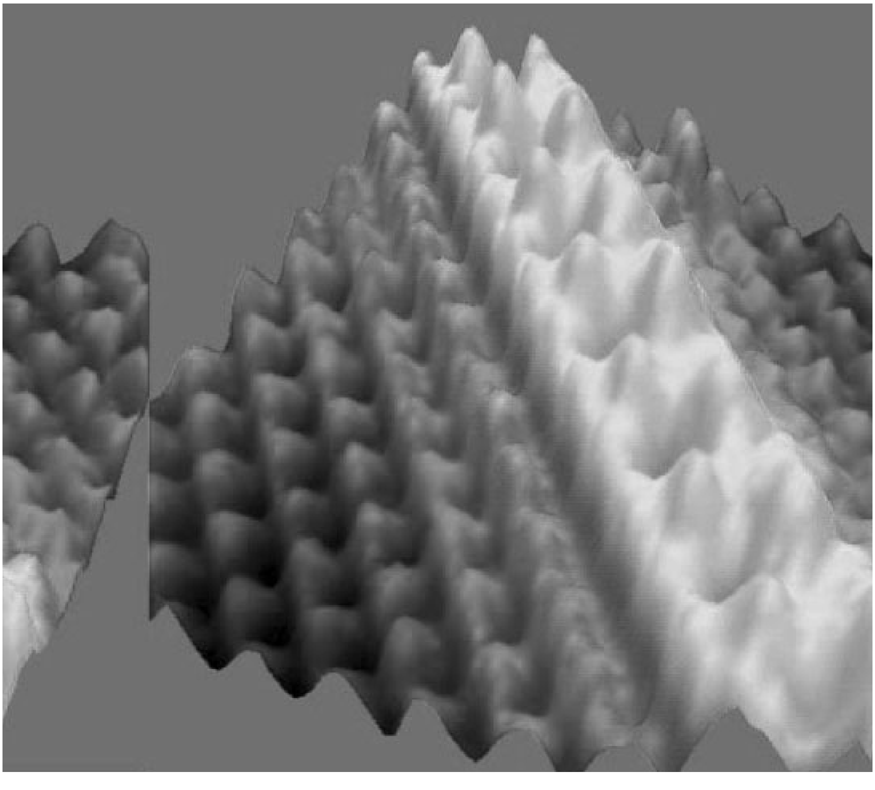


Figure 2.7 Reproduced from: L. J. Whitman, J. A. Stroscio, R. A. Dragoset and R. J. Celotta, *Geometric and Electronic Properties of Cs Structures on III-V (110) Surfaces: From 1-D and 2-D Insulators to 3-D Metals*, Physical Review Letters 1991, 66(10), 1338–1341, with permission.

of metal surfaces on the atomic scale (Figure 2.7). It is also used for control of microelectronic printed circuit cards.

The *3-D atom probe*, a development by research groups in Rouen and Oxford in the 1990s, is used in materials science for identifying and visualizing individual atoms, as shown in Figure 2.8.

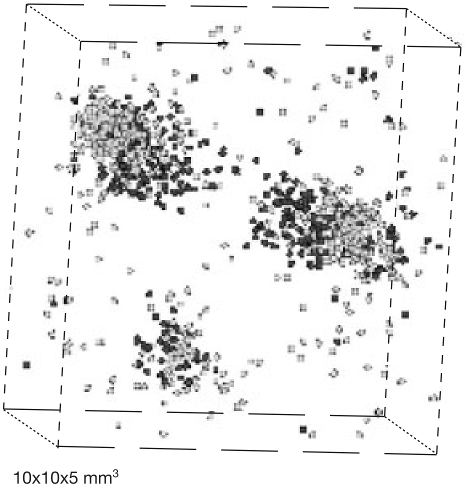


Figure 2.8 3-D atom probe picture of a high alloy stainless steel containing Fe, Cr, Ni, Ti, Al, Cu and Mo. For visibility only the atoms of copper (light) and aluminum (dark) are shown. These atoms are not evenly distributed but have formed Al-Cu particles, whereby the strength of the alloy is enhanced. (Reprinted with the permission of Dr Mats Hättestrand, Chalmers Institute of Technology, Gothenburg, and AB Sandvik Steel, Sweden.)

2.13
Alchemy for a new Millennium – Nanotechnology

So far we have considered:

- the origins of our knowledge of matter in chemical handicraft
- the development of atomism in natural philosophy
- experimental work in alchemy
- the discovery and identification of metals and other elements in experimental chemistry
- the clarification of the role of oxygen in combustion
- the formulation of an atomic theory
- the determination of atomic weights
- the evaluation of the structure and weight of the atom
- new knowledge about the structure of the atom itself; in spite of its name the atom is not indivisible
- methods for evaluating the atomic arrangement in minerals and the crystal structure of metals
- techniques for identification and observation of individual atoms

So do we now know all there is to know about matter? Of course not! But the knowledge about

- atoms and their electrons
- the binding forces between atoms in a molecule or in a solid
- the atom's own structure and its mass
- the atomic arrangement in the structure of matter

has created the base for a new "*handicraft, working on the atomic scale*", a new alchemy, with the possibility of synthesizing new materials atom by atom. A new designation, *nanotechnology* has been introduced[1]. It might be said that this is only a new name for chemistry. Chemists have made syntheses "atom by atom" for centuries. But the well established knowledge of matter nowadays is new and can help experimentalists and manufacturers in chemistry, biology and metallurgy to see what they are doing and see it on an atomic scale.

The term nanotechnology was introduced in 1974 to describe the machining of materials but it has also been applied to a wide field of small-scale engineering for manufacturing in the "nano" or atomic scale. The intention is to produce complex and valuable products from simple raw materials. A thesis in physics in 2001 [2.15] has an introductory chapter "Alchemy for a new millennium", and describes the designing of very hard materials. In these modern times some scientists have the goal – and the possibility – of changing some inexpensive base materials into substances more valuable than gold.

2.14
The Inorganic Chemistry of Life

2.14.1
Common Elements – Essential And Toxic

The dynamic nature of the processes involved is more obvious in living things than in any other field of activity on earth. Common chemical elements play the principal roles in this drama. Modern techniques of analysis reveal the presence of elements in all biological systems, human beings, animals and plants. The picture is reasonably clear. There are some elements, "*the eleven dominants*", that are present in quite high proportions in all biological systems. They constitute a group of elements necessary for all vital functions. A second group consists of "*essential trace elements*" while a third group has no biological role, at least as far as we know today. The elements in a fourth group are toxic. "Toxic" or "essential" is, however, a distinction without simple boundaries. For almost all of the essential trace elements there is a "right" level corresponding to health, while deficiency leads to disease and excess to poisoning.

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[1] 1 nanometer (nm) = 10 Å = 10^{-9} m = one billionth of a meter. As atomic radii and interatomic distances are of nanometer size the nanometer has become the new size measure in nanotechnology. *Nano* is strictly speaking a Greek word meaning dwarf or small.

2.14.2
The Eleven Dominants – Bulk Biological Elements

Examination of numerous plants and animals has shown that some elements are present, others not. It is said – and written – that the element carbon is absolutely essential to life. This is true but is only one part of the truth. Hydrogen and oxygen are principal elements, as they combine to form water and the chemistry of life mainly occurs in aqueous systems. Hydrogen and oxygen are also principal elements in the sense that they are covalently bonded in a large number of carbon compounds. The simplest hydrocarbons are, however, rare in biology. Almost all molecules essential for life also have bound oxygen and very frequently nitrogen, sulfur and phosphorus as well. The mnemonic CHNOPS indicates that living matter is composed of carbon, hydrogen, oxygen, phosphorus and sulfur. CHNOPS constitute the building stones from which the matter of life is built, the matter in a plant, an animal and even in a human being. Other elements, such as sodium, potassium and calcium, take part as positive ions in the vital processes and are essential for these. Chlorine dominates as the negative ion necessary for electrical balance. The element calcium is important, not only for ion formation but also in calcium phosphate for the skeletons. The eleven dominants constitute 99.9% of all atoms in the human body. The enormous importance of hydrogen is expressed by the fact that 63% of all atoms in the body are hydrogen atoms. The percentage by weight of the eleven dominants in the human body is shown in Table 2.3.

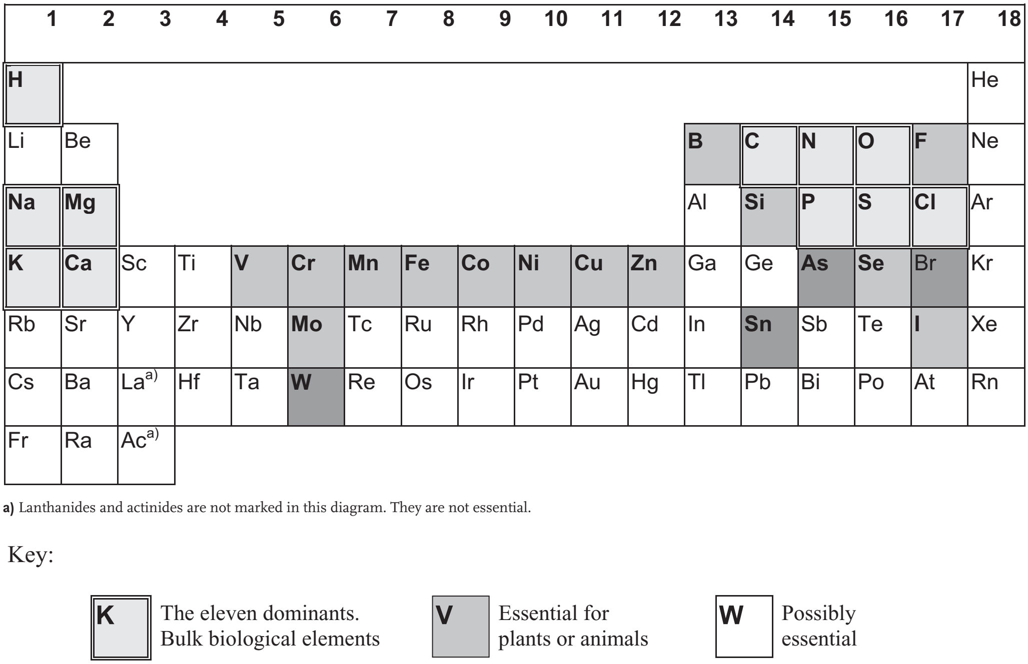
Table 2.3 Concentration of the eleven dominants in the human body

Element	**H**	**O**	**C**	**N**	**Na**	**K**	**Ca**	**Mg**	**P**	**S**	**Cl**
Weight percent	10[a]	61[b]	23	2.6	0.14	0.2	1.4[c]	0.027	1.1[d]	0.20	0.12

[a] Of which 7% is in water that makes up 65% of the body's weight.
[b] Of which 58% is in water.
[c] Of which 17% is in bones.
[d] Of which 7% is in bones and teeth.

2.14.3
Essential Trace Elements

Other elements are characterized as trace elements. They are designated essential if intake rate below a certain level leads to disease, impaired growth, failure of reproduction or other disturbances. At the end of the 19th century only two elements, in addition to some of the eleven dominants, were known to be essential for human health. These two were iron and iodine. Modern analytical chemistry has revealed that living matter contains many elements that are vital, although present in low concentrations. The essential trace elements are components of *enzymes* or *hormones*. The former catalyze chemical reactions in organic systems, the latter are messengers, controlling vital processes. Essential trace elements are marked in Figure 2.9. Some



a) Lanthanides and actinides are not marked in this diagram. They are not essential.

Figure 2.9 Main elements and essential trace elements [2.16]. Elements not marked in the diagram are not essential.

elements, such as strontium and barium, which are designated non-essential, *may* be essential for some species. Knowledge in this great field of matter is still incomplete.

2.14.4
Heavy Metals good for Life!

Iron and zinc are heavy metals but nature has selected them for vital functions. Almost one-third of all known proteins are *metal proteins*. They may contain iron, zinc, copper, cobalt, molybdenum, and/or manganese. With this in mind it is not fair to equate “heavy metal” with “environmental poison”. It is a part of the dynamics of life that elements, even heavy metals, that are available in the environment in safe amounts have been used for the development of organisms.

2.14.5
The Risk of Deviating from Just Right

Most elements, even essential ones, are injurious to an organism if the intake is too high. Selenium is typical. It is toxic to humans even in doses that only slightly exceed the recommended intake values. On the other hand it is definitely unhealthy if the intake is too low. Arsenic blocks sulfhydryl groups and is well known to all of us as a deadly poison. On the other hand for some animals it is an essential element that supports growth and reproduction. Some other elements are essential in one form and poisonous in another. Chlorine as chloride ion is extremely important for life but as chlorine gas it is extremely toxic. Chlorine transforms hydrocarbons to DDT (an insecticide) and PCBs (polychlorinated biphenyls), which are very injurious to the environment.

The biological functions of the specific elements are treated in the different element chapters. Some general information is collected in Table 2.4. A historical description, also containing fascinating anecdotes regarding trace elements, has been written by J. Lenihan [2.17].

Table 2.4 Examples of disturbances and diseases in humans and animals, caused by deficiency and excess of essential trace elements

Element	Effect of		Comments
	Deficiency	Excess	
Fluorine F	Increased incidence of dental caries	Fluorosis. Gives spots on the teeth	Fluorine favors structural resistance of teeth
Iodine I	Goiter and cretinism	Goiter and thyrotoxicosis	Iodine is a component of thyroid hormones
Selenium Se	Endemic cardiomyopathy or Kesham disease (a disease of the heart muscle). Osteoarthropathy or Kashin-Beck disease (broadening or thickening of the tips of the fingers)	Selenosis (hair and nail loss); blind staggers and chronic alkali disease (grazing-cattle)	Component of gluthathione peroxidase. Contributes to neutralizing free radicals
Iron Fe	Anemia. General weakness	Hemochromatosis, an inherited disorder that causes the body to absorb and store too much iron. especially in liver, heart, and pancreas	Iron is a component in hemoglobin and enzymes important for the respiratory function
Copper Cu	Anemia; ataxia; defective melamine production and keratinization	Liver necrosis, e.g. in Wilson's disease; hypertension	Copper is a component of oxidative enzymes involved in heme synthesis
Zinc Zn	Anorexia; growth reduction; sexual immaturity. Depression of immune response	Relatively non-toxic except at high doses	Zinc is a component in many enzymes

Table 2.4 continued

Element	Effect of		Comments
	Deficiency	**Excess**	
Manganese Mn	Skeletal and cartilage defects; depressed reproductive male function	Psychiatric disorders – manganism. Influences memory and speech. Gives hallucinations	
Nickel Ni	Growth reduction; Impaired reproduction; prenatal mortality (in animals)	Lung cancer; contact dermatitis, mostly in women	Nickel may replace other metals in their ordinary sites in enzymes
Cobalt Co	Anemia; anorexia; growth reduction. White liver disease (in sheep)	Heart failure; hypothyroidism	Cobalt is a component of vitamin B_{12} and involved in the synthesis of hemoglobin
Molybdenum Mo	Growth reduction; defective keratinization	Anemia; persistent dysentery (grazing animals)	
Chromium Cr	Impaired glucose tolerance; elevated serum lipids; corneal opacity	Hexavalent chromium, CrO_3, CrO_4^{2-} can give lung cancer. Chromium may cause contact dermatitis, mostly in men	
Vanadium V	Growth depression; failure of reproduction	Unknown except at high doses	Vanadate competes possibly with phosphate in important biological processes
Arsenic As	Impairment of growth and reproduction (animals)	Poisonous	Blocks sulfhydryl groups of enzymes

Data mainly from ref [2.16]

There are great areas on earth that are not suitable for farming owing to a deficiency of essential elements. The plants do not grow well and the crops produced will not be satisfactory as food for people or animals. In these cases necessary steps must be taken, mainly the addition of minerals with fertilizers. Even in normal areas, with good mineral access from the start, modern effective agriculture cannot go on without addition of essential elements. Besides the common additions of potassium, phosphorus, nitrogen and calcium, some soils need additions of copper, manganese, and so on. On sheep farms the animals lick cobalt sticks in order to build up vitamin B_{12}.

2.14.6
A dynamic Earth

Our earth is dynamic. Everything changes. Continental movements as well as formation of rocks and mountain chains occur over incredibly long times. The inland ice in glacial periods forms and melts away, also on a geological time scale. Volcanism and earthquakes have changed the crust as long as the earth has existed and has caused tragedies for people in the catastrophe zones. Humanity has given itself the right to optimize comfort and happiness. This has influenced the life conditions of people, animals and plants. Energy generation by fossil fuels has increased the contents of carbon and sulfur dioxides in the atmosphere. Sulfur dioxide has made the deposits (rain) acid with the negative effect that metals bound in soils have been dissolved and redistributed in nature, influencing organisms. The carbon dioxide emissions contribute to the greenhouse effect and may affect our future. These events in our time, a consequence of the industrial development, occur much faster than geological processes but yet so slowly that they can be detected only with uncertainty. Scientists measure and report, wise men and women debate and decide on policies at international conferences. Other processes, initiated by humans, rapidly change the conditions on earth. In an individual's lifetime we have seen how the streams in villages and cities can be changed to main sewers but we have also seen that they can be restored through political decisions and technical knowledge. What an experience to have the possibility to bathe in the water flowing through the Swedish capital and to see the salmon again migrate up the river Rhine! In the same human lifetime we have been told that birds may become silent for ever and that the white-tailed eagles brood their eggs in vain. Chemical knowledge has clarified the background and environmental legislation has saved several species in nature.

The elements on earth and combinations of them are the building blocks for soil, water and air and are also the material base for all life. Knowledge of the elements and of matter is vital for an understanding of nature and for the possibility of keeping the earth as a suitable and safe place for people, animals and plants.

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3
The Elements – Origin, Occurrence, Discovery And Names

3.1
The Synthesis Of Elements In Stars And In Supernova Explosions

One of the main theories in modern cosmology, the *Big Bang* theory, proposes that about 15 billion years ago the whole universe was concentrated to a *singularity* of extreme density. Time and space did not exist, nor did stars, planets, minerals or elements. Everything arose from “nothing”, initially just a hot plasma of quarks and electrons, which rapidly cooled down.

Then protons and neutrons were formed along with atoms of the elements hydrogen and helium. Ever since this creation the universe has continued to expand. About one billion years after the Big Bang large domains with enhanced concentrations of matter developed. Gravitational forces attracted still more matter to these regions. From the huge clouds of hydrogen and helium, which floated through space, large concentrations of rotating matter were formed, the forerunners of the galaxies. It has been calculated that after the Big Bang 77% of the mass of the universe consisted of hydrogen while 22% was helium. This is consistent with the present composition of our whole galaxy, the Milky Way. All the elements other than hydrogen and helium contribute only 1%. Oxygen amounts to 0.8% of the mass of the galaxy, iron, the most common metal, 0.1%.

Where the density of matter became high enough, stars were formed, the heat of which was created and maintained by thermonuclear reactions. This implies that hydrogen nuclei combine to helium nuclei while fusion energy is set free to maintain the temperature. As helium is formed hydrogen is consumed. When the “supply of fuel” begins to run out in the center of the star, it will be compressed. The temperature then increases and when it has reached an unimaginable 100 000 000 degrees, three atoms of helium can combine to one carbon atom. The synthesis of elements has started. (However, in our sun, small as it is, no atoms heavier than helium can be synthesized). In bigger stars carbon forms neon when helium runs out and the process continues: neon forms oxygen, oxygen forms silicon. When silicon finally starts to synthesize iron the star is close to catastrophe. Iron is the most stable of all atoms and no formation of heavier atoms is possible. Nuclear reactions cease, internal pressure falls off, and the gravitational force takes over. Thus iron is the heaviest

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element that can be created in a star, however big it may be! This gives rise to questions.

If iron has been created in big stars outside our planetary system where does the iron in Kirunavaara's big magnetite ore deposit in northern Scandinavia come from?

If no heavier elements than iron can be created in "sidereal furnaces" anywhere, where does the uranium in pitchblende come from?

The answer is *supernova explosions*.

When the nuclear reactions have come to an end, the central parts of the star collapse very rapidly and reach the same density as an atomic nucleus. At this point the collapse changes character to an explosion, which destroys the heart of the star and heats the components up to tremendous temperatures. During this supernova explosion the elemental contents of the star are spread out. In the very moment of explosion heavier elements are created and distributed into interstellar space. This matter is built into new stars and their planetary systems. Figure 3.1 shows the abundance of the elements in our own solar system.

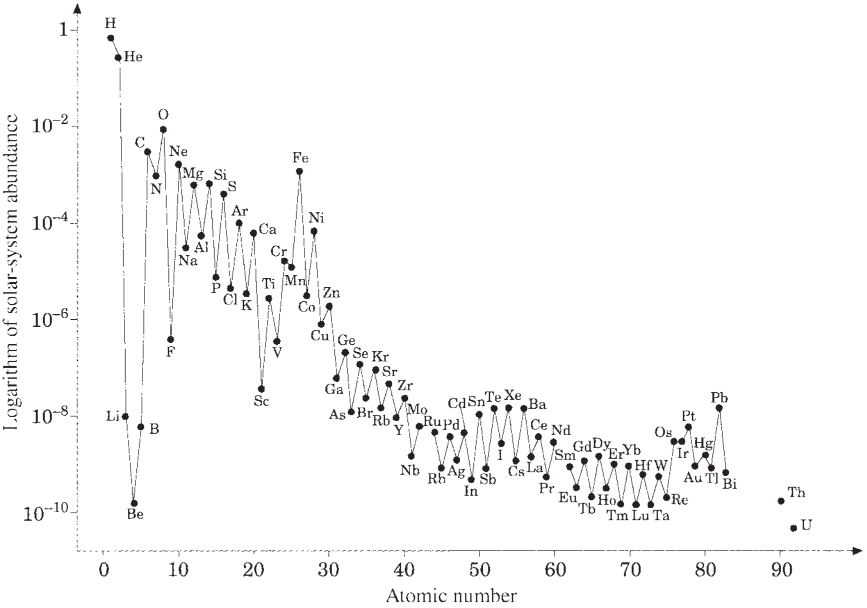


Figure 3.1 Abundance in the solar system of the elements versus their atomic number. Abundance is expressed as the logarithm of the numbers of atoms relative to 10^6 atoms of silicon. The zigzag pattern of the curve shows that elements with even atomic numbers are more common than those with odd atomic numbers (Harkin's rule) (Reprinted from A. H. Brownlow [3.1] and G. Faure [3.2])

3.2
The Earth

3.2.1
Building Up

Our own solar system was formed ca. 4.5 billion years ago out of matter from supernovas and other interstellar substances, and the earth is one of the nine planets in this system. The different zones within the planet are shown in Figure 3.2. The mantle constitutes ca. 83% of the earth's total volume and consists mainly of iron and magnesium silicates. The *lithosphere* is the solid portion of the earth as contrasted with the atmosphere and the hydrosphere. It includes the earth crust and the upper mantle. Between 100 and 400 km depth in the upper mantle is a plastic shell, the partially molten *asthenosphere*. Currents in that medium cause the movements of the continents. The core is believed to consist of an alloy of iron and nickel, and to contain also up to 10% of a lighter element, perhaps sulfur or oxygen. The inner central core is solid, the outer fluid. The temperature in the center is about 4000°C.

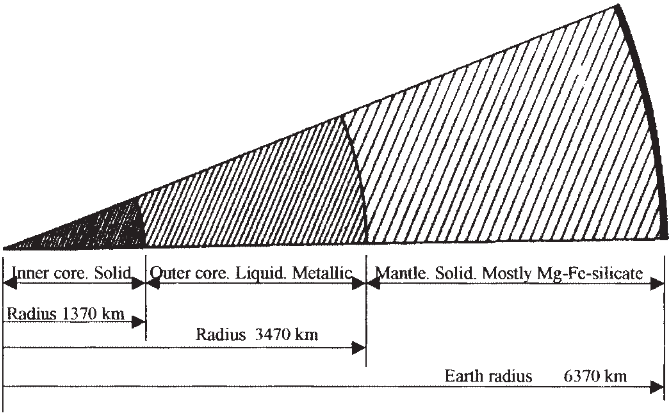


Figure 3.2 The inner structure of the earth (Based on a figure in Gunnar Hägg, General and inorganic chemistry, 8th edition, (in Swedish), 1984, Almqvist & Wiksell, Stockholm. With permission

The interior of the earth is almost inaccessible to direct observations. Deep drilling (on the Kola Peninsula) has reached a depth of 13 km at the very most. The radius of the earth is 6370 km. How is it then possible to know anything about the structure and composition of the interior of the earth? Gravitational and magnetic fields give some information. Most important, however, are techniques that study the pattern of motion for seismic waves. Vibrations from earthquakes and explosions propagate through the earth. They can be recorded by seismographs and give information of the interior of the planet.

Andrija Mohorovicic in Zagreb discovered the existence of zones with distinct boundaries within the earth. He analyzed seismic records after an earthquake in central Europe in 1909 and found that the results indicated an unexpected speed change for the seismic waves at a certain level within the earth. He concluded: "There must exist a sudden change in the matter of which the interior of the earth is built up".

What Mohorovicic originally discovered was the boundary between the earth's crust and the upper mantle. This boundary was named *Mohorovicic's discontinuity* or simply *Moho*.

The propagation of seismic waves depends on the properties of the rocks. According to the angle of incidence, waves are reflected or broken at a distinct interface. Nowadays hundreds of seismic observatories, spread round the earth, cooperate in recording seismograms from earthquakes and big explosions. From these results certain conclusions can be drawn about the structure of the earth, see Figure 3.3. At Moho the propagation speed of the seismic waves increases markedly.

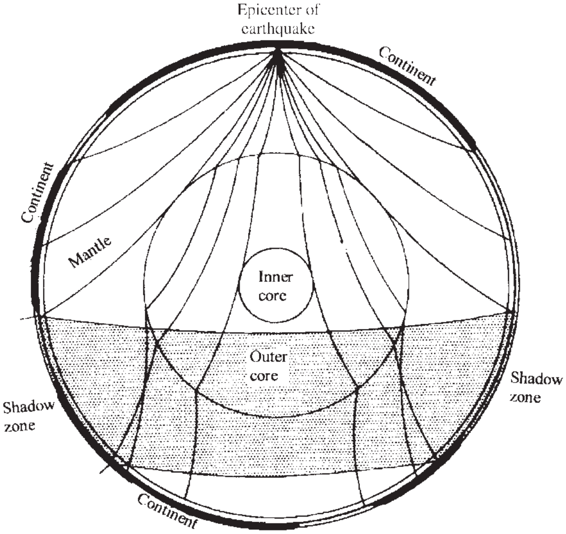


Figure 3.3 Seismic waves within the earth (From Jan Lundqvist Geologi. Processer-landskap-naturresurser. Studentlitteratur, Lund, Sweden, 1988. With permission.)

3.2.2
The Earth's Crust

The crust, with which we humans come in contact, constitutes only 0.4% of the earth's total mass. It is established that Moho lies at a depth of about 10 km beneath the oceans and 30–70 km (average 35) beneath the continents, and these figures also express the thickness of the earth's crust, see Figure 3.4.

The upper parts of the earth's crust are built mainly of light crystalline rocks (granites) while the lower parts (incompletely known) are dominated by dark rocks, diorites and gabbros.

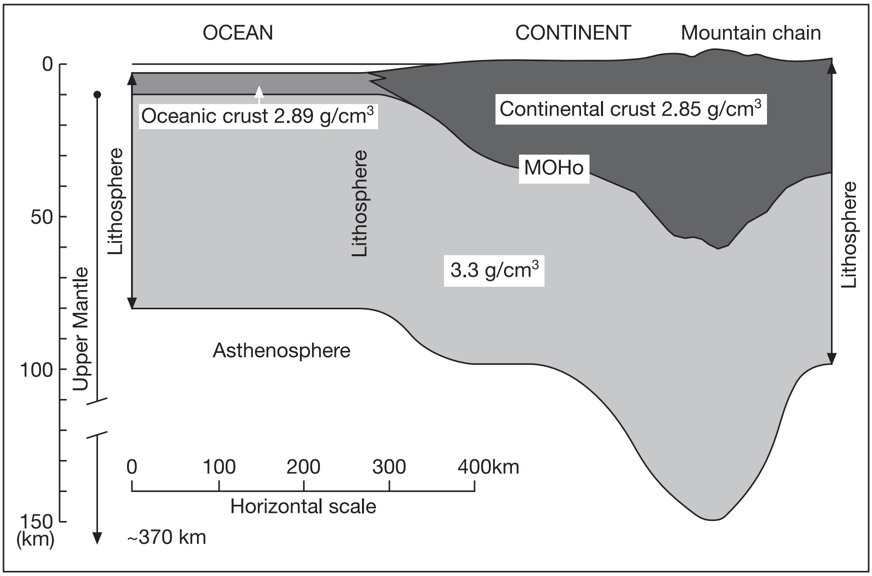


Figure 3.4 The thickness of the earth's crust and mantle. It is clear how much thicker the continental earth crust is below a mountain chain (From Bengt Loberg, Geology, Norstedts, Stockholm, 1993. With permission.)

The content of radioactive nuclides is largest in the granite layer.

On the very sea bed of the oceans there is loose matter – fine-grained mineral particles and remnants of organisms. The crust below consists mainly of dark basaltic rocks, formed from magma that has penetrated the mantle.

Within the crust a rock-forming activity is continuously going on. Remelting and recrystallization occur, rocks fold and break. Deep processes like these receive their energy from earthquakes and volcanism. Minerals and rocks thus generated are said to be *endogenous*, as they have been created within the earth. In contrast, *exogenous* rocks are those that have been formed by weathering, erosion, dissolving and transport processes on the surface of the earth.

In Table 3.1 the mean contents are given for all elements with a concentration of at least 0.001 g/tonne. The elements have been collected in groups each covers an order of magnitude of the selected concentration scale g/tonne. Within each group elements are arranged in order of decreasing content.

It is notable that elements regarded as common, e.g. copper and tin, are in reality quite rare while some "rare" elements, such as titanium, are very common.

Table 3.1 Mean contents of the elements in the accessible earth crust. Within each row the elements are arranged in order of abundance, those present at less than 0.001 ppm are excluded.

Concentration range		Elements within the concentration range
g/tonne (ppm)	%	
>100 000	>10	O, Si
100 000–10 000	10–1	Al, Fe, Ca, Na, K, Mg
10 000–1000	1–0.1	Ti, H, P
1000–100	0.1–0.01	Mn, F, Ba, Sr, S, C, Zr, Cl, V, Cr
100–10	0.01–0.001	Rb, Ni, Zn, Ce, Cu, Nd, La, Y, Co, Sc, Li, Nb, Ga, N, Pb
10–1		B, Th, Pr, Sm, Gd, Dy, Ar, Er, Yb, Cs, Hf, Be, U, Br, Sn, Eu, Ta, As, Ge, Ho, W, Mo, Tb
1–0.1		Tl, Lu, Tm, I, In, Sb, Cd
0.1–0.01		Hg, Ag, Se, Pd
0.01–0.001		Bi, He, Ne, Pt, Au, Os, Ir, Rh, Te, Ru
<0.001		Re, Kr, Xe, Pa, Ra, Ac, Po, Rn, Pm, At, Fr, Tc

3.2.3
The Oceans – The Hydrosphere

The earth is a watery planet and the hydrosphere is large. Land makes up less than one-third of the surface of the earth. The age of the oceans is probably of the same order as the age of the continents. The water has its origin in the mantle.

3.2.3.1 The Composition of the Oceans

The ocean water contains ca. 3.5% salts, mainly sodium chloride but also chlorides and sulfates of magnesium. It contains practically all elements even though in very low percentages (Table 3.2). The elements are present as individual ions, colloidal metals or oxides/hydroxides and as dissolved gases. The latter are mainly oxygen and carbon dioxide, the contents of which are determined by exchange with the atmosphere and by biological activity. For life in the oceans the presence of nitrogen and phosphorus as nutrients is important.

Table 3.2 Mean contents of the most common elements in the oceans

Concentration range		Elements within the concentration range
g/tonne (ppm)	%	
100 000–10 000	10–1	Cl, Na
10 000–1 000	1–0.1	Mg
1 000–100	0.1–0.01	S, Ca, K
100–10	0.01–0.001	Br

3.2.3.2 The Residence Time of Elements in the Oceans

The residence time is the average time an atom of an element spends in the ocean. Elemental flux through the oceans can be measured by river input and rate of removal into the deep-sea sediments. An argument against this first approach is the complexity of mixing in estuaries and the effect of human activities on some elements in river water. The alternative method is to use the composition of oceanic pelagic sediments as a measure of elemental flux. Residence times calculated by the two methods are highly correlated but not perfectly concordant. Calculated residence times are uncertain but some values from ref. [3.3] are shown in Table 3.3 to give some idea of their magnitude. The reasons for differences in residence time between different elements are discussed in Chapter 4, Geochemistry.

Table 3.3 Residence times for some elements in the oceans

Element	**Residence time τ**	
	log τ	**τ years**
Cl	7.9	$79 \cdot 10^6$
Na	7.7	$50 \cdot 10^6$
Mg	7.0	$10 \cdot 10^6$
Mn	4.0	$10 \cdot 10^3$
Al	2.0	100

Data from ref [3.1].

3.2.4
The Atmosphere

The lowest 11 km of the atmosphere is called the *troposphere*. It is in this layer we breathe and survive. Above the troposphere different layers are identified. At a height of several hundred kilometers the atmosphere gradually changes over to space.

The composition of the atmosphere varies with the height over the surface of the earth. The mean content is given in Table 3.4. Other than argon the noble gases are present in very low concentrations. Water vapor is of course also present.

Table 3.4 The mean composition of the dry atmosphere at the earth's surface

Component	**Content Volume %**
Nitrogen N_2	78.1
Oxygen O_2	20.95
Carbon dioxide CO_2	0.035
Argon Ar	0.93

3.3
The Periodic Table of the Elements

3.3.1
A Pattern for the Elements

In spite of the fact that elements and their atoms consist of different parts and can be decomposed, the elements are the building stones of which all matter is constructed. The same type of elements form the earth's crust, the water in the oceans, the high-temperature alloys in airplane engines, the material in plastic cups and the matter in the complicated structures of living things.

In the middle of the 19th century a pattern was observed in the properties of the elements known at that time. The development of *the periodic table of the elements* started. Berzelius' atomic weight determinations from 1815 onwards were a foundation. In 1829 *Johann Wolfgang Döbereiner* in Germany observed that some elements with similar properties occur in triads, groups of three. He mentioned chlorine, bromine and iodine; calcium, strontium and barium; sulfur, selenium and tellurium; iron, cobalt and manganese. When the British chemist *John A. R. Newland* listed known elements by increasing atomic weight he observed in 1864 that similar chemical properties return with a frequency of eight elements. He expressed this periodicity as the "law of octaves" as in musical scales. The fact that the properties of all elements seemed to be a periodic function of their atomic weights was developed independently and periodic systems were presented in 1869 by the Russian chemist *Dmitrij Ivanovitch Mendelejev* (Figure 3.5) and in 1870 by *Julius Lothar Meyer* in Germany.

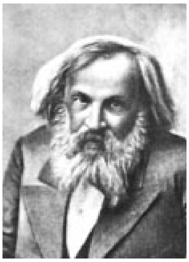
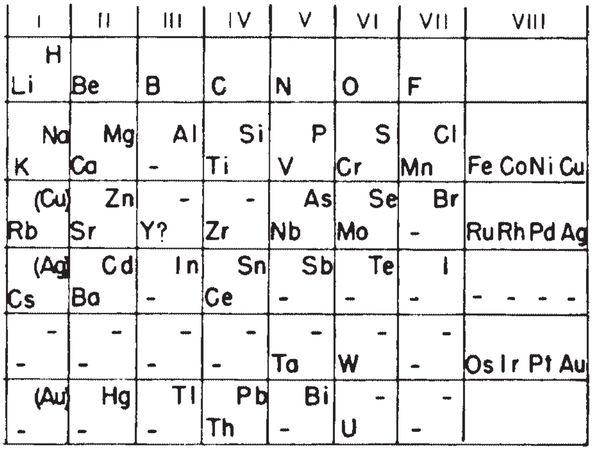


Figure 3.5 D. I. Mendelejev (1834–1907)

An early version of Mendelejev's table is shown in Figure 3.6, and in 1871 he presented a complete system with 12 horizontal periods and 12 vertical groups based on all 63 elements known at that time, including didymium but excluding terbium, the existence of which was disputed in the period 1860–1880.

> Dimitrij Mendelejev was born in Tobolsk, Siberia on February 7, 1834. He was the youngest of 14 children in one of the pioneer families, whose duty it was to transform the eastern provinces of the huge Russian empire. His father was Principal of the local high school in Tobolsk. He died and Dimitrij's



I	II	III	IV	V	VI	VII	VIII
H Li	Be	B	C	N	O	F	
Na K	Mg Ca	Al -	Si Ti	P V	S Cr	Cl Mn	Fe Co Ni Cu
(Cu) Rb	Zn Sr	- Y?	- Zr	As Nb	Se Mo	Br -	Ru Rh Pd Ag
(Ag) Cs	Cd Ba	In -	Sn Ce	Sb -	Te -	I -	- - - -
- -	- -	- -	- -	- Ta	- W	- -	Os Ir Pt Au
(Au) -	Hg -	Tl -	Pb Th	Bi -	- U	- -	

Figure 3.6 One of Mendelejev's early schemes (1870) for the periodic table of the elements [3.4]

> mother was left with the impossible task of providing for the large family. Perhaps the older brothers and sisters had to take care of each other. Their mother was determined to give young Dimitrij the opportunity to study science, and she tried, without success, to get him approved as a student at the University of Moscow. She traveled with him further to St Petersburg. There he was given the opportunity to study mathematics, physics and chemistry and was so successful that he was offered the chance to travel in Europe to further improve his knowledge. In Heidelberg he learned spectroscopy from Bunsen and Kirchhoff. At the age of 32, in 1866, he was appointed professor of chemistry at the University of St Petersburg. He wrote a book *Principles of Chemistry* and founded the *Russian Chemical Society* in 1868. Above all, however, he is remembered for *The Periodic System of the Elements.*

Mendelejev's work was admirable. The system he created made it possible for him to draw bold conclusions about facts beyond the actual experimental results, limited as they were at that time. Some examples:

- Beryllium, discovered in 1797 by Vauquelin in Paris, very much resembled aluminum, discovered by Oersted in Copenhagen in 1825. The similarity led chemists to suppose that beryllium was trivalent like aluminum. There was, however, no place in Mendelejev's system for a trivalent atom with beryllium's atomic weight. Because of that, Mendelejev placed Be in group 2, which would imply a normal oxidation state of 2 for the metal in spite of the similarity with aluminum. Later chemical research proved that his opinion had been right.
- During the early period, there were some gaps in the periodic table. Missing elements were given preliminary names, *eka-boron (*the gap after boron), *eka-aluminum* (the gap after aluminum), *eka-silicon* (the gap after silicon). *Eka* is Sanskrit and means "*one*". Mendelejev used it as "*the first after …*". Mendelejev anticipated

that these elements would be discovered and he made forecasts about their properties. When the elements were discovered and examined their real properties were in surprisingly good accordance with Mendelejev's predictions. The wise man in St Petersburg became considered as a prophet of his time.

Later the "eka" symbolism was used also for the missing elements after manganese. Table 3.5 contains the years of discovery and the names of the eka elements.

Table 3.5 Discovery years and names for the eka-elements

Eka-element	After discovery called	Discovery year
Eka-boron	Scandium	1879
Eka-aluminum	Gallium	1875
Eka-silicon	Germanium	1886
Eka-manganese	Technetium	1937
"Dwi-manganese"[a]	Rhenium	1925

[a] Dwi is also Sanskrit with the meaning "two". Thus the second after manganese.

At first, Mendelejev's system was not taken very seriously, but things changed in 1875 when Lecoq de Boisbadran discovered the element gallium in Paris. Mendelejev was able to show that this new element was just eka-aluminum and he also pointed out, without having seen gallium, that Lecoq's reported atomic weight was too low. A new investigation in Paris confirmed Mendelejev's statement.

3.3.2
The Modern Periodic Table

From the beginning the periodic table was built up by ranging the elements according to their atomic weights. It gradually became clear that the table ought instead to be based on atomic numbers. However, the atomic weights are transposed in relation to the atomic numbers only for three pairs of elements, see Table 3.6.

In all modern systems the elements are ranged according to their atomic number.

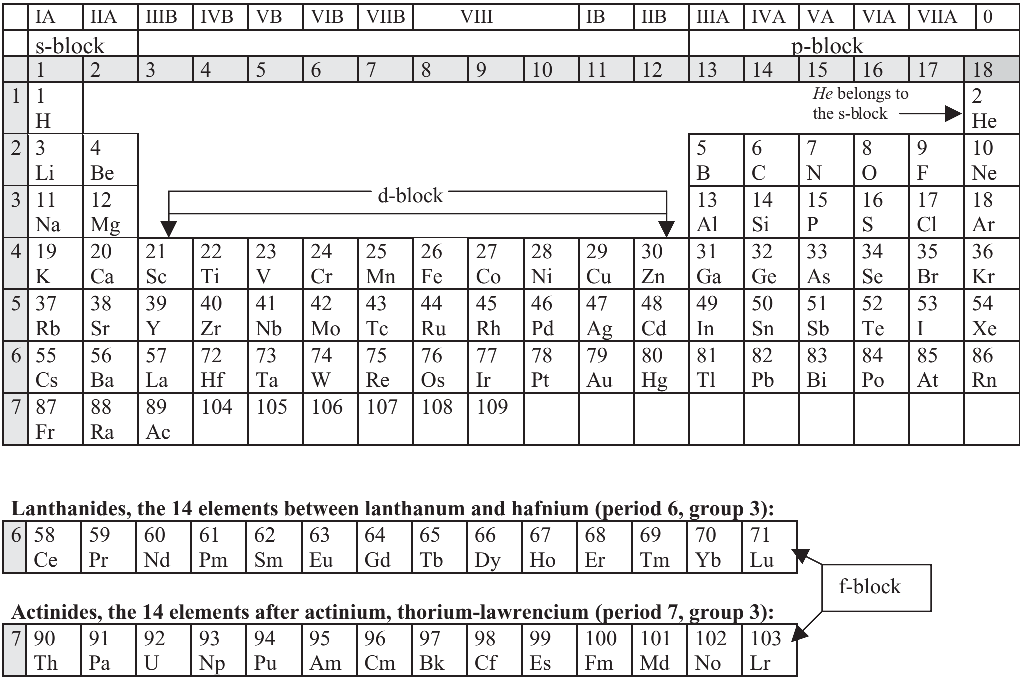
The periodic table has undergone an essential elaboration since its original formulation by Mendelejev. Many new elements have been discovered and found their positions in the system. A whole new family of elements, the noble gases, was quite unexpected in the 19th century and had to be given its own group. The noble gases are normally inert due to the fact that their electron shells are completely filled. Other elements have some shells only partially filled, which explains their chemical reactivity.

In the modern periodic table the elements are ranged according to their atomic number in seven horizontal periods. Periods 1–6 contain a maximum of 2, 8, 8, 18, 18 and 32 elements respectively. Period 7 can also be expected to have room for 32 elements although all these are not yet known.

Table 3.6 The three exceptions when atomic number increases while atomic weight decreases

Atomic number and element name	Atomic weight
18 argon	39.95
19 potassium	39.10
27 cobalt	58.93
28 nickel	58.69
52 tellurium	127.60
53 iodine	126.90

The vertical columns, the groups of the system, containing elements mutually related to each other, were earlier numbered IA –VIIA, IB – VIIB, VIII and 0 (marked in Figure 3.7). It was difficult to grasp and has now been replaced by the system recommended by the International Union for Pure and Applied Chemistry (IUPAC). In this the groups are numbered 1–18. These are also shown in Figure 3.7. In period 6 there are 32 elements but only 18 squares. This is solved for practical but also theoretical reasons (compare Chapter 17) by placing all 14 lanthanides in the square for group 3, period 6. In the same way, the actinides in period 7 are placed in one square.



	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	s-block												p-block					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H														*He* belongs to the s-block →			2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	d-block										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104	105	106	107	108	109									

Lanthanides, the 14 elements between lanthanum and hafnium (period 6, group 3):

6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

f-block

Actinides, the 14 elements after actinium, thorium-lawrencium (period 7, group 3):

7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 3.7 The modern periodic table

In 1927 *Erwin Schrödinger* suggested that an electron in a hydrogen atom should be described by a mathematical equation, now called the *Schrödinger equation*. Wave functions are in general analyzed in terms of the three variables required to define a point with respect to the nucleus. Using *three quantum numbers* for the solution of the Schrödinger equation we obtain solutions called *orbitals*. An orbital in a multielectron atom is of the same type as in the hydrogen atom. These hydrogen-like orbitals can "contain" one or two electrons, characterized by specific values of

- the principal quantum number n ($n = 1, 2, 3, 4, 5, 6, 7$)
- the second or orbital quantum number l ($l = 1, 2, 3 \ldots (n{-}1)$)
- the magnetic quantum number m ($m = 0, \pm 1, \pm 2, \pm 3, \ldots \pm l$)

With two electrons present in an orbital they must have different *spin quantum numbers* $= \pm 1/2$. Electrons occupy orbitals in a way that minimizes the energy of the atom.

From this quantum-mechanical viewpoint the elements in the periodic table are divided into four blocks, illustrated in Figure 3.7.

For the periodic table it is important that all orbitals with the same value of n are in the same principal electronic shell and all orbitals with the same n and l are in the same subshell. The number of orbitals in a subshell is the same as the number of allowed values of m. Instead of using numerical values for l it is customary to use letter symbols, as the spectroscopists did long before the introduction of the quantum mechanics (see Table 3.7).

Table 3.7 Orbital or second quantum number l and corresponding letter designations

The second quantum number l	Letter designation
0	s
1	p
2	d
3	f

The conventional way to designate the electron configuration in an atom is exemplified in Table 3.8.

The elements in groups 1 and 2 easily lose their outer electrons forming ions with the same electronic structure as the nearest preceding noble gas. The elements nearest the noble gases, groups 16 and 17, instead have a tendency to add electrons to form negative ions with the same electron configuration as the following noble gas. Boron, carbon, nitrogen, silicon, phosphorus, all from groups 13–15 are not inclined to form ions by electron loss or gain. In their compounds covalent bonds predominate instead. In the vicinity of these elements we find aluminum. It appears to be different and tends to form positive trivalent ions. So has Al been given the correct place in the periodic table? Habashi [3.6] has in fact recommended a change so that Al should be placed in group 3 above scandium.

Table 3.8 Examples of electron configurations in atoms

Element	Number of electrons	Designation	Explanation
Boron	5	$1s^2 2s^2 2p^1$	The lowest energy state 1s is filled with 2 electrons with opposite spin. The next 2 electrons go to the 2s subshell. With the 5th electron the 2p subshell begins to fill
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	The complete neon configuration is followed by 2 electrons in the 3s subshell. Alternative designation: $[Ne]3s^2$. The two 3s-electrons are the *valence electrons*
Titanium	22	$[Ar]3d^2 4s^2$	Electrons have begun to fill the d orbitals of the third shell. The d subshell has a capacity of 10 electrons
Neodymium	60	$[Xe]\ 4f^4 6s^2$	After Xe (54 electrons) the subshell 6s is first filled. Then the filling of the 4f starts, in the case of Nd with four electrons.

The elements in groups 3–12, the transition metals, either have atoms with incompletely filled d-subshells or can form ions with unfilled d-subshells. They show mutual similarities not only to elements in the same group but often also to elements in different groups but in the same period. This is true for Fe, Co, Ni and for the platinum metals.

3.4
Element Discoveries

3.4.1
Stable and Unstable Elements

There are at the moment 115 known elements with atomic numbers 1–115. Of these, 93–115 exist only as the results of nuclear reactions. Strictly speaking the “natural” elements are less numerous than 92 as some occur only as radioactive isotopes with such short half-lives that their concentrations in nature are extremely low. These special elements are: *43 technetium, 61 promethium, 84 polonium, 85 astatine, 86 radon, 87 francium, 88 radium* and *89 actinium.*

These exist or existed as intermediate products in radioactive decay series. It does not mean that they are unimportant. The gaseous element radon may, as is well known, be present as a dangerous air pollutant in houses built on radioactive ground. Because the element is gaseous the radioactivity can be removed by ventilation.

Some radioactive elements have isotopes with very long half-lives, for instance *90 thorium* and *92 uranium*. The element 91 *protactinium,* Pa, has an intermediate position. It has an isotope with the half-life $3.27 \cdot 10^4$ years. Traces of Pa result from its presence in uranium ores, which made its discovery possible.

3.4.2
Who Made the Discovery?

Who is the discoverer of an element? Is it the person who originally discovered the mineral and proved that an element, not earlier detected, is present?

> William Gregor and Martin Heinrich Klaproth at the end of the 18th century independently found titanium-containing minerals and isolated the oxide of an unknown metal. They could not solve the difficult task of preparing the metal itself, which occurred later. They are, however, both known as the discoverers of titanium, and their achievements were indeed important.

Or is the discoverer the scientist who first isolated the element oxide, reduced the oxide and had the new metal in his crucible?

> Carl Wilhelm Scheele discovered the tungsten mineral scheelite. He isolated and thoroughly described tungsten oxide, which he called tungsten acid. However, he did not have an adequate furnace in his pharmacy to reduce the oxide to metal. This was done by the two Spanish d'Elhuyar brothers who are always named as the discoverers. The history of element discoveries is rather random.

When titanium dioxide, TiO_2, had been prepared from ilmenite and rutile it became an important task for chemistry and metallurgy to produce the element in metallic form. The attempts met with great difficulties that we, with our present knowledge, can fully understand.

> Gibb's free energy, G, is a function of state, the value of which determines the direction of a chemical reaction.
>
> It is the tendency for the system to go to a state with lower G that is the driving force for every process at constant temperature and pressure. In a reaction the change of free energy is $\Delta G = \Delta H - T\Delta S$. Thus ΔG is composed of the energy term ΔH and the "disorder" term $T\Delta S$ (S is entropy). If we intend to reduce an oxide MeO with a reducing agent, for instance carbon C then if the experiment is to succeed the condition is that $\Delta G < 0$ for the reaction
>
> $$\mathrm{MeO} + \mathrm{C} \rightarrow \mathrm{Me} + \mathrm{CO}$$
>
> If we compare the possibilities to reduce nickel oxide NiO and titanium dioxide TiO_2 with carbon at a temperature of 1000 K and atmospheric pressure of oxygen we note that for the reactions
>
> (a) $2\mathrm{NiO} \rightarrow 2\mathrm{Ni} + \mathrm{O}_2$ (b) $\mathrm{TiO}_2 \rightarrow \mathrm{Ti} + \mathrm{O}_2$ (c) $2\mathrm{CO} \rightarrow 2\mathrm{C} + \mathrm{O}_2$
> ΔG^0 is (a) 301 kJ (b) 766 kJ (c) 400 kJ. Thus:

Reduction of NiO with carbon:

$$\begin{array}{ll} 2NiO \rightarrow 2Ni + O_2 & \Delta G^0 = +301\ \text{kJ} \\ 2C + O_2 \rightarrow 2CO & \Delta G^0 = -400\ \text{kJ} \\ \hline 2NiO + 2C \rightarrow 2Ni + 2CO & \Delta G^0 = \ -99\ \text{kJ} \end{array}$$

so the reaction can occur spontaneously.

Reduction of TiO_2 with carbon:

$$\begin{array}{ll} TiO_2 \rightarrow Ti + O_2 & \Delta G^0 = +766\ \text{kJ} \\ 2C + O_2 \rightarrow 2CO & \Delta G^0 = -400\ \text{kJ} \\ \hline TiO_2 + 2C \rightarrow Ti + 2CO & \Delta G^0 = +366\ \text{kJ} \end{array}$$

so the reaction is impossible.

An "impossible" reaction can, however, occur to some extent if the activities on the right hand side of the reaction equation are kept very low (see textbooks in physical chemistry). Unfortunately, some elements, such as titanium, have a strong tendency to form carbides or nitrides. In a carbon- or nitrogen-containing atmosphere at high temperature any traces of metal of this type that might be formed are immediately converted to carbide or nitride.

The difference in reducibility between different oxides, demonstrated above, influences which person will be designated the discoverer of the actual element. For titanium, niobium and similar elements, those who first isolated the oxides are regarded as the discoverers. Elements that are easily reduced from their oxides, such as nickel, cobalt, molybdenum and tungsten, are said to be discovered by those chemists who actually isolated the metal.

In general the work of discovery was greatly assisted by the development of spectroscopy about 1850 and by the use of the periodic table and Mendelejev's predictions of missing elements after 1870. In Tables 3.9A and B the elements are ranged by atomic number with the year of discovery and the discoverer (with the reservations expressed above).

The discovery of an element made the discoverer well known and also gave credit to his country, an honor that came abundantly to Sweden. A quotation from Mary Weeks illustrates the reasons for that:

> In the eighteenth century Sweden outstripped all other countries in the discovery of new elements. It is blessed with a rich supply of rare ores and, moreover, it had a long succession of brilliant chemists and mineralogists whose greatest delight was to investigate these curious minerals ….

During the second part of the 18th century France was also an important center for chemistry and there was certainly a stimulating competition between the two countries. When Peter Jacob Hjelm in Stockholm discovered molybdenum in 1781 (after considerable preparatory work by Carl Wilhelm Scheele) he was congratulated by Scheele, who in his letter says that he can already hear the French deny the existence of this new element "*as they themselves have not discovered it*". A salient feature in Table 3.9 is that so many gases, including the group of noble gases, have been discovered in England.

Table 3.9A The elements 1 hydrogen to 52 tellurium. Discoveries and discoverers

Atomic number and element	Discoverer and country	Year
1 Hydrogen	Cavendish, GB	1766
2 Helium	Ramsay, GB, Cleve, Langlet, Sweden	1895
3 Lithium	Arfvedson, Sweden	1817
4 Beryllium	Vauquelin, France Wöhler, Germany Bussy, France	1797 1828 1828
5 Boron	Lussac, Thenard, France Davy, GB	1808
6 Carbon	Prehistoric	–
7 Nitrogen	Rutherford, GB Scheele, Sweden	1772
8 Oxygen	Scheele, Sweden Priestley, GB	1774
9 Fluorine	Moissan, France	1886
10 Neon	Ramsay, Travers, GB	1898
11 Sodium	Davy, GB	1807
12 Magnesium	Black, GB Davy, GB	1755 1808
13 Aluminum	Oersted, Denmark	1825
14 Silicon	Berzelius, Sweden	1824
15 Phosphorus	Brand, Germany	1669
16 Sulfur	Prehistoric	–
17 Chlorine	Scheele, Sweden	1774
18 Argon	Rayleigh, Ramsay, GB	1894
19 Potassium	Davy, GB	1807
20 Calcium	Davy, GB	1808
21 Scandium	Nilson, Sweden	1879
22 Titanium	Gregor, GB Klaproth, Germany	1791 1795
23 Vanadium	del Rio, Mexico Sefström, Sweden	1801 1830
24 Chromium	Vauquelin, France	1797
25 Manganese	Gahn, Sweden	1774
26 Iron	Known since ancient times	–
27 Cobalt	Brandt, Sweden	1735
28 Nickel	Cronstedt, Sweden	1751
29 Copper	Known ca. 5000 BC	–
30 Zinc	Zn in brass known ca. 20 BC. Zinc AD 1500	–
31 Gallium	Boisboudran, France	1875
32 Germanium	Winkler, Germany	1886
33 Arsenic	Magnus, Germany	ca.1250
34 Selenium	Berzelius, Sweden	1817
35 Bromine	Balard, France Löwig, Germany	1825–1826
36 Krypton	Ramsay, Travers, GB	1898
37 Rubidium	Bunsen, Kirchhoff, Germany	1861
38 Strontium	Crawford, GB Davy, GB	1790 1808
39 Yttrium	Gadolin, Finland	1794
40 Zirconium	Klaproth, Germany	1789
41 Niobium	Hatchett, GB	1801
42 Molybdenum	Hjelm, Sweden	1781
43 Technetium	Perrier, Segré, Italy	1937
44 Ruthenium	Sniadecki, Poland Klaus, Estonia	1808 1844
45 Rhodium	Wollaston, GB	1803
46 Palladium	Wollaston, GB	1803
47 Silver	Known since ancient times	–
48 Cadmium	Stromeyer, Germany	1817
49 Indium	Reich, Richter, Germany	1863
50 Tin	Known ca. 2100 BC	–
51 Antimony	Known ca. 1600 BC	–
52 Tellurium	Reichenstein, Romania	1783
53 Iodine	Courtois, France	1811
54 Xenon	Ramsay, Travers, GB	1898
55 Cesium	Bunsen, Kirchhoff, Germany	1860
56 Barium	Davy, UK	1808
57 Lanthanum	Mosander, Sweden	1839
58 Cerium	Berzelius, Hisinger, Sweden Klaproth, Germany	1803
59 Praseodymium	Mosander, Sweden (Didymium) Auer, Austria	1840 1885
60 Neodymium	Mosander, Sweden (Didymium) Auer, Austria	1840 1885
61 Promethium	Marinsky, Glendenin, Coryell, USA	1945
62 Samarium	Boisbaudran, France	1879
63 Europium	Demarçay, France	1901

Table 3.9B The elements 53 iodine to 92 uranium. Discoveries and discoverers

Atomic number and element	Discoverer and country	Year
64 Gadolinium	Marignac, Switzerland	1880
65 Terbium	Mosander, Sweden	1843
66 Dysprosium	Boisbaudran, France	1886
67 Holmium	Cleve, Sweden. Delafontaine, Soret, Switzerland	1878
68 Erbium	Mosander, Sweden	1842
69 Thulium	Cleve, Sweden	1879
70 Ytterbium	Marignac, Switzerland	1878
71 Lutetium	Urbain, France Auer, Austria James, USA	1907
72 Hafnium	Hevesy, Hungary, Coster, Holland. In Bohr's Institute, Denmark	1923
73 Tantalum	Ekeberg, Sweden	1802
74 Tungsten	J. and F. Elhuyar, Spain	1783
75 Rhenium	Noddack, Tacke, Berg, Germany	1925
76 Osmium	Tennant, GB	1803
77 Iridium	Tennant, GB	1803
78 Platinum	Known AD 1500	–
79 Gold	Known since ancient times	–
80 Mercury	Known ca. 1500 BC	–
81 Thallium	Crookes, GB	1861
82 Lead	Known ca. 1000 BC	–
83 Bismuth	Known ca. 1500 BC	–
84 Polonium	Curie, Marie, France (Poland)	1898
85 Astatine	Corson, Mackenzie, Segré, USA	1940
86 Radon	Dorn, Germany Rutherford, Soddy, Ramsay GB	1900–1905
87 Francium	Marguerite Perey, France	1939
88 Radium	Marie and Pierre Curie, France	1898
89 Actinium	Debierne, France	1899
90 Thorium	Berzelius, Sweden	1829
91 Protactinium	Hahn, Meitner, Fajans Germany. Soddy, Cranston, Fleck, GB	1913–1918
92 Uranium	Klaproth, Germany	1789

3.5
Element Names

The background to the element name is as a rule described in the element chapter. This section gives some general overviews.

3.5.1
Elements Known in Antiquity

The origins of the names of antique and prehistoric elements cannot be derived. Nine elements were known in ancient time, see Table 3.10.

Table 3.10 Elements known in antiquity

Metal	Latin	Non-metal	Latin
Gold	*Aurum*	Carbon	*Carbo*
Silver	*Argentum*	Sulfur	*Sulfur*
Mercury	*Hydrargyrum*		
Copper	*Cuprum*		
Iron	*Ferrum*		
Tin	*Stannum*		
Lead	*Plumbum*		

The discovery of these elements cannot be mapped out as some of them have been known since prehistoric time. Perhaps carbon was the first element to be discovered and used. The discovery of gold and copper, the earliest known metals, dates from 5000 BC. Gold is available uncombined in nature and copper can easily be prepared by reduction of its oxide with charcoal. Mercury was the last of the metals known in antiquity. Aristotle mentions "the fluid silver" about 300 BC.

The Old Testament in the Bible gives much information about metals, minerals and other materials used in ancient times. Of the nine elements mentioned in Table 3.10, all except mercury are described in the Bible.

3.5.2
Elements from the Time of the Alchemistis

The most important elements from the time of the alchemists have names with known meanings (Table 3.11).

In more modern times it became generally accepted that the discoverer of an element is also entitled to give it a name. However, the International Union of Pure and Applied Chemistry, IUPAC, has the final decision about an element's name and symbol.

Table 3.11 Some alchemical element names

Element	Named after	Language	Meaning
Arsenic	*Arsenikos*	Greek	Male; masculine
Antimony	*Anti monos*	Greek	Not alone. Not one
Bismuth	*Weisse Masse*	German	White matter; white metal
Phosphorus	*Phosphorous*	Greek	Light-carrier. Venus as morning star

Taken from ref [3.5].

3.5.3
Element Names from Celestial Bodies

Many elements have been named after celestial bodies (Table 3.12).

Table 3.12 Elements named after celestial bodies

Element	Named after	Language	Meaning
Helium	*Helios*	Greek	Greek word for the sun. Helium was observed in 1868 in radiation from the sun. It was not discovered on earth until 1895
Selenium	*Selene*	Greek	The moon
Tellurium	*Tellus*	Latin	The earth
Cerium	*Ceres*	Latin	One of the minor planets between Mars and Jupiter, discovered in 1801. The metal cerium was discovered in 1803
Palladium	*Pallas*	Greek	Asteroid discovered in 1802. The new element was discovered in 1803

3.5.4
Element Names from Mythology

Greek and Nordic mythology have contributed some element names (Table 3.13). It seems to have been Klaproth who first used mythological names for elements. William Gregor, who discovered titanium in England in 1791 (see the titanium chapter), had given the element the name "menachanite" after the Menachan valley, the source of the mineral. The discovery was forgotten and the name did not spread. Martin Heinrich Klaproth discovered uranium in 1789 and rediscovered titanium in 1795. He accepted Gregor's priority but not the element name. He selected instead the name titanium with the explanation: "*As with the naming of uranium I select titanium from mythology, where the Titans were the first sons of the earth.*" Ekeberg continued with the element name *tantalum* in 1802, Berzelius with *thorium* in 1829, Sefström with *vanadium* in 1830 and Marinsky, Glendenin and Coryell with *promethium* in 1945.

Table 3.13 Element names with mythological backgrounds

Element	Named after
Uranium	Uranos, the first world ruler according to Greek mythology
Titanium	The Titans, sons of Uranos and the earth goddess Gaia in Greek mythology
Vanadium	The goddess Vanadis in Nordic mythology
Tantalum	Tantalus, son of Zeus in Greek mythology
Niobium	Niobe, daughter of Tantalus
Thorium	Thor, the god of thunder in Nordic mythology
Promethium	Prometheus, who in Greek mythology stole fire from the gods and gave it to humankind
Neptunium	Neptune, the god of the sea in Roman mythology
Plutonium	Pluto, god of the dead in Roman mythology. A Latin counterpart of the Greek god Hades

3.5.5
Elements With Color Names

During chemical reactions preceding the discovery of an element, chemists have often observed the characteristic color of an element or its mineral and have sometimes seen with astonishment the variety of colors that an individual element can have. Sometimes the typical colors of the element's spectral lines have been emphasized. These circumstances have dictated that many elements have names that express their color and color variations (Table 3.14).

Table 3.14 Element names from colors

Element	Named after	Language	Meaning
Cesium	*Cæsius*	Latin	Sky-blue
Chlorine	*Chloros*	Greek	Greenish-yellow
Chromium	*Chroma*	Greek	Color
Indium	*Indigo*	Latin	The blue color indigo
Iodine	*Iodes*	Greek	Violet
Iridium	*Iris*	Greek	Rainbow
Praseodymium	*Prasios didymos*	Greek	Green twin
Rubidium	*Rubidus*	Latin	Darkest red
Zirconium	*Zargun*	Persian	Gold colored

3.5.6
Names from Countries and Places as Element Names

In many cases the discoverer of an element has wished to recall his country or a province, a place, a river. The most remarkable example is the small village of Ytterby in the Stockholm archipelago. At the end of the 1780s a black mineral, never seen before, was found there. As described in Chapter 17 it contained the oxide of a new metal, which was given the name *yttrium*. Later, more elements got their names from Ytterby (Table 3.15). The same table also contains other names with geographical backgrounds.

Table 3.15 Elements with geographical names

Element	Named after
Alkaline earth metals	
Magnesium	Magnesia, a region in Thessaly in Greece
Strontium	Strontian, town in Scotland
Rare earth metals	
Scandium	Scandinavia
Yttrium	Ytterby
Europium	Europe
Terbium	Ytterby
Erbium	Ytterby
Thulium	Old Roman name for the far north of Scandinavia
Ytterbium	Ytterby
Holmium	Stockholm
Lutetium	*Lutetia,* an old name for Paris
Others, except transuranic elements	
Copper	Cyprus
Gallium	*Gallia,* France
Germanium	Germany
Ruthenium	*Ruthenia*, Russia
Hafnium	*Hafnia*, Copenhagen
Rhenium	The river Rhine
Polonium	Poland
Transuranic elements.	
Americium	*The Americas,* America
Berkelium	Berkeley in California
Californium	California
Darmstadtium	Darmstadt in Germany

3.5.7
The Family of Noble Gases

The noble gases have names alluding to their origin or properties (Table 3.16).

Table 3.16 Names for noble gases

Noble gas	Meaning of the name	Noble gas	Meaning of the name
Helium	From the sun	Krypton	Hidden
Neon	New	Xenon	Stranger
Argon	Slow, lazy	Radon	From radium

3.5.8
Personal Names as Element Names

Personal names are sparingly used in the etymology of element names. This probably has something to do with the fact that Berzelius very firmly took a definite position against the use of personal names as element names. When the metal tungsten was discovered and the chemical world disputed over the names wolfram or tungsten, the famous mineralogist A. G. Werner in Freiberg proposed the name *schelium* in honor of Scheele and his considerable preparatory work with "tungstic oxide". Berzelius rejected the proposal abruptly for two reasons: "*The name is not suitable from the viewpoint of the Swedish language and the immortality of our compatriot has no need of such support.*" After that the name became *tungsten* in England and the USA, *tungstène* in France and *wolfram* in Germany, Sweden and many other countries.

Two elements among the 92 have names that are connected with personal names, even if indirectly. The rare earth metal *gadolinium* got its name from the mineral *gadolinite*, and thus indirectly from the Finnish chemist Johan Gadolin. The Russian colonel and engineer E. Samarskii-Bykhovets discovered a mineral that was given the name *samarskite*. A rare earth metal found in this mineral was named *samarium* after the mineral.

When the transuranic elements were synthesized element names derived from personal names became usual:

- *Curium* after Marie and Pierre Curie.
- *Einsteinium* after Albert Einstein
- *Fermium* after Enrico Fermi
- *Mendelevium* after Dmitrij Mendelejev
- *Nobelium* after Alfred Nobel
- *Lawrencium* after Ernest O. Lawrence, the inventor of the cyclotron

3.6
Symbols for the Elements

The seven metals in antiquity early became connected with the symbols for heavenly bodies (Figure 3.8).

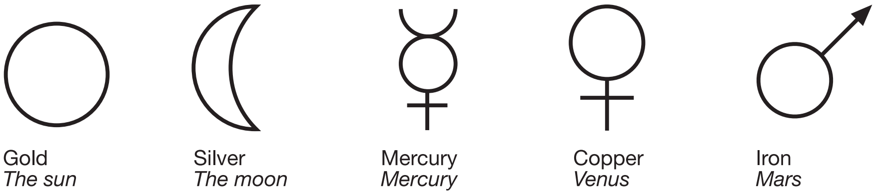


Figure 3.8 Ancient symbols for celestial bodies and corresponding metal names

These symbols (and many others for compounds) were used by the alchemists and also by artists (Figure 3.9).

Figure 3.9 Chemical symbols in art from the 17th century

During the powerful development of chemistry in the 18th century the need for appropriate symbols for the elements became obvious. Proposals were made, many of them of the same type as the old ones but with different geometric signs for different elements. J. J. Berzelius in 1813 formulated a simple, brilliant proposal: “Let the first letter in the name of the element be the symbol! Or two letters from the element’s name. But select the letters from the Latin name of the element. Then it will be intelligible in all countries”.

This proposal is illustrated in Table 3.17.

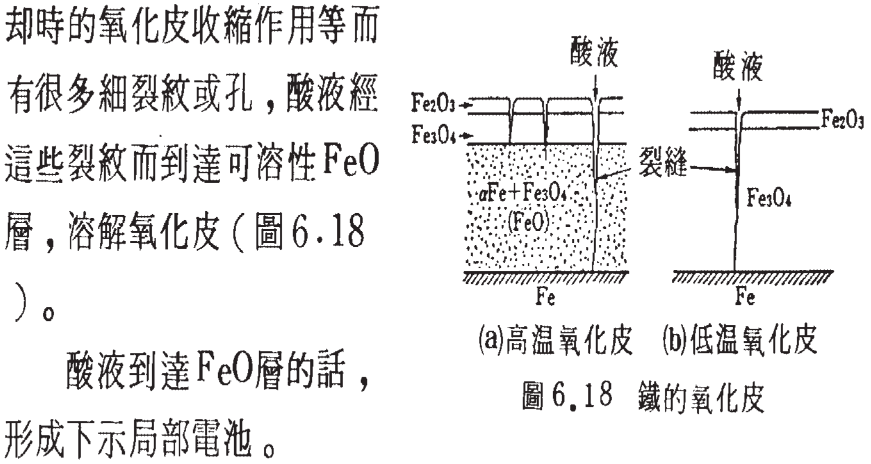
Table 3.17 Examples of Berzelius’ system for chemical element symbols

Element	Latin Name	Chemical Symbol	Element	Latin name	Chemical symbol
Iron	*Ferrum*	Fe	Hydrogen	*Hydrogen*	H
Copper	*Cuprum*	Cu	Oxygen	*Oxygen*	O
Gold	*Aurum*	Au	Nitrogen	*Nitrogen*	N
Silver	*Argentum*	Ag	Chlorine	*Chloros (Greek)*	Cl
Lead	*Plumbum*	Pb	Silicon	*Silicis silex*	Si
Mercury	*Hydrargyrum*	Hg	Carbon	*Carbo*	C
Tin	*Stannum*	Sn	Sulfur	*Sulphur*	S

The new system rapidly became accepted in Europe and America. As new elements were discovered and named they were given names and designations in accordance with Berzelius’ original principle. Only about element 41. niobium, have opinions differed right up to our own time. As described in the niobium chapter, the element has had the name columbium with the symbol Cb in America and niobium with the symbol Nb in Europe. Nowadays element 41 has the name niobium and symbol Nb according to decisions taken by IUPAC in 1949 and 1960.

It is very satisfactory that the same chemical symbolic language is used all over the world irrespective of the type of the national language.

In Russia, China, Japan and other countries with language systems quite different from the European/American system, all the same symbols are used, expressed with the Latin letters. This is exemplified in Figure 3.10, a picture from a Chinese textbook on metal manufacturing. Text and picture describe how different oxides are formed on an iron surface when the metal is heated to high temperatures. Which oxides? Chemists in all countries, even those with no knowledge of Chinese, can see that three oxide layers are formed. A thin layer of Fe_2O_3 farthest out, a thick layer of FeO farthest in and a layer of Fe_3O_4 in between.



却時的氧化皮收縮作用等而有很多細裂紋或孔，酸液經這些裂紋而到達可溶性FeO層，溶解氧化皮（圖6.18）。

酸液到達FeO層的話，形成下示局部電池。

(a)高温氧化皮　(b)低温氧化皮

圖6.18　鐵的氧化皮

Figure 3.10 Figure from a Chinese textbook of metal manufacturing

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4
Geochemistry

4.1
Common and Rare in the Earth's Crust

Humans have at all times made use of the components of the earth's crust. As a consequence of the discovery that even rare materials may have technically interesting properties, there has been a drive to widen the exploitation of natural resources. New separation methods have made the extraction of desirable elements possible. Such rare elements are often obtained as by-products of the mining of common ores. Gold and platinum, for instance, are present in the anode sludge from electrolytic copper refining. The mineral molybdenite, a sulfide, is "roasted" at 800°C to the oxide from which molybdenum metal and its alloys are produced. During the roasting process the oxide of a rare element, rhenium, volatilizes and its compounds can be extracted from the gas phase as a by-product. Several examples of this type are treated in the different element chapters of this book.

We have ingrained opinions about *common* and *rare* regarding the occurrence of elements. We know that the element *silver* is expensive, but it is so well known that we think it must be fairly common. On the other hand, many of us have perhaps never heard of the metal *gallium*, so we think it must be a very rare element. In the light of these experiences it is difficult to accept the statement in the chemical literature that the mean content of silver in the earth's crust is 0.07 g/tonne, (0.07 ppm) while the content of gallium is 18 g/tonne. Thus the "rare" element gallium is 250 times more common than the well-known silver. So why has silver been known and used since prehistoric times while gallium was not discovered until 1875 in Paris and thus got its French name? Some of the elements that have played big parts in our daily lives and have been well known for a long time are as a matter of fact very rare. Why is this so? More examples are given in Table 4.1.

Rare elements, such as silver, with a low mean content in the earth's crust are well known if two criteria are fulfilled:

- They are the main components in minerals that occur in only a few localities.
- They are easy to reduce to metals from their oxides or easy to convert to usable materials in other ways.

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Table 4.1 Well-known elements can be rare and rare ones common

"Common" element	Comments
Copper	Less abundant than zirconium
Lead	Gallium is equally abundant
Mercury	Less abundant than rare earth metals
Nickel	Rubidium is equally abundant
Arsenic	Not as abundant as scandium
Tin	Much less abundant than vanadium
Iodine	Not as abundant as hafnium, so difficult to discover

On the other hand we realize that there is a substantial difference between the mean content of an element in the earth's crust and its accessibility. Two reasons may be mentioned for *common elements* appearing to be rare:

- Some elements do not form their own minerals but are present in the minerals of other elements. For example, gallium has many similarities with aluminum and is widely present in aluminum minerals. In the same way, the alkali metal rubidium is present in practically all potassium minerals. The element germanium ("eka-silicon") is very like silicon. That is why the element is finely scattered among the silicates in the upper lithosphere.
- Other elements with a relatively high mean content in the earth's crust do form specific minerals but these are highly dispersed among other minerals. Local deposits with a high element content are missing. As a consequence the element is perceived as rare. Examples are titanium and zirconium.

Geochemistry takes up these issues and, to some extent, provides answers. This is why geochemistry is included in this book about the elements on earth and their discovery.

Geochemistry treats the earth as a chemical system. One of the main tasks for this rather young science is to determine the chemical composition of the earth. Another is to formulate the rules that control (and have controlled) the movements of the elements and their distribution between different minerals and rocks in the crust. The result is that geochemistry is to a high degree the chemistry of silicates. (Silicate chemistry is treated in Chapter 40 Silicon.) For the earth as a whole, size and composition are estimated and the same is true for its different parts: the core, the mantle, the crust, the hydrosphere and the atmosphere.

4.2
Analysis of the Earth's Crust – a Geochemical Task

The earth's crust is a thin shell with only 0.5% of the total mass of the earth. It has, however, a vital role in our existence, as the elements we use come mainly from this thin shell.

The distribution of elements between the different parts – core, mantle, crust, hydrosphere and atmosphere – occurred mainly when the planetary system was formed, but a continuous redistribution occurs through different chemical and geological processes.

In the investigation of the chemical composition of the earth the crust was naturally the target goal. During the 19th century, geochemical base data were received from mineral and rock analyses made in connection with ore prospecting.

4.2.1
Early Results from the US Geological Survey

In 1884 the US Geological Survey was formed. *F. W. Clarke* worked there from the beginning and he achieved much by collecting and analyzing a very large number of samples of minerals, rocks and ores. In 1889 he published the classic *The Relative Abundance of the Chemical Elements*. It was a first attempt to use his large number of rock analyses to express the composition of the earth's crust as a whole. A new work with new facts, *The Data of Geochemistry* was published in 1908, and was published in five editions over a period of twenty years. Table 4.2 contains the mean values of 5159 analyses that Clarke and Washington published in the USA in 1924. Clarke and Washington regarded the earth's crust as 10 miles thick (16 km).

Table 4.2 The main components of the earth's crust. Three analyses of the composition

Component	The Vernadsky Institute Mean values of many thousands of analyses	Clarke and Washington Mean values of 5159 analyses	Goldschmidt Mean values of 77 analyses	
	%	%	%[a]	%[b]
SiO_2	61.9	60.18	59.12	60.95
TiO_2	0.8	1.06	0.79	0.81
Al_2O_3	15.6	15.61	15.82	16.31
Fe_2O_3	2.6	3.14	6.99[c]	7.21
FeO	3.9	3.88		
MnO	0.1	–	–	–
MgO	3.1	3.56	3.30	3.40
CaO	5.7	5.17	3.07	3.16
Na_2O	3.1	3.91	2.05	2.11
K_2O	2.9	3.19	3.93	4.05
P_2O_5	0.3	0.30	0.22	0.23
H_2O			3.02	

a) Goldschmidt's mean value

b) Recalculated to anhydrous sample.

c) Goldschmidt gives the sum of Fe_2O_3 and FeO.

4.2.2
Findings at the Vernadsky Institute in Moscow

At the *Vernadsky Institute for Geochemistry* in Moscow (see below) a very extensive study of the composition of the earth's crust was made in the interwar period. The earth's crust was defined by the scientists at the Institute as the material mass that is situated above the surface of Mohorovicic's discontinuity. Many thousands samples from the vast Russian plate and the Caucasian geosyncline[1] were analyzed and the results were combined with values from other areas. Three types of the earth's crust were considered: continental, oceanic and subcontinental (the zone of transition between the continental shelf and the deep sea). The masses and mean compositions of each of these fractions were incorporated in the calculations in order to get a weighted mean value. The Russian investigations had been made with great care. The final values are shown in Table 4.2.

4.2.3
A Small Number of Samples but Important Results

The spirited *V. M. Goldschmidt* in Oslo pointed out that eight elements, O, Si, Al, Fe, Ca, Na, K, Mg, constitute 99% of the earth's crust ([4.1] and [4.3]). The crust consists almost entirely of oxygen compounds, especially silicates of aluminum, calcium, magnesium, sodium, potassium and iron. Thus it can be looked upon as a close packing of oxygen anions, bound to silicon and metal cations. According to Goldschmidt, because of the homogeneity of the crust, analysis of a large rock sample, selected in a proper way, should give a composition representative of the whole crust, even if the selected sample area is very local. He was of the opinion that a suitable sample could be the glacial clay that constituted the summer and winter deposits in the water in front of the edge of the inland ice, which occurs abundantly in southern Norway. The mean composition shown in Table 4.2 was obtained from 77 analyses of this clay. Goldschmidt claimed that the analysis gave a rather good value for the composition of the whole the earth's crust. A bold hypothesis! However, the good agreement with the American and Russian results, based as they were on a much larger number of samples, showed that the hypothesis was well founded as is evident from Table 4.2.

4.2.4
Odd and Even Elements. Harkin's Rule

In the whole universe, elements with even atomic numbers are more common than their nearest neighbors with odd atomic numbers. This phenomenon is known as *Harkin's rule*. An important exception is hydrogen, which undoubtedly has the odd number 1, but nevertheless is the most common element in the universe. This is a consequence of the proton's important function in the building-up of heavier nu-

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[1] Large inward bends in the earth's crust can arise from downward-directed magma streams. Such vast troughs, often filled with water, are called *geosynclines*. The sediments in these ocean basins are transformed into sedimentary rocks.

clides. Even for the elements in the earth's crust Harkin's rule is often valid, but exceptions are more common than for the element distribution in the universe. Some examples of agreement with the rule and exceptions are shown in Table 4.3.

Table 4.3 Element abundance in the earth's crust

Element[a]	Atomic number	Abundance in earth crust ppm (g/tonne)
Boron	5	10
Carbon	6	200
Nitrogen	7	19
Aluminum	13	82 300
Silicon	14	282 000
Phosphorus	15	1050
Potassium	19	20 900
Calcium	20	41 500
Scandium	21	22
Manganese	25	950
Iron	26	56 300
Cobalt	27	25

[a] In agreement with Harkin's rule.

Element[b]	Atomic Number	Abundance in earth crust ppm (g/tonne)
Lithium	3	20
Beryllium	4	2.8
Boron	5	10
Vanadium	23	120
Chromium	24	102
Manganese	25	950

[b] Exceptions to Harkin's rule.

4.3
The Development of Geochemistry

As other branches of chemical and physical science developed on the basis of principles and fundamental laws it was not satisfactory to let geochemistry remain simply as a collector of test results. Even geochemical science started to use physicochemical ways of looking at things.

4.3.1
Rare Elements in the Earth's Crust – Compounds and Contents

Determination of the rare-element content in rock samples is a more difficult analytical problem than determination of the main components. The development of optical spectroscopy, X-ray fluorescence analysis, atomic absorption spectrophotometry (AAS), mass spectrometry and other analytical methods from the middle of the 20th century made careful mapping of the composition of the crust possible, even for the rarer elements. The content of each element is given in the corresponding element chapter.

The year 1912 was memorable for the whole of materials science. As described in Chapter 2, it was in that year that von Laue at the University of Munich discovered that the regular atomic arrangement in crystals can act as a diffraction grating for X-rays. This made it possible to determine the atomic structure of minerals and other solids. However, a long time elapsed before this new possibility was used within geochemistry. In the fifth (1924) edition of Clarke's *The Data of Geochemistry*, X-ray diffractometry was not mentioned. But Goldschmidt in Oslo saw the enormous possibilities of the new technique. Between 1922 and 1926 he determined the crystal structures of a large number of compounds. In fact a new branch of science, *crystal chemistry*, was developed. His co-workers in this research were among others *T. Barth, W. H. Zachariasen, L. Thomassen, G. Lunde* and *I. Oftedahl*. The results were published as a series of reports *Geochemische Verteilungsgesetze der Elemente I-IX*.

In 1922 *Assar Hadding* at the Swedish University in Lund began to use X-ray analysis to determine the composition of minerals. Goldschmidt also rapidly applied the new technique of X-ray fluorescence analysis and confirmed that Harkin's rule is also valid for rare elements.

4.3.2
Goldschmidt and the Modernizing of Geochemistry

Modern geochemistry had its origin in Norway. *Viktor Moritz Goldschmidt* was a professor at the universities in Oslo and Göttingen. He changed the character of geochemistry by applying physicochemical principles to its problems. He formulated a *phase rule for mineralogical systems* and analyzed in a new way the different driving forces in crystallization from stone melts and the physical chemistry of weathering and sedimentation [4.3]. What circumstances led him to work with geochemical research in Norway? The story of VMG is a remarkable one.

> *Viktor Moritz Goldschmidt* (Figure 4.1) was born in Zürich in 1888. He was the only child of Heinrich Jacob Goldschmidt and Amelie Köhne, a Jewish family. His father was a distinguished expert in physical chemistry and became professor in Amsterdam and Heidelberg, where the young Viktor Moritz began his schooling. In 1900 Heinrich Jacob Goldschmidt was offered a professorship of chemistry in Oslo, which he accepted. He succeeded Peter Waage, well known to all chemists as one of the enunciators of the *Law of Mass Action*. The Goldschmidt family moved to Oslo and became Norwegian subjects in 1905.
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> VMG studied mineralogy, geology and inorganic and physical chemistry at the University of Oslo. He took a doctor's degree in 1911 with a thesis that later became a classic: *Die Kontaktmetamorphose*[2] *im Kristiania-Gebiete* [*Contact Metamorphism in the Oslo Region*] (483 pp.). In view of his interest in physical chemistry and its accentuation of the idea of "system" he was bold enough to see the whole earth as a single system. In the monograph VMG applied physicochemical ways of looking at geological phenomena.
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> His thesis attracted much attention and he was offered a professorship in Stockholm. VMG's previous teacher, W. C. Brögger, a famous geologist and also a politician, arranged for Goldschmidt to stay in Oslo. At the age of 26

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[2] Metamorphism is a process by which rocks are altered in composition and structure. Pressure, heat and the introduction of new chemical substances are the principal causes. Contact metamorphism takes place in rocks in close contact with a body of gneiss or granite. The phenomenon is related to the intrusion or extrusion of magmas.

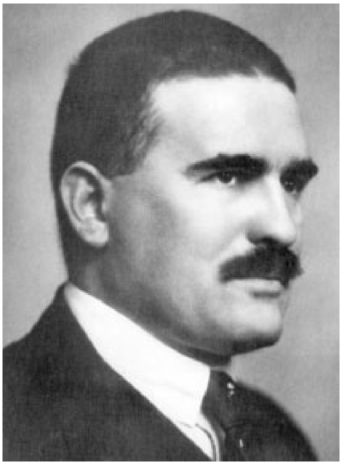

Figure 4.1 V. M. Goldschmidt (1888–1947). (Photo: E. Rude. Reprinted with permission of professor emeritus Nils Spjeldnäs, University of Oslo, once one of Goldschmidt's students.)

(1914) he was appointed professor and director of the mineralogical institution at Oslo University.

As World War I raged, Norway was neutral but isolated, so imports were stopped. In 1917 the government decided to set up a commission to make a thorough investigation of the mineral resources of the country. Young VMG was appointed leader of the commission and of the attached materials laboratory. The intention was primarily to guarantee the supply of materials during the blockade. After the war the activity continued, though now with a more general remit. It became of great importance, both practically and theoretically, for the new science of *geochemistry*.

In 1929 VMG was appointed professor and director of a new mineralogical institution in Göttingen, Germany. He accepted and immediately began to organize its activities with the Oslo laboratory as a model. He started a series of geochemical investigations into the less common elements on earth. Analytical methods were tested and developed. Optical spectroscopy with an arc between carbon electrodes made a detection limit of 0.001% possible. The intention was to learn how these rare elements had been distributed among different phases in the geological development ever since the first magma. This led to analyses of igneous and sedimentary rocks and of the sea itself. He spared no pains to obtain minerals and rocks from all over the world for investigation. These activities resulted in a series of publications about gallium, germanium, scandium, beryllium, boron, noble metals and the rare alkali metals. The results were revolutionary for knowledge of the distribution in the earth's crust of the less common elements, based as they were on a careful selection of material of both terrestrial and meteoritic origin.

Germanium has obviously been enriched in the plants that in prehistoric times were the origin of the earth's coal deposits. Goldschmidt discovered germanium in coke ash. But this discovery did not arise from a serious sample selection – he found germanium in the ash from the fireplace in his own institute. The biochemical processes behind enrichment of this type have not been fully elucidated.

In 1933, when the Nazis came to power, the situation changed drastically. The position of a Jewish professor like VMG became precarious. In 1935, after a surge of anti-Semitism, he left his chair and returned, in a state of destitution, to Norway. He was again provided with an opportunity for research at the University of Oslo. Then he published the last volume, No IX, of the big series *Geochemische Verteilungsgesetze der Elemente* [*Geochemical Distribution Laws for the Elements*]. In this he summarized his geochemical and cosmochemical research from previous years. He reported not only the distribution of the elements but also, to some extent, the contents and distributions of their isotopes. In this way, in fact, he laid the basis of the important parts of geochemistry that later became *isotope geology*.

This interwar period was a rather happy time and he was able to pursue his spectroscopic studies vigorously. He planned to design and manufacture a mass spectrometer for the determination of the ratio between isotope masses. The outbreak of World War II stopped these plans.

With the German occupation of Norway in 1940 a hard time began. During his last months in Göttingen, VMG always carried a capsule of hydrocyanic acid as an emergency exit. This habit he took up again during the German occupation of Norway. It is said that a colleague at the university asked VMG to get him such a capsule as well. Goldschmidt's answer, typical of his special sense of humor, was that *"this poison is only for professors of chemistry; you are a professor of mechanics and you have to procure a rope"*.

VMG was arrested and brought, in October 1942, to the Grini concentration camp. In November he was sent to Oslo harbor and a waiting ship that was to take him and other Norwegians of Jewish descent to Poland and the gas chambers. At the last moment he was set free. There are different versions of the rescue operation. One version is that men from the resistance movement in stolen Gestapo uniforms fetched him, the reason being that the authorities had been aware of his scientific capacity and had decided to use him in the production of heavy water in Rjukan for the development of an atomic bomb. What is clear, however, is that men from the resistance movement smuggled him out to Sweden.

Goldschmidt did not stay long in Sweden. He preferred to work in one of the allied countries and in his own way to take part in the fight against Nazism. In the spring of 1943 he got the opportunity to go to England and obtained a position at the Macaulay Institute for Soil Research near Aberdeen in Scotland. In spite of precarious health, VMG took an active part in the new work and he was very well received by Dr William Ogg, the director of the institute. When Ogg was appointed leader of the Rothamsted Experimental Station VMG moved with him. The research work there, *the distribution of trace elements in earths*, suited him perfectly. It was also after an appeal from Dr Ogg that VMG started to write his last *magnum opus,* a statement and conclusion of geochemistry in the English language. He wrote 700 folio sheets but did not have enough strength to finish it. His co-workers continued and after his death published the book *Geochemistry* with Viktor Moritz Goldschmidt as author.

The war ended in 1945 and Goldschmidt returned to Norway in 1946. His health was however undermined, and he died 1947 at the age of 59.

Goldschmidt received many honors in his lifetime. The Geological Society of London conferred on him its highest distinction, the Wollaston Medal. It is said that he deeply appreciated the fact that he was elected as one of the fifty foreign members of the Royal Society in London.

4.3.3
The Russian Geochemical School

In the 18th century the Empress Catherine II of Russia initiated a search for valuable minerals in the vast Russian Empire. Perhaps this can be seen as the beginning of a tradition, leading to the strong development of geochemistry in both Russia and the Soviet Union in the 20th century.

After 1917 *Vladimir Ivanovich Vernadsky* (1863–1945) became a pioneer and led an essential development of theory and principles within geochemistry. In his classic book *Essays on Geochemistry* he emphasized the fact that it is important to abandon the old static approach to minerals and instead study the atoms and the pattern of their movement on earth and in the universe. Of course, practical geochemistry continued to be concentrated on creating conditions for the exploitation of raw materials for the mineral and metal industry in Russia. These efforts were successful.

Vernadsky was also a pioneer in another domain, bio-geochemistry, the science that studies the distribution of elements among plants and animals. This new science inspired *A. I. Oparin,* who became a leading expert in this field publishing his book *The Origin of Life on Earth* in 1936.

Other young colleagues of Vernadsky, also internationally known within geochemistry, were *A. E. Fersman* and *A. P. Vinogradov*. Fersman, who, like his teacher Vernadsky, died in 1945, published a thorough treatment of geochemistry in four volumes [4.2].

After the war geochemistry continued to be energetically pursued in the Soviet Union. It is reported that 25 000 geochemists were educated between 1945 and 1990. The *Vernadsky Institute for Geochemistry* in Moscow was founded in 1947.

4.4
Some Geochemical Principles and Results

4.4.1
The Geochemical Classification of Elements

Goldschmidt formulated a *phase rule for mineralogical systems*. Like Gibb's phase rule in physical chemistry, it is based on the equilibrium between solid phases in contact with solutions, a situation that occurs during both crystallization from a stone melt and dissolution of rock components in a water system (weathering). Goldschmidt presupposed that the elements were distributed among the phases, solid, liquid and gaseous, in early geological processes. The liquid phases could be characterized as metal melt (iron, nickel), sulfide melt and molten silicates. According to the tendency of a specific element to be part of one molten phase or another the elements are designated as

– siderophilic (preferring a metal melt)
– chalcophilic[3] (preferring a sulfide melt)
– lithophilic (preferring a silicate melt)

Later the concept of *atmophiles*, elements tending to go to the atmosphere, was introduced. Examples of elements belonging to the different groups are given in Table 4.4.

Table 4.4 Typical elements in different geochemical groups

Typical siderophile	Typical chalcophile	Typical lithophile	Typical atmophile
Ru, Rh, Pd, Os, Ir, Pt, Au	Zn, Cd, Hg, Ga, In, Ta, Pb, Bi, S, Se, Te	Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, Al, RE-metals, Si, Ti, Zr, Hf, Th, P, V, Nb, Ta, Cr, Mn, U, O, F, Cl, Br, I	H, N, O, He, Ne, Ar, Kr, Xe

Some elements can be assigned to more than one group. Besides oxygen the following examples can be given:

- Fe, Co, and Ni are all both siderophilic, chalcophilic and lithophilic.
- W and Mo are both actually siderophilic. However, in the earth's crust W is a lithophile while Mo is a chalcophile.
- Elements that are very rare in the earth's crust, such as gold and the platinum metals, migrate from the lithosphere and are enriched in the siderosphere. Similar behavior can be expected for Ni and Co.
- Strictly speaking, siderophilic elements such as Fe and Ni are concentrated in the core but they are also present in the crust as chalcophilic sulfides and lithophilic oxides.

A complete geochemical classification of the elements is given in Figure 4.2.

A fifth group, the *biophiles*, has been introduced for elements that concentrate in living systems, both plants and animals.

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[3] The elements in group 16 (mainly oxygen and sulfur) are called chalcogenes, meaning "ore former". The word comes from Greek *chalcos*, copper, which later took the meaning ore and metal in general. Within geochemistry the designation *chalcophile* is used for an element that has a strong affinity for sulfur and is commonly found in sulfide ores. Copper, silver, zinc and mercury are chalcophilic.

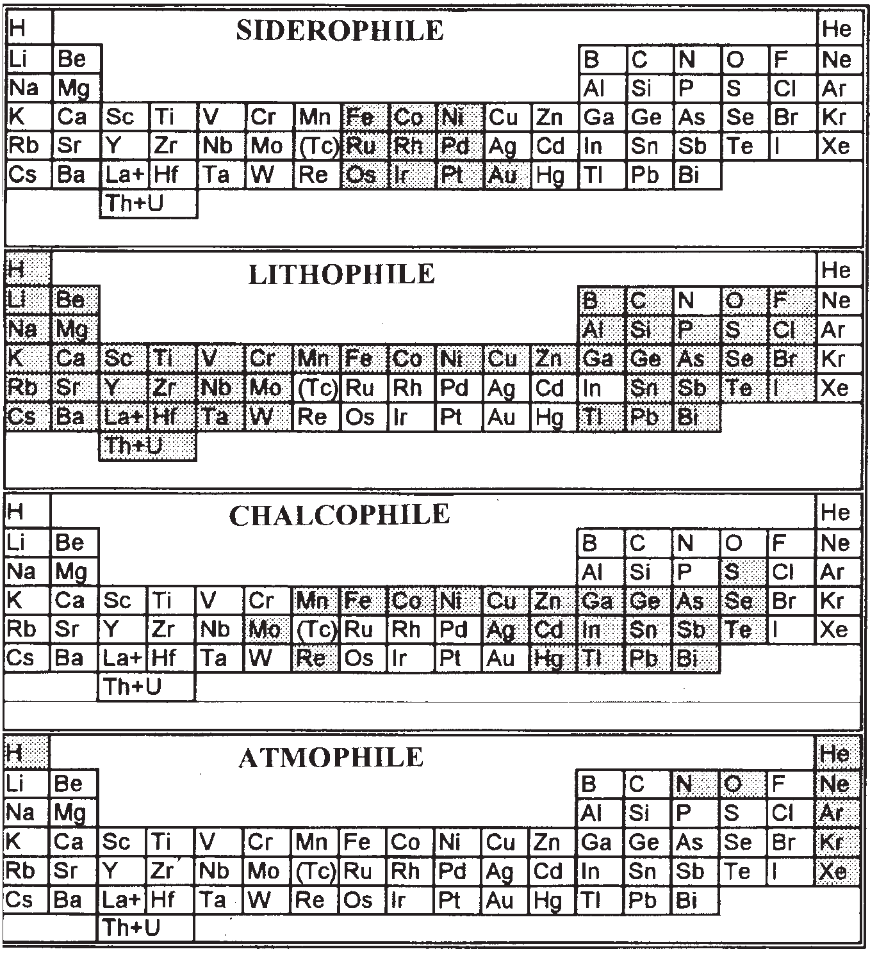

Figure 4.2 A complete geochemical classification of elements. *Notes:* La+ is the element lanthanum and lanthanides; of the naturally radioactive elements only Th and U are included. (From Svend V. Sölver, General mineralogy – a compendium 1993 for the School of Mining and Metallurgy, Filipstad, Sweden.)

4.4.2
… if the Atomic Sizes are Suitable

When crystallization occurs when stone melts solidify, aggregates of solid matter form with a three-dimensional structure. Atoms and ions of rare metals are caught in this growing crystal structure if, and only if, their sizes are suitable. Atoms that are too big or too small remain in the melt. The aluminum/gallium pair is a classic example. The ion Ga^{3+}, with a radius of 0.61 Å, is easily "hidden" in a structure in which

Al ions, radius 0.53 Å, predominate. All aluminum minerals contain up to 100 g/tonne of gallium, and gallium is found with aluminum in all industrial processes. This explains why gallium is, in fact, common but is perceived as rare.

A common definition is that *trace elements* are elements with a concentration in the crust of less than 0.1%. A trace element is, as a rule, not a significant component of a given mineral and does not occur in the mineral formula. Goldschmidt's development of principles for trace element geochemistry is, according to *A. H. Brownlow* [4.7], one of the reasons he is considered the father of modern geochemistry. From a knowledge of ionic sizes and mineral abundances it was possible to postulate a set of rules for trace element distribution during magmatic crystallization. These rules as formulated by Brownlow are:

1. If two ions have the same radius and the same charge, they will enter into a crystallizing mineral with equal ease.
2. If two ions have similar but unequal radii and the same charge, the smaller ion forms a stronger bond and will preferentially be concentrated in the early formed parts of a crystallizing mineral. However, extensive substitution does not occur between elements whose radii differ by more than 15%.
3. If two ions have similar radii but different charges, the ion with the higher charge will be preferentially concentrated in the early formed parts of a crystallizing mineral. Thus a trace element with a higher charge than the main element can be *captured* by the structure. On the other hand a trace element with a lower charge than the main element may be *admitted* to the structure in a later phase of the crystallization process.
4. If two elements have similar radii and the same charge, the one with the lower electronegativity will be preferentially concentrated in the early formed parts of a crystallizing mineral.

According to the first rule a hafnium ion with radius 0.72 Å can substitute for a zirconium ion, radius 0.73 Å. Bohr predicted that hafnium might well be found concealed in zirconium, and hafnium was indeed discovered in a Norwegian zirconium mineral at Bohr's institute in Copenhagen. This is described in Chapter 20 Hafnium.

The second rule predicts that when crystallization occurs from a stone melt containing potassium, radius 1.52 Å, and rubidium, radius 1.66 Å, rubidium will be concentrated in the later formed parts of the potassium feldspar.

Examples of the third rule are: (a) the capture of Ba^{2+} (1.49 Å) in place of K^+ (radius 1.52 Å) by potassium feldspar and (b) the admittance of Li^+ (0.73 Å) into biotite as a replacement for Mg^{2+} (0.71 Å).

Numerous exceptions to Goldschmidt's rules have been found and it has been necessary to modify them, since it is not the ion size alone that determines if a metal ion occupies place in the growing crystal.

4.4.3
Charge Intensity – Ion Potential in Water Solutions

Positive and negative ions in *water solutions* attract water molecules because of their dipole character. The number of water molecules that can be bound to a cation depends on the size of the ion, and the strength of the bond depends on the electrical charge Z in relation to the ion radius r. The hydration of an ion thus depends on Z/r.

Goldschmidt used calculated Z/r values to forecast and explain sedimentation and weathering reactions. He introduced the designation *ion potential* for Z/r, a term also used by Mason and Moore [4.4]. Cox [4.5] gives a thorough treatment of the relationship between ion radius, ion charge and water solubility but does not use the expression *ion potential* for Z/r. Some calculated Z/r values are shown in Table 4.5.

Table 4.5 Z/r-values for different ions

$Z/r<3$					Z/r 3–12				
Ion	**Z**	**Coordination number**	**Ion radius r Å**	**Z/r**	**Ion**	**Z**	**Coordination number**	**Ion radius r Å**	**Z/r**
Li^+	1	6	0.90	1.11	Be^{2+}	2	4	0.41	5.81
Na^+	1	6	1.16	0.86	Al^{3+}	3	4	0.53	5.66
K^+	1	6	1.52	0.66	Al^{3+}	3	6	0.675	4.44
Cs^+	1	6	1.81	0.55	Cr^{3+}	3	6	0.755	3.97
Ca^{2+}	2	6	1.14	1.75	Fe^{3+}	3	4	0.63	4.76
Ba^{2+}	2	6	1.49	1.34	Ta^{3+}	3	6	0.86	3.49
Fe^{2+}	2	4	0.77	2.60	Ta^{5+}	5	6	0.78	6.41
Mn^{2+}	2	4	0.80	2.50	Mn^{5+}	5	4	0.47	10.64
La^{3+}	3	6	1.17	2.56					
Y^{3+}	3	6	1.04	2.88					
Cu^{2+}	2	4	0.71	2.82					

The ionic radii are expressed in Å with values from ref. [4.6]

At pH 7 and Z/r values <3 the ions are water soluble. Sodium, potassium, calcium, barium, iron (ferrous) and copper stay in solution during sedimentation processes (provided, of course, that carbonates and sulfates with low solubility are not formed). The least soluble elements in neutral water solutions are those that form ions with Z/r values between 3 and 12. They have the greatest tendency to form hydroxides with low solubility, $Al(OH)_3$ for instance. The fact that beryllium resembles aluminum although they belong to different groups in the periodic table is explained by their close Z/r values. When beryllium was discovered, its similarity to aluminum was observed. Because of that there was strong opinion in favor of placing beryllium in group 3. There was, however, no room for a group-3 metal with the atomic weight of beryllium. Beryllium belongs to group 2 and its ion is Be^{2+}. The small ion radius makes Z/r large, almost equal to the value for the aluminum ion. Because of that, beryllium tends to resemble aluminum instead of is natural “relatives” magnesium and calcium.

Taking another example from among the rare earth metals, the ion Y^{3+} has the Z/r value 2.88 and has a somewhat lower solubility in water than La^{3+} with Z/r 2.56.

Ions like manganese and iron that occur in different oxidation states have different values of Z/r in their low and high oxidation states. They are more soluble in the lower state (lower value of Z/r), less soluble in the higher state (higher value of Z/r). Geochemical theory thus implies that precipitation and sedimentation presuppose an oxidizing environment, completely in accordance with practical experience.

Hypothetical ions like C^{4+}, N^{5+}, P^{5+} or S^{6+} would have Z/r values far greater than 12. The repulsion of the protons in water is so strong that oxoanions of the type CO_3^{2-}, NO_3^-, PO_4^{3-} and SO_4^{2-} are formed instead.

In ocean water there is a very wide range of element concentrations. The elements that dominate are, in accordance with the previous discussion, cations from groups 1 and 2 in the periodic table, anions from group 17 and oxoanions of non-metals such as sulfates, nitrates and so on. Intermediate elements of the type Al, Fe, Be, Mn are present in very low concentrations.

4.4.4
Not Only Ionic Radius and Charge

Ionic radius and charge are important for the distribution of trace elements among phases in the earth’s crust. There are, however, additional factors to be considered. Ionic bonding, presupposed by Goldschmidt’s rules, is not the whole truth. There is a strong component of covalent bonding, at least in the silicate minerals. Although Goldschmidt’s approach provides an indication of the distribution of the elements during magmatic crystallization, simple electrostatic theory cannot account for the distribution of cations between the different sites, tetrahedral and octahedral, in minerals. Nor can the simple theory explain the many distortions from highly symmetrical structures that are found in crystals containing transition metals as central atoms with non-bonding d and f electrons. A promising new approach has been to describe the behavior of the transition elements in terms of *crystal-field theory*. This considers the effect on the central atom of the electric field due to the surrounding ligands. The interaction has consequences for the orbital energy, and an energy splitting of the electrons may occur in some transition metal electron states. This in turn allows a prediction of the relative affinity of an ion in a magma for a particular site in a crystalline silicate mineral. A discussion of the use of crystal-field theory in mineralogy can be found in ref. [4.8].

4.5
Isotopes and Geochemistry

4.5.1
Isotopic Variations

Isotopes are elements whose atoms have the same number of protons but different numbers of neutrons in their nuclei. Within chemistry it is, as a rule, possible to disregard the fact that the elements are not uniform but mixtures of isotopes. The reason for this is partly that the chemical properties are almost entirely determined by the proton number and partly that, for most of the elements, the mixture of isotopes shows very little variation. However, the isotopic composition is not completely constant, and the small variations are studied and used within geochemistry. Observation of the differences in isotopic composition for an element in different minerals makes it possible to draw conclusions about the conditions at the formation of the mineral. Geochemical isotope research also tries to gain information on long-term environmental and climate changes.

The content of a special oxygen isotope ^{18}O in relation to the dominant ^{16}O in a certain substance can be expressed as the ratio $^{18}O/^{16}O$, measured by mass spectrometry[4]. A special method is used for expressing the relative isotope abundance in relation to some selected standard substances, some of which are shown in Table 4.6.

Table 4.6 Standard substances used in examinations of isotope variations [4.4]

			δ-value for the heavier isotope ‰	
Element studied	**Isotopic standard**	**Isotopes measured**	**Minerals and rocks**	**Natural water**
Hydrogen	SMOW, Standard Mean Ocean Water	$^{2}H/^{1}H$ (D/H)	−180 to +20	−410 to +50
Carbon	PDB, belemnite, a carbonate	$^{13}C/^{12}C$	−35 to +5	
Oxygen	SMOW, Standard Mean Ocean Water	$^{18}O/^{16}O$	−2 to +36	−50 to +15
Silicon	Quartz vein “Mother Lode”, California	$^{30}Si/^{28}Si$	−2.2 to + 3.2	
Sulfur	Meteorite troilite (FeS), “Canyon Diablo”	$^{34}S/^{32}S$	−45 to +60	

In the standard sample the isotope ratio R_{standard} is determined by mass spectrometry. Then, for the actual sample, the isotope ratio R_{sample} is determined. As a measure of the deviation from the standard sample regarding isotope composition the δ-value is calculated from

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[4] Mass spectrometry is dealt with in more detail in Chapter 10.

$$\delta = (\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1) \cdot 1000$$

The δ-value is expressed in per mil (‰) or parts per thousand. A high positive δ-value means that there is more than the "normal" amount of the heavy isotope present.

Isotope variations are most pronounced in atoms with low atomic weights: hydrogen, carbon, oxygen and sulfur.

4.5.2
Hydrogen isotope variations

The relative mass difference between the two stable isotopes ^{1}H and ^{2}H (deuterium, D) is larger than for any other isotope pair. Because of that hydrogen shows the greatest isotopic fractionation. The content of heavy water HDO in ocean water corresponds to 0.015 atomic% ^{2}H and a δD-value near 0. Light water, H_2O, has the higher vapor pressure and is to some extent enriched in the vapor. The difference becomes greatest when the temperature is low. Measurements of precipitation show that water near the equator has a hydrogen isotopic composition near that of ocean water whereas snow near the poles may have δ^D-values below –300‰.

4.5.3
Oxygen Isotope Variations and Temperature Variations 400 000 Years Ago

Oxygen is the most common element in the earth's crust and many systems containing oxygen are available for isotope studies. As a rule, determinations are made of the rare isotope ^{18}O in relation to the main isotope ^{16}O. Oxygen produced in photosynthesis has the δ-value 0. During breathing, organisms use the lighter 16-isotope preferentially and the atmosphere will be enriched in the ^{18}O isotope. Therefore the δ-value for oxygen in the atmosphere is +23.5.

Water molecules rich in ^{18}O vaporize more easily from ocean water during warm periods than during cold. The water left in the ocean in a warm period thus has a low δ^{18}O-value. Similarly, the δ^{18}O-value is high during cold periods. The carbonate sediments of the oceans are in equilibrium with the water and "freeze in" the isotopic relation from the water. δ^{18}O-values have been determined by mass spectrometric methods from sediments whose age has been determined by geological methods. When sedimentary carbonates are investigated in the present, their ^{18}O-values tell us about the temperature in the period in which the sediments were formed. During warm periods the δ^{18}O-value is more negative than during cold. When the δ^{18}O-values are plotted against time a diagram of the type in Figure 4.3 is obtained. The vertical δ^{18}O-axis is therefore also a temperature axis. High values indicate low temperatures and a glacial period, low values indicate high temperatures and a warm period. The underlying causes for the variations are, according to the so-called *Milankovitch theory,* changes in the declination of the axis of the earth and in the eccentricity of the earth's orbit. This involves changes in the distance between earth

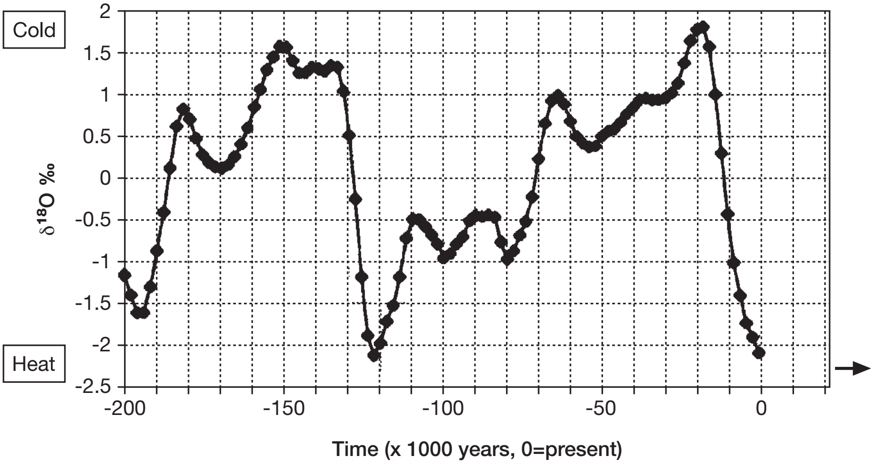

Figure 4.3 Isotope variations over 200 000 years. Oxygen isotope data from marine carbonate sediments. Cyclic variations correspond to periods of global heating and cooling.

and sun. This theory does not take into account the greenhouse effect or magnetic changes in the sun.

The minimum values in the diagram (the most negative $\delta^{18}O$-values) correspond to warm periods while the maximum values correspond to glacial periods. The periods of warming occur quite regularly while cooling is interrupted by periods of heating but the cooling process soon takes over again. By extrapolation forwards from 0 (today) it is possible to estimate the time of the next glacial period.

4.5.4
Carbon Isotope Variations and a Bold Hypothesis for Life

Carbon has two stable isotopes, ^{12}C and ^{13}C. Natural diamond has $\delta^{13}C$-values between –3 and –5. Diamonds have been formed from carbon in the mantle with an isotopic composition that can be supposed to be in accordance with what existed for the newly created planet earth. The isotopic composition for carbon in meteorites also corresponds to a $\delta^{13}C$-value of –5‰. Inorganic carbonate sediments have the value 0 while organic sediments have the value –25‰. To give a total mean value of –5 the latter must constitute 20% of all sedimentary carbon. Modern estimates [4.9] assert that this value has been constant in almost 4 billion years. That implies that living organisms have been active since very early in the history of our planet.

4.6
Radioactive Methods for Age Determination

The rate of radioactive decay of some unstable elements is supposed be constant and independent of chemical state and environmental factors such as temperature and pressure Radioactive isotopes, according to Table 4.7, decay to stable ones as described in Chapter 52 Radioactive Elements.

Table 4.7 Some nuclides used in geochronology [4.4]

Nuclide	Half-life Years	Effective range for age determinations. Years	Materials studied
$^{238}U \rightarrow ^{206}Pb$	$4.47 \cdot 10^9$	$10^7 - 10^9$	Zircon, uraninite, Monazite, titanite
$^{235}U \rightarrow ^{207}Pb$	$0.70 \cdot 10^9$	$10^7 - 10^9$	Zircon, uraninite, Monazite, titanite
$^{232}Th \rightarrow ^{208}Pb$	$14.0 \cdot 10^9$	$10^7 - 10^9$	Zircon, monazite
$^{87}Rb \rightarrow ^{87}Sr$	$48.8 \cdot 10^9$	$10^7 - 10^9$	Micas, igneous and metamorphic rocks
$^{147}Sm \rightarrow ^{143}Nd$	$106 \cdot 10^9$	10^9	Igneous rocks
$^{40}K \rightarrow ^{40}Ar$	$1.25 \cdot 10^9$ (total)	$10^4 - 10^9$	Micas, hornblende, sanidine ($KAlSi_3O_8$), igneous and metamorphic rocks
$^{14}C \rightarrow ^{14}N$	5730	$0 - 10^5$	Wood, charcoal, bone, shells

The table contains actual figures (for 2002) compiled by Å. Johansson, Swedish Museum of Natural History, Stockholm.

The long half-lives of the first six examples make dating of very old minerals possible, even an estimation of the age of the earth. The ^{14}C method for investigating old wood and bone material is presented in Chapter 39 Carbon.

A radioactive isotope can be useful for geochronology if some criteria are satisfied:

- The half-life must be in the same range as the age of the material that is dated.
- The rate of decay of the parent nuclide must be known.
- The initial content of the parent and daughter nuclides must be known.
- The system must be closed so that no parent or daughter isotopes are added or subtracted by any process other than radioactive decay. The potassium–argon method is especially risky as argon is a gas that can disappear.
- In special cases, e.g. for ^{14}C, the radioactive isotope is continually replenished.

If a rock is subjected to high pressure or temperature or exposed to hot water solutions, new minerals may be formed. In such cases the system is not closed and the dating methods do not show the original age of the rock but instead the time counted from the metamorphic transition.

Radiometric investigations of meteorites have shown that the age of the solar system, and correspondingly the age of the earth, is about 4.6 billion years. Direct measurements of the age of the earth are difficult because the original crust is not preserved. The oldest rocks found in the crust are younger than the age of the earth. The oldest rocks examined, found in Canada and in western Greenland, have an age of almost 4 billion years.

> Zirconium silicate, the mineral zircon, contains uranium in a concentration high enough to make a radioactive age determination possible. The mineral is present, finely scattered, in acid silicate rocks and can act as a clock for measuring the age of the rock. Determinations on magmatic rocks are the most reliable. For the examination of granite a sample of 10 kg is collected. After crushing and separating the minerals, good zircon crystals are picked out under a microscope [4.10]. The crystals are dissolved in strong acid and uranium and lead are separated chemically from the solution. Their isotope compositions are analyzed in a mass spectrometer and the ratios ^{206}Pb/^{238}U and ^{207}Pb/^{235}U are calculated. When the zircon mineral was formed it contained no radioactive lead isotopes and both values were 0. The lead contents and the ratios increase with mineral age. The age is evaluated by special graphical methods.

A thorough treatment of isotope geology is given in ref. [4.7].

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5
Gold

5.1 Au
Facts about Gold

5.1.1 Au
The Element

Symbol:	Au
Atomic number:	79
Atomic weight:	196.97
Ground state electron configuration:	[Xe]$4f^{14}5d^{10}6s^1$
Crystal structure:	Cubic fcc with $a = 4.08$ Å

5.1.2 Au
Discovery and Occurrence

Discovery: Gold occurs native as a rule and the metal was used in prehistoric times, at least as far back as 4000 BC. Gold ornaments have been found in Egyptian tombs with inscriptions dating back to 2600 BC.

Most important mineral: Gold occurs native (Figures M1–M3) in solid rocks, often together with quartz. Most of the gold is won from *alluvial* deposits, made up of gold particles in sediments (*placers*). In addition gold is also present in sulfide ores, mostly of copper, zinc and lead.

Ranking in order of abundance in earth crust:	75
Mean content in earth crust:	0.004 ppm (g/tonne)
Mean content in oceans:	$4 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	$100 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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5.1.3 Au
Chemical Characterization

Of all the metals, gold has the lowest tendency to react with air to form oxides. In nature it is found in its metallic state, associated with quartz, pyrite and other minerals. Gold is a bright yellow metal with a high luster and is a good conductor of heat and electricity. Finely divided gold, colloidally suspended, ranges in color from ruby red to purple. Gold is the most malleable and ductile of all metals. It can be rolled to a thickness of 0.1 μm and one gram could be drawn into a wire more than 3000 m long. The metal is very inactive and unaffected by air, heat, moisture and most solvents. However, a mixture of nitric and hydrochloric acids (*aqua regia*) dissolves gold, the *King of Metals*. Because it is very soft, gold is usually alloyed in jewelry and dentistry to give it more strength. The term *carat* describes the gold concentration (24 carats is pure gold).

Oxidation states:	**Ionization energy (kJ mol^{-1}):**	**Electron affinity (kJ mol^{-1}):**
Au^{I} as in AuBr and $KAu(CN)_2$	$Au(g) \rightarrow Au^{+}(g) + e^{-}$ 890	$Au(g) + e^{-} \rightarrow Au^{-}(g)$
Au^{III} as in $AuCl_3$	$Au^{+}(g) \rightarrow Au^{2+}(g) + e^{-}$ 1980	–222.8
Au^{I} and Au^{III} as in Au_4Cl_8		
Au^{V} as in AuF_5		

Standard reduction potential: $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$ $E^0 = +1.52$ V

Electronegativity (Pauling): 2.54

Radii of atoms and ions: (WebElements™)		
	Atomic:	135 ppm
	Covalent:	144 ppm
	Au^{1+} (6-coordinate, octahedral):	151 pm
	Au^{3+} (4-coordinate, square-planar):	82 pm
	Au^{3+} (6-coordinate, octahedral):	99 pm
	Au^{5+} (6-coordinate, octahedral)	71 pm

5.1.4 Au

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
19 300 kg m^{-3} 19.30 g cm^{-3}	10.21 cm^3	1337.4 K 1064.2 °C	3129 K 2856 °C	129 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
324	319	313	299	272

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$11.8 \cdot 10^{-6}$	$14.2 \cdot 10^{-6}$	$15.4 \cdot 10^{-6}$	$17 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1336 K**
5	20.5	28.8	46.3	86	310

Mass magnetic susceptibility χ_{mass} at 293 K	$-1.78 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
78 GPa	27 GPa	234 GPa	0.44

5.1.5 Au
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	13.0 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	325 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	366 kJmol^{-1}
Entropy S^0 at 298 K	47.40 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	21.4	25.42	26.8	28.9	29.3	29.3

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
4/3 Au + $O_2 \rightarrow$ 2/3 Au_2O_3	+53.3	–	–	–	–

5.1.6 Au
Nuclear Properties and X-ray

Isotope range, natural and artificial	172–205

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{197}Au	Stable	100	3/2+	0.1482

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{97}Au
Reference compound	–
Frequency MHz (^{1}H = 100 MHz)	1.754
Receptivity D^P relative to ^{1}H = 1.00	$2.77 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.158
Magnetogyric ratio, radT^{-1}s^{-1}	$0.4731 \cdot 10^7$
Nuclear quadropole moment, barn	0.547

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
78	Pt	65.123
79	Au	66.990
80	Hg	68.894

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	205
17.37 keV (Mo$K\alpha_2$)	113

Neutron absorption	Thermal neutron capture cross section	98.8 barns

5.2
Gold in History

5.2.1
Most Prominent Among Metals

Gold occurs throughout the world although only in small quantities. Gold may have been the first metal with which people came into contact[1]. Among the gray pebbles at the bottom of shallow streams the shining yellow grains of gold could be seen – so different from the stones! The most salient properties of gold, found by the early discoverers, were the possibility of beating the metal to a thin foil and drawing it out into a thin wire. These inspired the human artistic imagination. Using fire the gold grains could be sintered or melted to form bigger pieces, from which craftsmen prepared cult objects and adornments.

Egypt had the status of the leading gold country from predynastic times and it exerted an influence in neighboring countries. In the Sumerian civilization, in the Euphrates-Tigris region, gold was being forged into ornaments of high aesthetic value as early as 3000 BC. Near the modern city of *Varna*, on the Bulgarian coast of the Black Sea, pieces of ceramic decorated with small gold grains have been found. They are probably 5000 years old. The gold had been fastened with a glue of resin or egg albumen.

The word for *gold* in different languages is as a rule connected to the yellow color or to the sun. The German word *gelb* (yellow) is derived from an old Germanic word *gulth* and it may be the origin of the word *gold*. The Slavonic gold word *soloto* is obviously related to the Indo-European word *sol* (sun). The Latin *aurum* (which has given us the chemical symbol Au) is connected with Aurora, the goddess of the light of dawn and thus with the sun. In the old Egyptian language gold was called *nub*, which gave the name Nubia to the gold country south of Egypt.

The special properties of gold have made it a peaceful metal. It is very soft and cannot be used for tools and weapons. However, its great value has caused robberies with bitter fights and sudden deaths, as well as several wars. It is perhaps not an accident

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[1] It is not quite certain that gold was the first known metal everywhere. At least in Egypt, copper seems to have been known earlier.

that Alexander the Great (356–323 BC) had obviously gold-rich countries as goals for his major wars of conquest: Anatolia in Asia Minor, Nubia and India. Alexander also captured great quantities of gold from the Persian Empire.

5.2.2
Gold from the Mysterious Country of Ophir and from the Queen of Sheba

According to the Old Testament the people in biblical times got their gold and precious stones mainly by import. Solomon, king of Israel 971–931 BC, together with Hiram, king of Tyre on the Mediterranean, built a fleet at the Gulf of Aqaba and manned it with people from Tyre, experienced in seamanship.

> Then Solomon went to Ezion Geberon and Elath on the coast of Edom. And Hiram sent him ships commanded by his own officers, men who knew the sea. These, with Solomon's men, sailed to Ophir and brought back four hundred and fifty talents of gold, which they delivered to King Solomon.
> (2 Chronicles 8:17)

The ancient Greek unit of weight, the *talent*, is said to correspond to ca. 26 kg. The real weight of 450 talents of gold in King Solomon's time is unknown but seems to have been an impressive quantity. The country of Ophir has not been identified. Different possibilities have been mentioned: India, Midian (Arabia) and the East Coast of Africa. If simply Nubia is meant, then it was not so far away.

In the far south of the Arabian peninsula, in present-day Yemen, lay the country of Sheba. Its connections with India were good, with trade in gold, precious stones and spices. The authorities in Sheba were aware of Solomon's policy of expansion, which had resulted in the king of Israel gaining control of the caravan routes from the Mediterranean Sea down to the Red Sea and the Arabian peninsula. For a trading nation such as Sheba it became important to establish connections with the new great power. The Queen of Sheba, famous not only for power and wealth but also for beauty, made the 2000-km journey to Jerusalem. Then, as now, at meetings between sovereigns gifts were important. Gold was highly esteemed as an expression of wealth and power.

> When the Queen of Sheba heard about the fame of Solomon and his relation to the name of the Lord, she came to test him with hard questions. Arriving at Jerusalem with a very great caravan – with camels carrying spices, large quantities of gold, and precious stones – she came to Solomon and talked with him about all that she had on her mind. (1 Kings 10:1–2)

5.2.3
Nubia – The Gold Country

At the first cataract of the Nile, now known as Aswan, the geology changes. Hard rocks are found, which have resisted the creation of the broad river channel that is so typical of the flow of the Nile through Egypt. The Nubian desert begins there and extends through the country of Nubia. Unlike Egypt, Nubia had always been sparsely populated and culturally underdeveloped. But it was a country with gold.

The most powerful Pharaoh of Egypt, Thothmes III, conquered Syria in the 16th century BC and also captured Nubia as far as the 24th cataract, “where the land of the Negroes begins”. Egypt thus came into possession of the gold country. This was apparent in the tomb of the Pharaoh Tutankhamen. At his death in 1350 BC he was placed in a gold coffin and his mummy was ornamented with a portrait of the young sovereign’s face in pure gold. One hundred years later Rameses II, Pharaoh at that time (1279–1213 BC), had to fight hard to keep Syria, but Nubia was still firmly in Egyptian hands.

Our knowledge of gold extraction at this time is fairly well documented. Even detailed mining maps, showing wells, roads, and temporary houses, are known [5.1]. Rocks containing gold were hammered into pieces, pounded in mortars and ground to powder.

This was treated in a gentle water flow on wooden tables. The water carried the light mineral particles with it while the heavy gold grains remained. For gold refining the cupellation process (described in Chapter 6 Silver) was probably adopted from silver metallurgy, in which it had been used some centuries earlier.

Gold production was a state affair. The noble metal was won by expeditions, conducted by experts, to the different desert regions. Slaves and prisoners, guarded by soldiers, worked under inhuman conditions. At this time alternative gold suppliers, Arabia, India, the Caucasus, Persia, Asia Minor and the Balkans, were available. The yearly deliveries of gold from Nubia were, however, bigger and more regular than those from the other gold regions.

Goldsmiths bought their gold from the state or worked in the temples under the supervision of the priests. Gold objects in this distant Egyptian time were nearly always contaminated with metals such as silver, copper and iron. The color varies with the content of these impurities, a fact that the Egyptian craftsmen skillfully exploited in their designs.

5.2.4
The Golden Fleece

Native gold follows quartz in veins. After weathering the larger gold particles can be found as gold grains in streams and extracted by panning. Very fine gold particles form *alluvial* or *placer* deposits after erosion and subsequent concentration by the action of water. This is the case for the Caucasian alluvial deposits. On the eastern shore of the Black Sea, finely dispersed gold was found in the sand. Only a primitive method was needed to win the gold. When the sand was suspended in water over fleeces, the small gold particles adhered to the grease in the wool, a behavior with similarities to ore dressing by flotation. After drying, the fleece was shaken and the gold dust was loosened and used. This is the background to the tale of the Golden Fleece.

> The heroes of the tale sailed in the ship *Argo* through the Hellespont (the ancient name of the Dardanelles) into the Black Sea. Jason, son of the king of Thessaly, intended to fetch the Golden Fleece, the hide of a ram, guarded by a dragon. After many terrible adventures the Argonauts arrived at Colchis. Jason succeeded in putting the dragon to sleep and in fulfilling his task. Medea, the daughter of the local king, helped him and followed him on the dangerous journey back to Thessalia. This tale was first mentioned in *The Odyssey*.

5.2.5
Esmeralda – The Gold Country

The indigenous South American peoples were very skilful metallurgists in pre-Hispanic times. They used gold for adornment and for cultic purposes as was done in the Middle East. However, these South American peoples are the only ones who have used gold for tools, or we might even say weapons! Gold was so plentiful that it could even be used for fishhooks!

Esmeralda is a province in present-day Ecuador. The people there worked gold, copper, silver and platinum. The numerous streams running from the Andes brought gold-sand with them and the gold grains were collected by panning. To get gold with the right color, a "contaminant" of a white metal had to be removed by hand. This was platinum, which was thus known long before it began to be investigated in Europe in the 18th century AD. The gold was melted with blowpipes on a bed of charcoal. In that process, alloys with varying copper contents were made. Some silver and platinum were always present, so a gold-copper-silver-platinum alloy was the final product. Small pieces of alloy were forged and hammered into foils and wires and used for ornaments and tools, see Figure 5.1. Pieces could be joined by heating them together, obviously without solder.

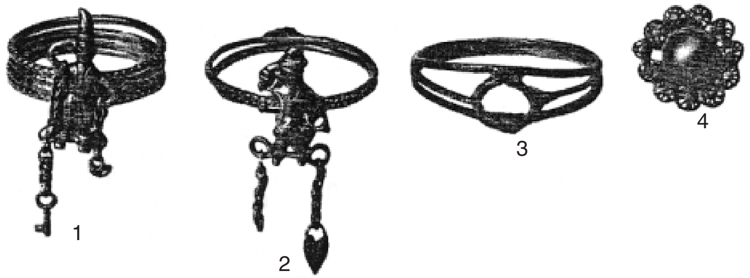

Figure 5.1 Indian gold jewelry found at La Tolita in Esmeralda [5.2].

5.2.6

Gold Coins

In about 2700 BC gold rings were introduced for payment purposes. In 1090 BC small squares of gold were legalized for payments in China. Around 1500 BC the *shekel* became the usual coin in the Middle East. It weighed 11.3 g and was made from the alloy naturally obtained after purification of gold by the cupellation process. The silver content was high, often 30%. This alloy was called *electrum*. The silver chapter describes how coinage was introduced in Asia Minor and how the use of coins spread. Silver coins became a Greek specialty, as Greek was a silver country. In the same way gold became an important coinage metal in Macedonia, a country with good supply of gold in its mountains. Philip II, father of Alexander the Great, introduced the "*gold stater*", a coin weighing 8.6 g. It became a universal coin, not least through Alexander.

When the Roman Empire took over, the coinage metal was initially copper. However, Spanish gold and silver deposits were incorporated with Rome through the Punic Wars in the third century BC and 40 000 slaves were forced into the mines. Noble metal coins were reintroduced and the silver *dinar*, weighing 4 g, became widespread. About the year 60 BC Julius Caesar led a campaign in Gaul and returned with so much gold that he was able to pay all the debts of Rome and in addition give every soldier in his army 200 gold coins.

Caesar Augustus, who issued a decree that a census should be taken of the entire Roman world, tried to reorganize the monetary system and introduced the gold *aureus*, weighing 8.19 g. Caesar Nero devalued it to a weight of 7.3 g and in the following two centuries the deterioration of the Roman monetary system continued. Constatine the Great in the Eastern Roman Empire installed a new gold standard, the *solidus,* with a weight of 4.55 g. At the beginning of the era of the Great Migration, minting coins continued in the name of the emperor of the Eastern Empire. With the decline and fall of the Roman Empire, however, the Arabs had begun to coin their own gold dinars. The kings in the Merovingian country issued a gold coin, the *trient*. In the middle of the 6th century, gold coining ceased within the Frankish confederation and towns and private individuals minted coins using cheaper metals. Charles the Great (Charlemagne; king of the Franks 800–814) restored order and claimed energetically that coining is a royal obligation. Silver now became the principal coinage metal and the dinar a national standard. King Charles was, however, also interested in gold coins. During the 8th century he attacked his eastern neighbors, the Avars, a Mongolian people and successors of the Huns, and captured a very great gold treasure.

Gold eventually returned to Europe as a coinage metal. In Italy, two coins weighing 3.5 g were created in the 13th century: the *florin* (Florence) and the *ducat* (Venice). At the end of the century, Great Britain issued its first gold coin, also called a *florin*. In the following years gold coins were even more important than silver ones, especially for international transactions. In France, Louis IX in 1266 introduced a gold coin, the *ecu*, weighing 4 g. That name was used for a time in the 1990s for the European Currency Unit (ECU) but in 1999 this was replaced by the Euro as the means of payment within the European Monetary Union (EMU).

From the 18th century, gold coins became still more important because new gold deposits were discovered, most notably in Brazil. In 1787 the first gold money was coined in the USA, and in 1792 *The Coinage Act* defined the value of the US dollar as 24.75 grains fine gold (= 1.683 g). In Great Britain, the gold *sovereign* with a value of 1 pound sterling was issued in 1817. Gradually it became common to use a gold standard without gold coins. Banknotes, paper money and other means of payment were guaranteed a value in gold. The introduction and the phasing out of the gold standard are outside the scope of this book. Today the gold standard is not used, and coins are no longer made of gold or silver.

It may be mentioned as a curiosity that South Africa introduced the gold *Krugerrand* in 1967, weighing 1 troy ounce = 31 g. It was an internationally appreciated object of investment for many years.

5.2.7
Gold and Gold Rushes in the Modern Era

5.2.7.1 South America and Mexico

As previously mentioned, knowledge of gold, its winning and use, goes back to prehistoric times. With the 16th century and the New Era in history a considerable inflow of noble metals from America into Europe began, treasures which the Spanish conquistadors robbed from the Aztecs and Incas, and – above all – from mines in Mexico, rich in silver but also in gold. The efforts of the new masters to increase gold mining were, however, not very successful. Most of the finds consisted of silver. But in 1725 large gold deposits were discovered in Brazil, and for the rest of the century that country became the leading gold producer with almost two-thirds of the world production.

In the 1970s a discovery that attracted much attention was made in Brazil. In Sierra Pelada, several nuggets weighing more than 10 kg were found. They contributed very much to the gold rush that has been going on since the 1980s in the whole Amazonian region in Brazil, and in Venezuela and Guyana.

5.2.7.2 North America

In the United States gold has mainly been produced in two regions, the eastern region along the Appalachian Mountains and the western region along the Rocky Mountains and Sierra Nevada. Production began in the east.

The discovery in 1803 of native gold at Meadow Creek in North Carolina started the gold fever and legendary gold rushes of that century as well as the more ordinary mining and gold deliveries. In 1804 the first gold for coinage was shipped from North Carolina to the United States Mint.

The western gold fields extend from Mexico to Alaska. The first discovery was made in 1848 at Sacramento, California, during excavation for a sawmill. A gold rush started and people from all parts of the world hastened to the gold district. Characteristic of another Californian gold area, Carson Hill, were the rich quartz lodes found in the hill. The method adopted to win the gold was to explode a charge in the vein and, after the explosion, go round and pick up the pieces in hand baskets. Carson Hill became famous on November 29, 1854, when a miner hit a rock too large to be picked up by hand. It was, indeed, a gold nugget with a weight of 195 pounds (88 kg), the largest in the world at that time.

The different discoveries were in fact contributory causes of the historically important development of the western USA. New findings of importance occurred in Nevada (1859), Colorado (1875), Alaska (1886) and Canada (1896).

At the end of the 19th century, gold rushes continued in the border district between Canada and Alaska, at Yukon River, Bonanza Creek and Klondike River. In the first decades of the 20th century important discoveries of gold mixed with copper were made in northwestern Quebec.

5.2.7.3 **The Gold Coast in Africa**

The Gold Coast in western Africa, now Ghana, has gold deposits, partly as ore in the mountains of Ashanti and partly as gold that can be panned from the rivers. The presence of gold was known long before European colonization. In fact it was reports about the gold wealth of the country that enticed the Portuguese to go there at the end of the 15th century. After colonial wars over centuries, the Gold Coast became a British Crown Colony in 1874. Gold deliveries from the country have been considerable.

5.2.7.4 **Russia**

Gold has been won from the eastern slope of the Ural Mountains since 1745, when a mineralogical laboratory was built up in the neighboring city of Yekaterinburg. Here, at the crossroads between Europe and Asia, a city was founded in 1723 and named for Peter the Great’s wife, Catherine. In the middle of the 19th century the winning of gold near Yekaterinburg and in other parts of the huge country made Russia an important gold exporter.

5.2.7.5 **South Africa**

In 1868 George Harrison found gold in South Africa when he was digging the foundations of his new house. It was a simple beginning for a development that changed South Africa into the biggest gold producer in the world. An extremely rich deposit was revealed when the goldfields of Witwatersrand in South Africa were discovered in 1885, which soon made South Africa the leading gold country.

5.2.7.6 **Australia**

In 1850 a giant nugget (70 kg!) was found in Victoria, Australia, situated just below the surface of the ground. It was seen when a carriage wheel passed and was given the name *Welcome Stranger*.

5.2.8

How Much Gold?

Australian Mineral Economics and Geological Survey of Sweden have tried to estimate the total production of gold in history. The result is shown in Table 5.1.

Table 5.1 Estimated total gold production in history

Period	Time	Production tonne	Mean production tonne/year[a]	Cumulative production tonne
The copper age	3900 – 2000 BC	920	0.5	920
The bronze age	2000 – 1200 BC	2645	3.3	3565
The iron age	1200 – 50 BC	4120	3.6	7685
The Roman period	50 BC – 500 AD	2572	4.7	10 527
Older Middle Ages	500 – 1000	934	1.9	11 191
The Middle Ages	1000 – 1492	1538	3.1	12 729
The New Era	1493 – 1680	8163	43.7	20 892
	1681 – 1850	3072	18.2	23 964
	1851 – 1900	3523	70.5	27 487
	1901 – 1950	34 172	683	61 659
	1951 – 1980	31 341	1045	93 000
	1981 – 1995	27 028	1802	120 028

a) Not in the original estimate. Values calculated for this table.

The US Geological Survey [5.3] has extended the calculation to the year 2002 and estimates the total quantity ever mined as 140 000 tonnes. About 15% of this is thought to have been lost, dissipated after industrial use, while 120 000 tonnes remain, 33 000 tonnes in central banks as official stocks and 87 000 tonnes held privately as bullion, jewelry and coins.

5.3
Is it Possible to Find Gold – Today?

For people in general, the metal gold has kept its fascination. Panning for gold in our day is a tourist hobby in mountain streams and is also practiced by amateur mineralogists. They expect to find free gold grains from weathering rocks and then a recurrence of what happened in the gold country, Esmeralda. The conditions for big finds are, however, not often very promising. Yet, if gold grains are present, it may be a motive also for professional prospecting in adjacent mountains. The situation is simply described in Figure 5.2.

In sedimentary deposits, gold may occur as microscopic scale-like grains, impossible to detect with the naked eye. But gold grains may also be larger. If they weigh some grams or more they are called *nuggets*. Some substantial finds have been made.

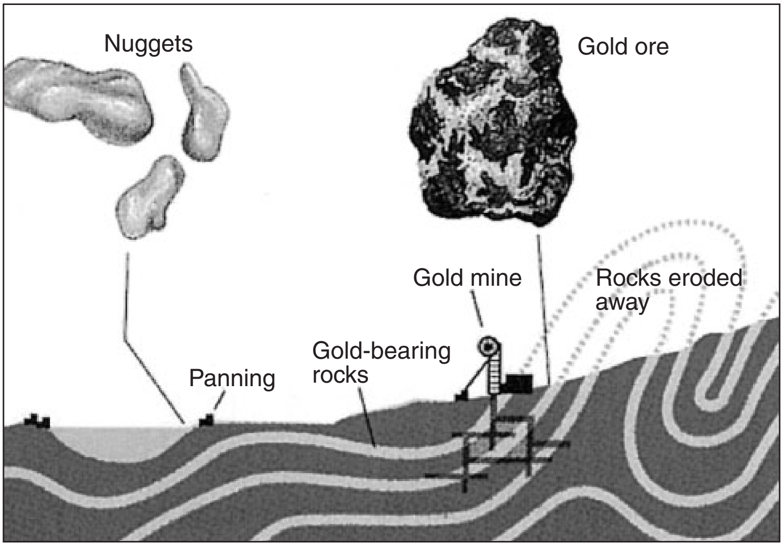

Figure 5.2 The principles of the recovery of native gold from mountains. (From a picture in Bonnier Lexicon, Stockholm. With permission.) Copyright Lidman Production AB

5.4
Gold Ores and Gold Reserves

5.4.1
Gold Prospecting

Ore prospecting is searching rocks for metals suitable for mining economically. Prospecting for gold has been carried on very actively all over the world in recent years. One contributory cause for this is that many countries has changed their mineral laws to facilitate prospecting and investment in the own country. The use of advanced geological, geophysical and geochemical techniques in the modern search for gold has led to significant finds.

5.4.2
Gold Reserves

Gold is a rare element in the earth’s crust. Abundances vary from 0.001 to 0.006 ppm (g/tonne). How rare gold really is, in comparison with other elements, may be concluded from Table 5.2.

Table 5.2 Gold is a rare metal

Metal	Concentration in earth crust ppm or g/tonne
Gold	0.0035
Silver	0.091
Uranium	1
Lead	10
Copper	85
Zinc	120
Manganese	1800
Iron	47 000

(compilation by Li and Yio; Australian Mineral Economics AME 1966)

In geological processes gold has been concentrated locally, and gold ores have been formed in which the gold percentage is many times greater than the mean content of the crust. In spite of this, there are no rich ores used for extraction of gold. The ores in South Africa generally contain 6 g/tonne but richer ores are also known, yielding 20 g/tonne. Gold ores in the USA contain ca. 3 g/tonne. Some ores that are mined for copper may also be important gold ores, even if the gold content is as low as 0.2 g/tonne.

Gold occurs mostly native as pure gold. The alloy *electrum*, gold and silver, is not uncommon. Important gold compounds in ores are tellurides of the type $(Ag,Au)Te_2$. They weather easily and the metal is set free. When it occurs in nature the heavy gold is concentrated in some parts of the sediment as gold sand.

There are different types of gold ore.

- With native gold as particles:
  - The *primary* occurs in solid rocks, often together with quartz on the surface of cracks in the upper crust.
  - The *secondary*, also called *alluvial*, are made up of gold particles in sediments (*placers*). The particle size can vary from big nuggets to microscopic grains, impossible to detect with the naked eye. Most gold is won from these secondary deposits.
- With gold impregnated in sulfide ores, mostly of copper, zinc and lead.

Within the different types there are many subgroups, as illustrated in Table 5.3.

Calculations of gold reserves in the world have changed very much in recent years owing to the discovery of new regions rich in gold. In the early 1960s South Africa was considered as possessing almost 90% of the global reserves. In 1992 the corresponding share was down to 43% and in 2000 to 38%. Actual values for the gold reserves are given in Table 5.4 and Figure 5.3. Table 5.4 also shows the values for the gold *reserve base* that includes known deposits that can be mined in the future.

Table 5.3 Gold ores of different types

Ore type	Geological comment	Example of deposit
Native gold in quartz gangues	Fissure veins partly filled with native gold in weakness zones in volcanic and sedimentary rocks	Several of the biggest gold ores are of this type: *Super Pit* in Australia, *Golden Giant* in Canada, *Björkdal* in the Skellefte Field in Sweden
"Paleo-placers"	Conglomerates of quartzite and mica in precambrian sedimentary rocks. May contain gold, silver, platinum and uranium	The biggest gold producer in the world, *Witwatersrand* in South Africa has several mines with this ore type
Carlin type	Gold embedded in younger sedimentary rocks. The metal is so fine grained that not even a content of 400 g/tonne can be detected, even if a simple magnifier is used. This ore type was discovered in Nevada at the beginning of the 1960s	Deposits in Gold strike in Nevada: *Carlin* (1960), *Betze* (1988), *and Miekle* (1996). There is a gigantic activity in the region. A total rock quantity of 400 000 tonne is mined every day, of which 35 000 tonne is gold ore
Epithermal gold deposits.	Epithermal deposits are formed in and along fissures in rocks by deposition at shallow depths from ascending hot solutions.	Several gold ores, discovered since the end of the 1980s of this type: *El Indo* and *Tambo* in Chile, *La Joya* in Bolivia, *Porgera* and *Lihir* in Papua New Guinea
Porphyry copper gold deposits	Disseminated copper minerals and gold in a large body of porphyry. Gold in quartz gangues. This ore type is of great economic importance for copper production in the world	The ore in the deposit *Grasberg/Ertsberg* on Irian Jaya in Indonesia is of this type. The mine was discovered and built in the period 1985–95. The deposit, probably the biggest in the world with Cu and Au, is situated at an altitude of 3500 m
Gold in complex sulfide ores	Gold is impregnated in sulfides of copper, lead or zinc	Many deposits, mined for Cu, Pb and Zn are of this type. Gold is an important by-product

Table 5.4 World mine reserves and reserve bases

Country	Reserves Tonnes	Reserve base Tonnes
South Africa	19 000	36 000
United States	5600	6000
Australia	5000	6000
Russia	3000	3500
Indonesia	1800	2800
Canada	1500	3500
China	1000	4300
Peru	200	650
Other countries	13 000	16 000
World total	50 000	78 000

Source: ref [5 3].

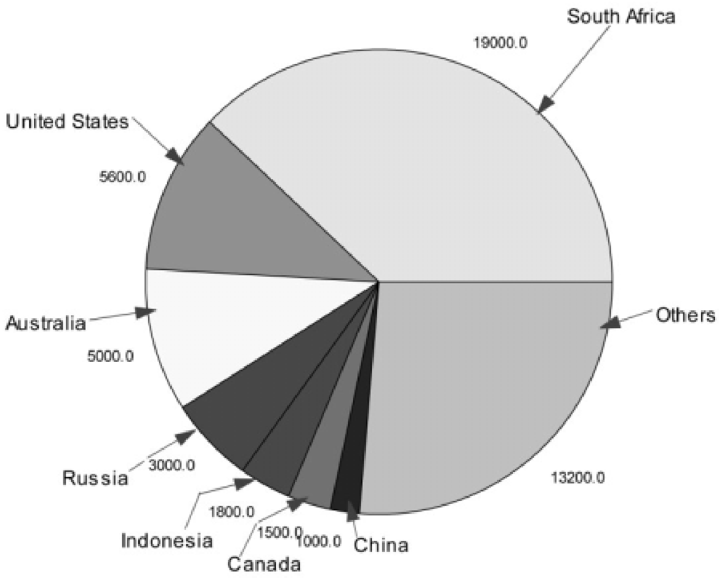

Figure 5.3 World gold reserves in tonnes.

The oceans have a certain low gold content, yet it is large enough to state that the total weight of gold in the oceans is greater than all known deposits in the earth's crust together. The cost of recovery would, however, be far greater than the value of the gold recovered.

5.5
Gold Production in Mines

As mentioned, gold is found as fine particles in *gold ores* and in *complex sulfide ores*, containing – besides gold – copper, lead and zinc. Modern mining for special gold ores may occur in very deep mines, in South Africa down to 4000 m. Gold-containing sulfide ores are worked with traditional techniques in both opencast and underground mines. The ores are dressed near the mine. Flotation is the process mainly used for the sulfide ores, giving concentrates of the different ore minerals. Gold concentrates with copper. The special gold ores, with gold as very fine particles, are ground and pretreated with gravity concentration.

The world production of gold in mines is shown in Table 5.5.

Table 5.5 World mine production of gold in 2000 by country

Country	Production, counted as gold metal		Country	Production, counted as gold metal	
	kg	**% of total**		**kg**	**% of total**
South Africa	430 780	16.9	Mexico	26 375	1.0
United States	353 000	13.8	Argentina	26 000	1.0
Australia	296 410	11.6	Mali	25 000	1.0
China	180 000	7.0	Korea, Republic	25 000	1.0
Canada	153 780	6.0	Zimbabwe	22 070	0.9
Russia	140 000	5.5	Kazakhstan	20 000	0.8
Peru	132 585	5.2	Kyrgyzstan	20 000	0.8
Indonesia	124 600	4.9	Colombia	19 000	0.7
Uzbekistan	85 000	3.3	Guyana	13 500	0.5
Papua New Guinea	74 000	2.9	Guinea	13 000	0.5
Ghana	72 080	2.8	Bolivia	11 000	0.4
Chile	54 140	2.1	Mongolia	10 000	0.4
Brazil	52 000	2.0	68 other countries	138 680	5.4
Philippines	30 000	1.2			
			Total	2 550 000	100

Source: ref [5.3]

5.6
Gold Manufacturing by Chemical and Metallurgical Methods

5.6.1
Older Techniques

The *cupellation method* is described in Chapter 6 Silver. In earlier times this separated gold from less noble metals such as lead, tin, iron and zinc. Any silver present, however, remained with the gold.

The *amalgamation process* was also an early technique. It was based on the fact that mercury easily forms alloys, amalgams, with gold. As far back as Roman times the mercury ore *cinnabar* was found in Spain and mercury was obtained by distillation. Crushed and ground gold ore was treated with mercury, amalgam was formed and pressed out from the gangue. Afterwards, when the mercury was distilled off, gold remained. The Spaniards in South America used this technique. Many native peoples, commandeered as forced labor, died of mercury poisoning. In subsequent times the amalgamation process has been adapted so that finely ground ore, suspended in water, passes over copper plates coated with mercury.

5.6.2
The Cyanide Method – Environmentally Friendly!

Around 1900 a technical breakthrough was made in gold extraction. The cyanide method was invented. After grinding, the gold ore is leached in a water solution containing 0.05% sodium cyanide. Some lime is added to keep the pH value high enough to avoid release of the deadly poisonous hydrocyanic acid. Gold is dissolved as a cyanide complex. After filtering, the gold is precipitated with zinc chips. As an alternative the gold cyanide complex is adsorbed on active coal and is eluted as a concentrated solution from which gold is precipitated in an electrolytic process. The cyanide process is, in spite of the cyanide, markedly more environmentally friendly than the amalgamation method. The excess of cyanide is easily removed by oxidation to ammonia and carbon dioxide.

5.6.3
Gold Manufacture from Sulfide Ores

Copper and other sulfide ores with gold are concentrated by flotation, when gold concentrates with copper. In the final step, in which anode copper is dissolved in an electrolytic process (and copper is precipitated on the cathode) gold is not anodically dissolved but stays with the silver in the slime. This is melted to a raw silver, which is used as an anode in a new electrolytic process in an electrolyte containing nitric acid. Silver is dissolved but gold, and platinum, stay in a new anode sludge, from which gold is extracted.

5.6.4
Separation of Gold and Silver

Raw gold, prepared from gold ores, normally contains 85–95% gold, 5–15% silver, and small percentages of copper, zinc and other metals. To separate gold from silver is a classic assignment. Attempts at gold/silver separation were made in antiquity. Addition of salt (sodium chloride) in the cupellation process transformed silver to silver chloride, which was dissolved in the slag. The remaining metal was gold. A similar effect was obtained by addition of sulfur or antimony sulfide. Silver combined with sulfur to silver sulfide, which passed into the slag. When mineral acids became available the important discovery was made that gold is insoluble in all acids with the exception of a mixture of hydrochloric and nitric acids, *aqua regia*. Silver, unlike gold, is soluble in nitric acid. This acid, *aqua fortis*, could thus be used to separate gold and silver. In the middle of the 19th century AD platinum became available and the *parting* (the gold/silver separation) was performed in vessels of this noble metal. All metals in an alloy except gold were dissolved and the vessel material was not attacked.

Cheaper methods were sought and one was developed by F. B. Miller in Australia in 1867 and used by the Sidney Mint. In that process gold was refined by chlorine in special crucibles, as shown in Figure 5.4. Chlorine was passed through the molten gold. At first fumes of volatile chlorides of different metals, except gold and silver, were emitted. Then silver started to react with chlorine forming molten silver chloride. At the end of this process step, and before gold reacted with the dry chlorine, the crucible was cooled until the gold solidified. The molten silver chloride could then be poured off.

After many essential improvements, this technique, the Miller process, has been introduced in all big gold refineries [5.4].

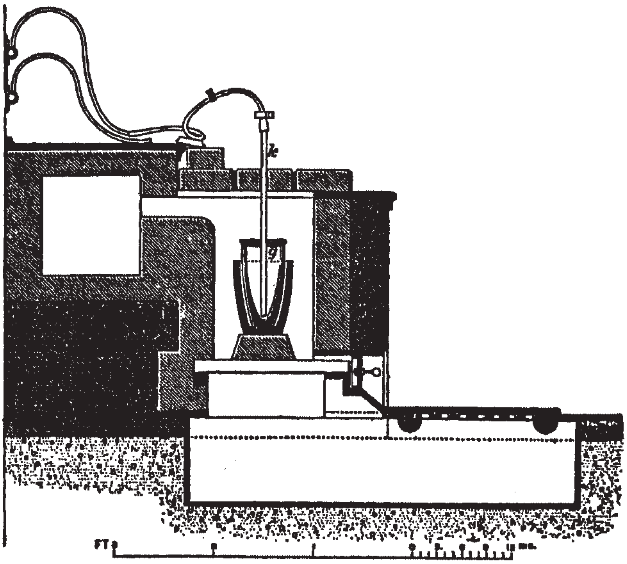

Figure 5.4 Purification of gold by chlorine [5.1].

5.7 Properties

5.7.1
A Ductile and Noble Metal

Gold is the most ductile of all metals. It can be rolled to foils with a thickness of 0.1 μm (0.1 micron; 0.0000004 in) and drawn to wire with a diameter of 10 μm (0.00004 in).

Gold is bright yellow but finely divided it is black like other metal powders. Suspended as a colloid in water the color ranges from ruby red to purple.

Chemically gold is a noble metal. It does not react with oxygen and ozone, sulfur, fluorine and iodine. Dry chlorine gas, however, attacks gold. The metal is inert to nitric acid but is attacked by hydrochloric acid if oxidizing agents are present. *Aqua regia*, a mixture of concentrated hydrochloric acid and concentrated nitric acid in the ratio 3:1 is the classical solvent for gold. In the solution, gold is present as a trivalent ion. Cyanides of alkali metals also dissolve gold if oxygen is present, and this is the basis for the cyanide leaching process.

5.7.2
Why is Gold so Noble?

A noble gas like argon is noble because its outer electron shell is complete and stable. By that definition, gold is not a noble element. Ten electrons are present in 5d-orbitals and one electron in the 6s-orbital farthest out. It seems from this electron configuration that gold is not a noble metal. The single 6s-electron may be lost, with the formation of monovalent ions. This is in fact the case in solutions containing cyanide for complex formation and air for oxidation. In the complex, the dissolved ion $[Au(CN)_2]^-$ contains gold in the oxidation state (valency) +1. In contact with a very strong electron acceptor such as chlorine in *aqua regia*, two d-electrons can be set free together with the 6*s*-electron, a process that is responsible for the +3 valency for gold in solution.

But, gold *is* noble! Why?

Between silver in period 5 (atomic number 47) and gold in period 6 (atomic number 79) 32 electrons have been added, 14 of them in the 4f subshell. The number of positive protons in the nucleus has, of course, also increased by 32. Electrons in an f subshell are, however, not very effective in screening outer-shell electrons from the nucleus. As a result the outer-shell electrons are held tightly by the nucleus. If we go from an atom with 47 electrons (Ag) to one with 79 (Au) an increased atomic radius would be expected. Surprisingly, this is not the case. The covalent radii are 1.5 Å for silver and 1.44 Å for gold. As a consequence, the outer electrons are strongly attracted by the nucleus and the tendency to form ions is extremely small.

The contraction of the d and s subshells farthest out explains the great affinity of gold atoms for other gold atoms. Interaction between the 5d and 6s orbitals leads to especially stable configurations with gold–gold bonds at a low energy level [5.5]. This strong bonding prevents the metal from being attacked by air, moisture, nitric acid or alkalis. It is also the reason for the tendency of gold to occur native in quartz veins and in nuggets.

5.8
Uses

Gold is important to the total world economy. In the whole world about 500 000 employees work in gold production. Of the gold on the market, about 75% comes from mining and 25% from recycling processes, including quantities sold by government monetary authorities.

The two biggest demand sectors are jewelry and electronics. In 1997, 2360 tonnes (86%) were used for jewelry while 184 tonnes (6.7%) were used for electronics. Dental materials used 2.4% of the total gold supply, 2750 tonnes, that year [5.6].

The mean gold price in 2000 was $280 per troy ounce[2].

5.8.1
Pure Gold and Gold Alloys

5.8.1.1 Alloying for Hardness

In almost all applications gold is used alloyed with other components. The alloy is harder and has better abrasion resistance. This is, for instance, important for gold in teeth. *Dental gold,* used mainly for preparing gold crowns, consists of at least 75% gold. The rest may be palladium, iridium, silver and copper. For aesthetic reasons the visible gold parts are nowadays coated with plastic or porcelain. For *jewelry purposes* mainly gold–silver–copper alloys are used. As solders in jet engines, used at temperatures above 500 °C, gold–copper alloys are used. *Coinage gold* was composed of 90% gold and 10% silver.

5.8.1.2 Gold is Yellow – But Also Green and White

By adding different metals to gold, alloys with different colors can be created. Silver has a very good reflecting power over the whole spectrum and because of that is experienced as the whitest of all metals. A high enough silver content makes gold or gold–copper alloys white, but such a high silver content is needed that the "white gold" may be regarded as a silver alloy. Another way to get white gold is to use palladium, platinum or nickel as alloying metal. The alloy gold–palladium has very good formability and is preferred by jewelers. It is also appreciated by allergy suffererers, as it is free from nickel. White gold of gold–nickel type is, of course, the least-expensive variant, but that alloy is not completely white. A very faint green or yellow color is visible. Zinc or even copper may be resorted to. A common composition of *white gold* is 75% gold, 10% nickel, 10% copper and 5% zinc. White gold can also simply be platinum or pure gold plated with rhodium.

When gold is alloyed with silver the effect of silver on the color begins to be evident at a content of 10%. In the range 10–20% silver the alloy color is not pale yellow, as might be expected. Instead, the alloy is *green gold* with a faint green color. Wavelength measurements show that there is a blue component in the light that is reflected by

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[2] Troy weight is a British weight system for noble metals and precious stones.
1 troy pound = 12 troy ounces = 373.242 g.
Thus 1 troy ounce = 31.1 g.
Compare 1 "ordinary" ounce = 28.35 g.

silver. Gold itself reflects a distinct yellow color. The combination of yellow and blue gives an impression of green. However, the alloy does not have a clear green color. It is about as green as pure nickel is yellow and pure chromium is blue.

5.8.2
Gold Surfaces

Gilding for decoration has been used from time immemorial. The gold gave beauty and luster. In genuine *gilding* of *furniture* and *books* the object was given a coating of varnish or albumen. Then gold leaf was pressed against the gluey surface. *Copper objects* were dipped in an acidic mercury nitrate solution. Metallic mercury was precipitated on the surface, which also was smeared with gold amalgam. The mercury was driven off by heating, leaving a raw gold surface, which was polished to a luster. From the environmental point of view this method was, of course, clearly undesirable. More modern and acceptable is the coating of copper by roll plating a thin gold layer on the object. This technique is in fact very important, partly for making filled gold for jewelry and partly for corrosion-resistant electric contacts in industry.

Gold coating of *glass surfaces* is carried out by modern vacuum deposition (PVD, physical vapor deposition) and also with an old method, painting with a gold pigmented lacquer, followed by burning.

Plating with pure gold is important in modern high-technology components. In, for example, printed circuit cards for computers and mobile telephones the gold gives corrosion resistance and solderability. The plating is as a rule made by electrolysis in a bath, containing gold as a complex cyanide ion $[Au(CN)_2]^-$ and potassium cyanide, KCN.

5.8.3
The Gold Content of Gold

For assaying, the cupellation test is used. The method is described by Agricola and is in principle used even in our day for testing [5.7].

> 0.25 g of the alloy to be examined is weighed and mixed with a quantity of silver 2.5 times the estimated gold quantity in the sample. A small quantity of copper is added and the mixture is laid in a lead foil. The "packet" is melted at 1050 °C in a bowl called a *cupel*. The less noble metals are oxidized by excess air, leaving a silver-white metallic bead of a gold–silver alloy on the bottom of the cupel. This bead is hammered or rolled to a strip. The silver is dissolved by treatment with nitric acid and the remaining metal is pure gold. It is sintered and weighed and the gold content of the original sample is calculated.

Taking out a sample for chemical analysis would destroy valuable gold jewelry. A very old testing technique, with roots in the Greco-Roman world, can by used for a simple estimation of the gold content. The gold–silver alloy was rubbed on a touchstone and the color of the mark was compared with the color obtained from an alloy of known composition. In a modern variant a mark from the actual sample is made on a touchstone of slate. A quantity of only 1–2 mg is transferred from sample to stone. Parallel marks are made with a number of gold–silver alloys with known compositions. A thin layer of a suitable acid is applied straight across all the marks and may act during 10–30 sec. The lower the gold content, the faster the acid attacks the mark. By comparison the gold content of the sample can be estimated.

In a modern laboratory, spectroscopic methods are of course used for determining the gold and silver contents of alloys.

5.9
The Biological Role of Gold

Gold metal as foil or sand was in older times used as a remedy for different illnesses. Such elementary gold is, however, quite ineffective. On the other hand, gold salts may be absorbed by an organism and are toxic in too great concentrations. In correct concentrations they have been used for therapeutic purposes against tuberculosis and rheumatoid arthritis.

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6
Silver

6.1 Ag
Facts about Silver

6.1.1 Ag
The Element

Symbol:	Ag
Atomic number:	47
Atomic weight:	107.87
Ground state electron configuration:	$[Kr]4d^{10}5s^1$
Crystal structure:	Cubic fcc with $a = 4.09$ Å

6.1.2 Ag
Discovery and Occurrence

Discovery: Silver has been known and valued as an ornamental and coinage metal since ancient times, at least as far back as 4000 BC. Silver mines in Anatolia (present Asia Minor) were probably worked before 2500 BC. Metallurgical techniques were developed and silver could be exported to different parts of the ancient world.

Most important mineral: *Native silver* (Figure M4) rarely occurs in nature. The main occurrence of silver is as sulfide minerals. Argentite Ag_2S is geologically connected with deposits of lead, copper and zinc and with gold in veins. Silver minerals containing antimony and arsenic, *pyragyrite* Ag_3SbS_3 and proustite Ag_3AsS_3, form local deposits.

Ranking in order of abundance in earth crust:	68
Mean content in earth crust:	0.075 ppm (g/tonne)
Mean content in oceans:	$4 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	$100 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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6.1.3 Ag
Chemical Characterization

Silver is stable in pure air and water, but tarnishes when exposed to hydrogen sulfide, or eggs, which contain a considerable quantity of sulfur as a constituent of protein. It is insoluble in sulfuric and hydrochloric acids but dissolves in concentrated nitric acid. Next to gold, silver is the most malleable and ductile of all metals. Of all metals silver has the highest thermal and electrical conductivity, the highest reflectivity and the whitest color.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**	**Electron affinity (kJ mol^{-1}):**
Ag^{I} as in AgCl, $AgNO_3$ and AgCN	$Ag(g) \rightarrow Ag^{+}(g) + e^{-}$ 731	$Ag(g) + e^{-} \rightarrow Ag^{-}(g)$
Ag^{II} as in AgF_2	$Ag^{+}(g) \rightarrow Ag^{2+}(g) + e^{-}$ 2070	–125.6
Ag^{I} and Ag^{III} in AgO ($Ag^{I}Ag^{III}O_2$)	$Ag^{2+}(g) \rightarrow Ag_3+(g) + e^{-}$ 3361	

Standard reduction potential:	$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $E^0 = +0.800$ V	
Electronegativity (Pauling):	1.93	
Radii of atoms and ions:	Atomic:	160 ppm
(WebElements™)	Covalent:	153 ppm
	Ag^{+} (4-coordinate, tetrahedral):	114 pm
	Ag^{+} (4-coordinate, square-planar):	116 pm
	Ag^{+} (6-coordinate, octahedral):	129 pm
	Ag^{+} (8-coordinate):	142 pm
	Ag^{2+} (4-coordinate, square-planar):	93 pm
	Ag^{2+} (6-coordinate, octahedral):	108 pm
	Ag^{3+} (4-coordinate, square-planar):	81 pm
	Ag^{3+} (6-coordinate, octahedral):	89 pm

6.1.4 Ag
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
10 490 kg m^{-3} 10.49 g cm^{-3}	10.27 cm^3	1235 K 961.8 °C	2435 K 2162 °C	235 J K^{-1} kg^{-1}

Thermal conductivity Wm^{-1}K^{-1}

173 K	**273 K**	**373 K**	**573 K**	**973 K**
432	428	422	407	377

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$14.2 \cdot 10^{-6}$	$18.9 \cdot 10^{-6}$	$20.6 \cdot 10^{-6}$	$23.7 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
3	14.7	20.8	33.4	61	194

Mass magnetic susceptibility χ_{mass} at 293 K	$-2.27 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
82 GPa	30 GPa	103 GPa	0.37

6.1.5 Ag
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	11.30 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	255 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	284.5 $kJmol^{-1}$
Entropy S^0 at 298 K	42.55 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	20.10	25.35	26.99	29.67	33.40	20.79

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4\ Ag + O_2 \rightarrow 2\ Ag_2O$	–22.4	–	–	–	–

6.1.6 Ag
Nuclear Properties and X-ray

Isotope range, natural and artificial	94–128

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{107}Ag	Stable	51.84	–1/2	–0.1136
^{109}Ag	Stable	48.16	–1/2	–0.1307

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{107}Ag	^{109}Ag
Reference compound	$AgNO_3/D_2O$	
Frequency MHz (^1H = 100 MHz)	4.048	4.654
Receptivity D^P relative to ^1H = 1.0	$3.50 \cdot 10^{-5}$	$4.95 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.0	0.200	0.282
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-1.0889 \cdot 10^7$	$-1.2519 \cdot 10^7$
Nuclear quadropole moment, barn	–	–

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
46	Pd	21.021
47	Ag	21.991
48	Cd	22.985

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	214
17.37 keV (MoKα_2)	26.9

Neutron absorption	**Thermal neutron capture cross section**	63.8 barns

6.2
Silver in History

Figure 6.1 illustrating ancient time periods may be of help in discussions about silver in history.

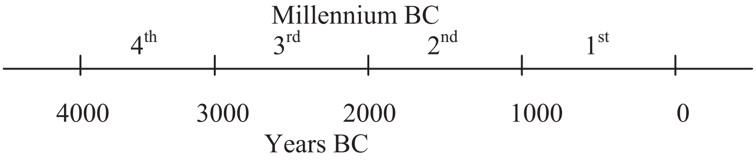

Figure 6.1 Designations for ancient times.

6.2.1
Knowledge of Metals Gradually Increased …

The division of prehistoric times into the Stone Age, the Bronze Age and the Iron Age expresses the importance of materials for tools and weapons. The Stone Age covers the longest part of the prehistory of mankind. In the latter part of the Stone Age, the Neolithic, humans acquired knowledge of agriculture and stock farming. In the Mediterranean region this began at the end of the ice age in Northern Europe. Flint could be worked into tools and earthenware vessels could be fired. Gradually people got to know metals and started to use them. Some could be found native in nature: yellow gold, very apparent among the gray stones in the streams; silver, less noticeable, as thread-shaped “schlieren” or veins in some rocks.

> The word metal itself may, according to Pliny as cited by Meyer [6.1], be derived from this manner of occurrence – not in big blocks but in small units, μετ αλλα, “met all”, “after each other”. This interpretation is, however, uncertain. The Greek word métall-on means “mine” and was adopted into Latin as metallum.

While gold was a reminder of the sun, silver, with its matt surface, was like a reflection of the moon. Both materials were surprisingly formable and really special compared to stone and flint. That they kept their colors after heating in fire was also a source of astonishment.

6.2.2
The Bellows Puff and Blow in the Cupellation Process

Some native silver could be found, but never in amounts great enough to meet the demand. Silver became more and more sought after and demand increased. The big change came with the discovery that silver occurs with lead in its sulfide mineral galena. Many galena deposits rich in silver were found in Asia Minor and in the Armenian mountains. It is often said, and this is mentioned in Chapter 8 Iron, that the alloy steel was invented in the Hittite country. But the same region, a real metallurgical center in Asia Minor, was also the birthplace of silver manufacture. This started at the beginning of the third millennium BC. At this very early time, what method was available to prepare pure silver from a mineral that was mainly lead sulfide?

The technique is known as the cupellation process. The galena ore was roasted, which converted it to lead oxide, litharge, which was easily reduced by charcoal. If silver was present in the galena it stayed in the lead metal. The separation process worked in the following way:

Air was blasted onto the surface of the molten lead that contained silver. Lead and other non-noble metals were oxidized and formed a slag, which floated to the surface or was absorbed by the walls of the earthenware furnace in which the process was performed. A residue of pure silver remained at the bottom. The cupellation process was described by Agricola in De Re Metallica [6.2] in 1556. The principle, shown in Figure 6.2, is the same as the ancient method for separating silver from lead.

The ancient civilizations of Egypt, Israel and India were all familiar with silver and gold, and with methods for winning and working them. They are mentioned in old documents, describing the cupellation process for separating silver (and gold) from lead. Different findings and historical data indicate that cupellation was invented in Asia Minor in the first half of the third millennium BC.

A more detailed description of methods and problems in ancient silver production is given by Habashi [6.3].

If the task was to purify lead-contaminated silver metal, the same process was used but lead was added in excess from the beginning before the furnace operation started. The silver content of the alloy could then be taken up from the furnace bottom. If the supposed silver alloy did not in fact contain silver, blowing, however long it might be for, was no use. No silver was formed on the furnace bottom. In the time of the Old Testament, people were obviously so familiar with this refining process that the prophets of Israel could use it in their pictorial language. Ca. 750 BC the prophet Jeremiah refers to the process in a severe lecture to his audience:

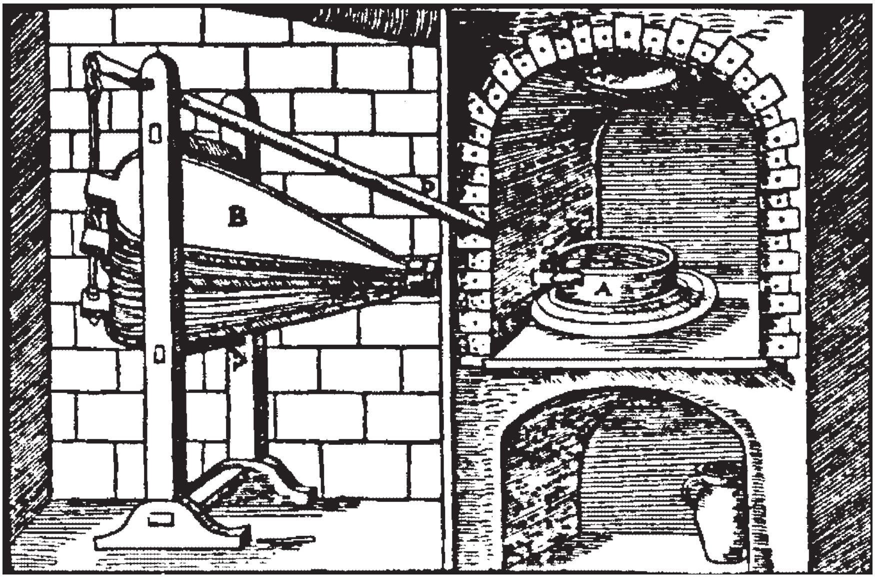

Figure 6.2 Furnace for the separation of silver from a lead-silver alloy according to Agricola.

> I have made you a tester of metals and my people the ore, that you may observe and test their ways. They are all hardened rebels, going about to slander. They are bronze and iron; they all act corruptly. The bellows blow fiercely to burn away the lead with fire, but the refining goes on in vain; the wicked are not purged out. They are all rejected silver, because the Lord has rejected them. (Jeremiah 6:27–30)

This manner of speaking is forceful for anyone who, perhaps daily, has come into contact with the trade of the silversmith in their own village. For people in our own time the speech is certainly less easily understood. And how do the theologians of our time interpret the text? Perhaps theological education today needs elements of chemistry and metallurgy to make texts of this type understandable.

6.2.3

Crete and Mycenae

In the third millennium BC, Mesopotamian merchants sent out by Sumerian and Assyrian cities settled in Asia Minor, bought metals in the land of the Hittites and delivered the valuable materials to their home country in the Euphrates–Tigris region. A sophisticated craft in silver (and gold) developed and the ability of the craftsmen there became known in different parts of the ancient world, Egypt and Syria for instance, and was passed on to Anatolia in Asia Minor. The manufacture of articles, drinking-vessels, pans and cult objects began there after 2500 BC and reached the Greek mainland via Troy and the Cyclades islands. In the highly developed Minoan culture on Crete, with the great princely palace at Knossos, the new metals were highly appreciated. Through the extensive contacts that the shipping created, the Cretans acquired the noble metals and also a knowledge of metalworking. From the prosperous time of the Minoan culture about 2000 BC and up to ca. 1400 BC many finds show excellent handicraft. However, at this latter time the glory days of Crete ended, perhaps after a huge eruption of the volcano on Thera in about 1500 BC, followed by an invasion of mainland conquerors. The Knossos palace was finally destroyed in about 1400 BC. Before these disastrous happenings, Cretan energy had exerted a great influence on large parts of Greece. The gold-rich Mycenae on Peloponnesos was according to Homer a palace for the Greek kings. Excavations have exposed six shaft graves from ca. 1600 BC, revealing immensely rich findings of pieces of jewelry. Memories from these times are retained in the myths about the Trojan War in about 1250 BC. In The Iliad Homer tells how Odysseus won a wine cup of silver as the first prize in a competition held in connection with the funeral of a well-known king.

A Doric tribe armed with weapons of iron invaded the Greek peninsula around 1100 BC and conquered the Mycenaean Greeks, equipped only with bronze weapons.

At the beginning of our chronological times, Spain had taken over as the main supplier of silver ore and silver metal. Native silver was found, but usually the mined silver was a sulfide mixed with lead sulfide.

6.2.4
King Croesus Coins Silver and Becomes a Proper Croesus

Lydia was a mountainous province in Asia Minor, around the valleys of the rivers Hermos and Kaytros. The capital was Sardis while another large town was Magnesia. The coastal land was colonized early by emigrants from Greece and was known as Ionia. Etymologically this small area has a strong connection to modern science. The name of the capital we find in the mineral names sard and sardonyx, the town name Magnesia in the element magnesium. Charged atoms, migrating in an electric field, are ions. Croesus became the king of Lydia in 560 BC. He had an ambivalent attitude to Greek people, religion and culture. Partly he made war against the colonized coastal towns and conquered all but Miletos; partly he devoted himself to giving his country a Hellenistic spirit and he gave generous gifts to the Greek temples.

The first simple coins in the ancient Near East consisted of weights, rings and bars of copper or lead. Croesus and his authorities introduced separate silver and gold coins and these were given a kind of official status. The silver coins in particular spread rapidly among the Mediterranean countries. The conditions for this were favorable, as both Asia Minor and Greece were important silver regions. Coins of silver gained a strong position in the Greek world and provided the financial base for Athens' period as a great power. Silver continued to be used for coins right up to the 20th century but is now substituted by other coin-metals1).

1) The composition of modern coin-alloys is described in Chapter 31 Nickel.

King Croesus himself became enormously rich from his invention. Ever since then a very rich man is said to be "a proper Croesus". According to Herodotos[2] Croesus once asked Solon[3] if he knew any person more rich and happy than the king himself. The wise Solon's answer is often quoted: "Nobody should be praised as happy before his death". This the king also experienced. In a war against Persia the Persian king Cyrus conquered him. The captured Croesus was condemned to be burnt at the stake. At the first flames Croesus cried: "Oh Solon, Oh Solon". This aroused Cyrus' curiosity and he wondered about the meaning. When the whole situation was explained to him he discharged the prisoner and made Croesus his collaborator. Perhaps this helps to explain why the Persian coin weighing 8.4 g, the dareik, became the most used gold coin in its time.

6.2.5

Athens a Basis for the West – Silver a Basis for Athens

On the island of Attica in the southeast the big Greek silver mine Laurion was situated. Silver had been won there since the beginning of the second millennium BC. When silver coins became so important after Croesus' achievement, the mine was especially valuable and its production reached a peak around 500 BC. The silver tetradrachm became a common coin in the eastern Mediterranean countries. The growing Athenian State then ran the mine. After the victory over the Persians at Marathon in 490 BC a big Persian revenge attack was expected. In that situation, the Athenians decided that the returns from the silver mine in Laurion should be used for building up a fleet of a new type of ship, the trireme, "three-oarsmen", big ships with a crew of 200 men. They were intended for ramming, the new marine battle-tactic in the Mediterranean. In 483 BC a new silver vein was found in Laurion, so rich that the mined metal was sufficient to provide coins for both fleet building and common trade.

Greek culture stood for humanism and aspired towards a rational explanation of our world and all its phenomena. This attitude has permeated the western world. The aim was and remained: freedoms, moderation, balance. The Athenians laid the foundation. The element silver was a part of the spadework. The mineralogists of antiquity, who searched and found the silver veins in the mountains, and the 30 000 slaves doing the hard work of mining, created the material basis for Athens position as a great power among the Mediterranean countries. They should be remembered when Greek culture and its intellectual characteristics are described and assessed.

When the Roman Empire took over in the Mediterranean region, the silver deposits in Laurion were insufficient. In Cartagena in southern Spain, a big deposit of lead and silver was discovered. These mines were incorporated with Rome about 200 BC in connection with the Punic Wars.

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[2] Herodotos, 485–425 BC, Greek learned man and writer. His language is said to show that he was Ionian.

[3] Solon, active round 600 BC, Athenian statesman and writer. Official conciliator appointed to avert the acute crisis that threatened the population after the victory of the monetary economy.

6.2.6
Early Silver Supply in Central and Northern Europe

In the Harz region in central Germany a silver deposit was discovered in Rammelsberg in the middle of the 10th century AD. This mine became the most important source of silver, lead and copper in central Europe. Silver was found somewhat later in Erzgebirge, the ore mountains in the borderland of Bohemia, between Germany and the Czech Republic. The deposits at Schneeberg, Annaberg and Joachimsthal became, like Rammelsberg, important sources of the silver used in Europe during the Middle Ages. In Kongsberg in Norway a large deposit of native silver was discovered in 1623.

In Sweden, the most important silver deposit has been the Sala Silver Mine, Figure 6.3. Like many other silver mines it was actually a lead mine. The pure galena contained 0.1–1% silver, but in some parts the lead glance contained more silver sulfide, Ag_2S, as well as native silver. There the silver content of the ore could increase to 2–3%. There are many myths about the discovery and first mining of this deposit. Historically it is clear that the mine was active at the beginning of the 16th century, when it was taken over by the king, Gustavus Vasa. By his personal and energetic commitment, the mine was established on a sound basis and in some years could give 4000 kg silver, a valuable contribution to the finances of the state.

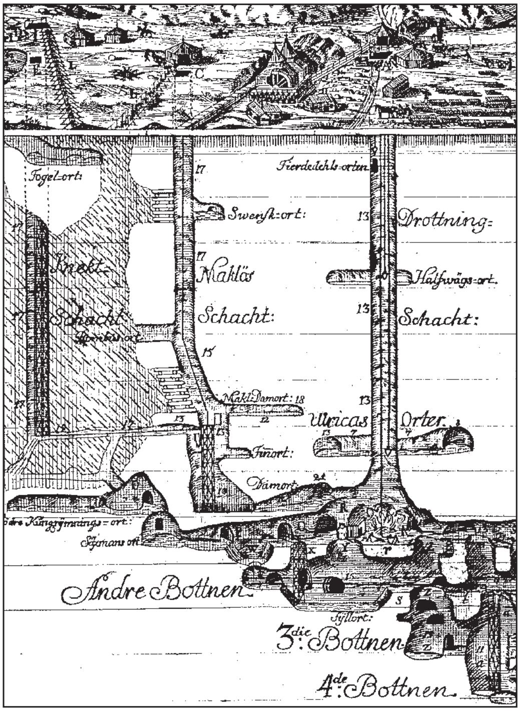

Figure 6.3 Longitudinal section through the Sala Silver Mine in a mine map, drawn in 1724 by Johan Tobias Geisler. Three shafts can be seen: a drainage shaft to the left and two working shafts in the middle and to the right. The depth of the mine is 250 m.

As in all mines at this time, the rock was broken up by a method which involved heating it with fire and then pouring water over it. The following description from 1642 recounts the hard conditions for miners in Sala, but is certainly typical for all mines in the time before the use of explosives.

> After midday at five o'clock they make a fire. Then all the workers climb up, out of the mine. In the nighttime, at one o'clock, two men go down to put out the fire. When they pour out the water on the fire a smoke of moisture and sulfur rises straight up, for which they cannot remain standing but must throw themselves down to the floor. It is a dangerous work and so detrimental to their health that those men who take this job do not live for a long time. Yet, they are paid much better than other laborers in the mine."

From the old careful Swedish mining statistics we can see that from the start and up to 1920 as much as 189 173 kg metallic silver was produced. Mining continued with reduced activity after World War II but stopped in 1962. For some years in the 1950s, a labor force of 15 men could annually produce as much silver as 1000 people did during the palmy days of the 16th century.

6.2.7
Silver Regions in South and Central America

Colonization led to the discovery of large silver deposits in South and Central America. From the middle of the 16th to the beginning of the 19th century, a quantity of about 100 000 tonnes of silver was transferred from America to Europe. One of the biggest cities of the time grew up near the silver mountain of Potosi in Bolivia. The silver was extracted from the ore with mercury (the method is described in Chapter 5 Gold). In the Huancavelica mine in Peru a high proportion of the native peoples died of mercury poisoning in forced labor.

6.3
The Geology of Silver

6.3.1
Silver Minerals

Native silver (Figure M4) occurs in nature, but very rarely. It is presumably formed in earth by the reaction

$$3Ag_2S + 2H_2O \rightarrow 6Ag + 2H_2S + SO_2$$

and is deposited on the walls of cracks within a metamorphic zone of calcite, quartz or fluorite. Native silver has also been found in arsenides of nickel and cobalt, together with calcite. Famous localities are Kongsberg in Norway, Annaberg in Erzgebirge, Cobalt in Canada and in Peru. Native silver is also found in nature with gold in an alloy called electrum.

The main occurrence of silver in the ground is as sulfide minerals. Silver glance, argentite, Ag_2S is geologically connected with lead, copper and zinc. Silver minerals containing antimony and arsenic, pyragyrite Ag_3SbS_3 and proustite Ag_3AsS_3, form local "primary" deposits.

The mineral cerargyrite, horn-silver, AgCl, is interesting from a historical point of view. It was in crystals of this mineral that Carl Wilhelm Scheele first observed the blackening effect of light on silver halides.

6.3.2
Silver Resources and Reserves

In Mexico, ores are available containing pyragyrite and proustite, mined entirely for silver extraction, and Mexico derives 50% of its silver production from mines containing these so-called primary silver minerals The other half is, as in the rest of the world, a by-product of copper, zinc and lead production.

The important silver mineral argentite, silver glance, Ag_2S, is part of two types of silver resources. In one silver sulfide is associated with lead, copper and zinc deposits, often at great depths. In the other silver follows gold in vein deposits. In both cases silver is a by-product at extraction of the other metals. Two-thirds of the resources are of the first type, one third of the second type. Global reserves of silver are estimated by the US Geological Survey at 280 000 tonnes. The reserve base (including marginally economic resources) is 430 000 tonnes [6.4].

An additional resource is industrially used silver that is recycled. Most important are scrapped photographic film and paper as well as used photographic baths. Reclamation of scrap from the electronics industry and catalysts from chemical industry contribute to modern silver manufacturing and dental scrap, silver amalgam, is also important.

Global consumption of silver in the year 2000 was estimated to be 25 000 tonnes (with an average price of $5.00 per ounce). Mine production was 18 300 tonnes, which indicates that the recycling of used silver products was considerable.

6.4
Mine Production of Silver

"True" silver ores, mined entirely for silver, are in our day worked mainly in Mexico and to a small extent in the USA (Utah). Most silver is obtained as a by-product after mining of ores for copper, lead and zinc production. However, as much as 10–15% of the total silver amount comes from vein deposits in which gold is the most valuable element.

Figures for silver production in mines in the year 2000 are collected in Table 6.1.

Table 6.1 World mine production of silver by country in 2000

Country	Production, counted as silver metal Tonnes	Percentage of world total production
Mexico	2620	14.3
Peru	2440	13.3
Australia	2060	11.3
Unites States	1860	10.2
China	1600	8.7
Chile	1240	6.8
Canada	1160	6.3
Poland	1100	6.0
Kazakhstan	930	5.1
Korea, Republic	590	3.2
Bolivia	435	2.4
Russia	370	2.0
Sweden	300	1.6
Morocco	290	1.6
South Africa	145	0.8
Turkey	110	0.6
Japan	105	0.6
More than 40 other countries	945	5.2
Total	18 300	100

Data from ref. [6.4].

6.5
Silver Manufacture – Metallurgical and Chemical

6.5.1
Extraction from Lead Ores

6.5.1.1 Older Methods

Lead ores, poor in silver, are first concentrated by flotation. Lead is then produced by roasting and reduction. The content of silver in the lead metal is low. A metallurgical concentration occurs by the so-called Pattinson process (pattinsonizing). The method relies on the fact that silver–lead alloys have a eutectic composition with a silver content of 2.7%, see Figure 6.4. A melt of an alloy with a silver content lower than 2.7% is allowed to solidify slowly. The solid lead formed is gradually removed mechanically and the silver content of the melt increases. In theory a residual alloy with 2.7% Ag can be obtained. In practice it is possible to obtain at least 2% silver. Lead and silver can be separated from this residual alloy by the cupellation process.

For lead ores with higher silver contents the amalgam and cyanide methods described for gold are possible, but little use is made of them today.

6.5.1.2 A Modern Method for Lead Ores, Poor in Silver

Silver is much more soluble in zinc than in lead. In the Parkes process, zinc is added to a lead melt. A silver-rich zinc phase forms on the surface and is drawn off. When zinc is removed by distillation, raw silver remains. Very pure silver is obtained by a subsequent electrolytic process.

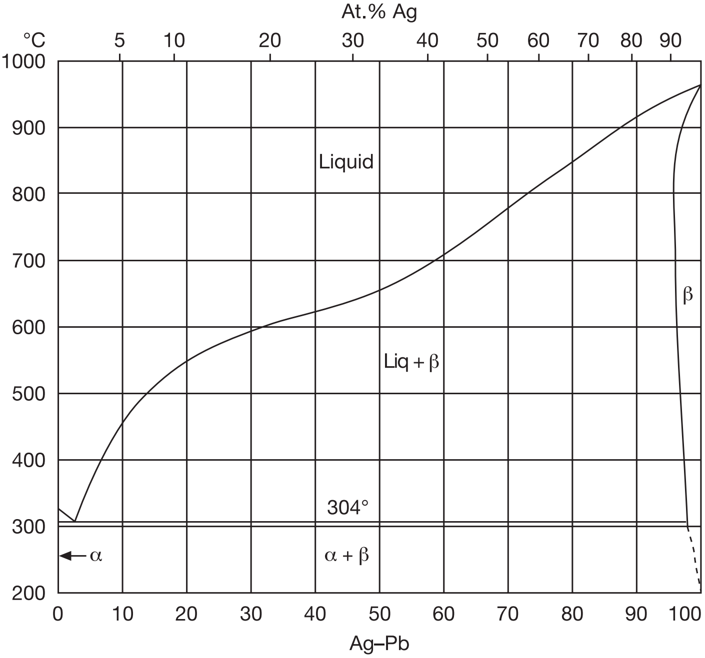

Figure 6.4 The equilibrium diagram for silver and lead.

6.5.2
Silver from Copper Ores

During the electrolytic step of copper production an anode slime is obtained, containing the noble metals of the ore. They are extracted by a complicated process. Raw silver is obtained by melting, and is used as a new anode material. In an electrolytic process with nitric acid as electrolyte silver dissolves from the anode while gold and platinum form a new anode slime. Silver is precipitated from the electrolyte as silver chloride. This is melted with soda and saltpeter at 1000°C. The molten silver is cast into bars and remelted in vacuum to yield very pure, gas-free silver.

6.6
Properties and Uses

Silver is very ductile and malleable, almost as much as gold. It does not react with water and air at ordinary temperatures. Silver is resistant to alkalis and most acids. In contrast to gold, however, it is dissolved by nitric acid. Sulfur and sulfides tarnish silver owing to the formation of black silver sulfide. Contact between silver objects and eggs must be avoided as they contain much sulfur in their protein.

In the year 2000 the consumption of silver in the world was 25 000 tonnes, 18 300 tonnes produced from mining, the rest from recycling processes including quantities sold by government monetary authorities. The silver was mainly used within three areas of about the same size: Silverware/jewelry, photography, and different industrial applications, including electronics.

In a strong period for silver between 1979 and 1988 the price reached a high of \$49.45 per ounce in 1980. By the end of the 20th century, silver had lost much of its image as a precious metal and become more of an industrial metal. The price is nowadays fairly stable, averaging around \$5.00 per ounce.

6.6.1
Alloys for Different Purposes

Of all metals, silver has the highest thermal and electrical conductivity, the highest reflectivity and the whitest color. Pure silver is too soft for most purposes. However, it can be used as a catalyst in oxidation reactions. One example is the production of formaldehyde from methanol. Pure silver is also used in electrical connectors because of its very good conductivity and oxidation resistance. When greater hardness is required, alloys of silver with, for example, copper, nickel and tungsten are used. Sterling silver for tableware, jewelry and different instruments has the composition 92.5% silver and 7.5% copper.

Coin silver was in earlier periods a support for the monetary system, and an alloy of 90% silver and 10% copper was used for coins in the USA until 1965. After a transitional period, the use of silver in coins came to an end in 1970.

Amalgam for dental filling is composed of 32% silver and 52% mercury, with tin, copper and zinc in addition.

6.6.2
Oxides for Batteries and Bromides for Photography

In modern batteries silver oxide is used as the positive pole while zinc is the negative. An increasing quantity of silver is used for this purpose.

A large quantity of silver is used within photography. The photosensitive layer, which darkens on exposure to light, is mainly silver bromide in a gelatin emulsion. Digital imaging may be a threat to this sector of silver use.

6.6.3
Silver Plating

A silver coating is applied to many components. Practically all baths for electrolytic silver plating contain the complex ion $[Ag(CN)_2]^-$ and potassium cyanide, KCN. After plating the silver layer is normally matt but mechanical polishing makes the surface lustrous. Plating baths with special additives directly give brightness to the surface.

6.7
The Biological Role of Silver

Silver has no essential function in biology and its compounds have a very low toxicity, acute or chronic. Both silver and its compounds have a bactericidal effect that has been used for water cleaning and the treatment of wounds. For prophylactic reasons, silver nitrate, lapis, has been dropped into the eyes of newborn children in order to prevent inflammation caused by gonococci.

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7
Copper

7.1 Cu
Facts about Copper

7.1.1 Cu
The Element

Symbol:	Cu
Atomic number:	29
Atomic weight:	63.55
Ground state electron configuration:	$[Ar]3d^{10}4s^1$
Crystal structure:	Cubic fcc with $a = 3.615$ Å

7.1.2 Cu
Discovery and Occurrence

Discovery: Copper was known in prehistoric time, at least as far back as 5000 BC. The word copper is derived from the island of Cyprus in the Mediterranean Sea. Objects of the red metal have been found among the remains of many ancient civilizations, including those of China, Egypt, Asia Minor and Crete. It was also known to the native Americans as copper ore and also as native metal

Most important mineral: Chalcopyrite $CuFeS_2$ (Figure M6)
Copper glance, chalcocite Cu_2S
Malachite $Cu_2(OH)_2(CO_3)$ (Figure M5)
Cuprite Cu_2O
Bornite $CuFeS_4$
Azurite $Cu_3(OH)_2(CO_3)_2$ (Figure M5)

Ranking in order of abundance in earth crust:	26
Mean content in earth crust:	60 ppm (g/tonne)
Mean content in oceans:	$2.5 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	1 ppm
Content in a man's body (weight 70 kg):	70 mg

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7.1.3 Cu
Chemical Characterization

Copper is a reddish metal with a bright metallic luster. After silver it has the best electrical conductivity among metals. This, and its high conductivity of heat, resistance to corrosion and good formability, have made the metal suitable for a wide variety of applications. Its alloys, brass and bronze, are also very important.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
Cu^{I} as in Cu_2O and $CuCl$	$Cu(g) \rightarrow Cu^{+}(g)$	745.5	$Cu(g) + e^{-} \rightarrow Cu^{-}(g)$
Cu^{II} as in CuO and $CuSO_4$	$Cu^{+}(g) \rightarrow Cu^{2+}(g)$	1958	–118.4
	$Cu^{2+}(g) \rightarrow Cu^{3+}(g)$	3555	
	$Cu^{3+}(g) \rightarrow Cu^{4+}(g)$	5536	

Standard reduction potential:	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $E^0 = +0.340\ V$	
Electronegativity (Pauling):	1.90	
Radii of atoms and ions:	Atomic:	135 ppm
(WebElements™)	Covalent:	138 ppm
	Cu^{+} (4-coordinate, tetrahedral):	74 pm
	Cu^{+} (6-coordinate, octahedral):	91 pm
	Cu^{2+} (4-coordinate, tetrahedral):	71 pm
	Cu^{2+} (4-coordinate, square-planar):	71 pm
	Cu^{2+} (6-coordinate, octahedral):	87 pm

7.1.4 Cu
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
8960 kg m^{-3} 8.96 g cm^{-3}	7.08 cm^3	1357.8 K 1084.6 °C	2835 K 2562 °C	384 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
420	403	395	381	354

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$10.3 \cdot 10^{-6}$	$16.5 \cdot 10^{-6}$	$18.3 \cdot 10^{-6}$	$20.3 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1356 K**
2	15.5	22.3	36	67	213

Mass magnetic susceptibility χ_{mass} at 293 K	$-1.081 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
130 GPa	48 GPa	149 GPa	0.35

7.1.5 Cu
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	13.14 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	300.5 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	338 kJmol^{-1}
Entropy S^0 at 298 K	33.15 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	16.01	24.44	26.48	28.70	32.80	32.80

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4Cu + O_2 \rightarrow 2Cu_2O$	–292	–265	–195	–117	–
$2Cu + O_2 \rightarrow 2CuO$	–257	–220	–140	–	–

7.1.6
Nuclear Properties and X-ray

Isotope range, natural and artificial	57–79

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{63}Cu	Stable	69.17	–3/2	2.223
^{65}Cu	Stable	30.83	–1/2	2.382

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{63}Cu	^{65}Cu
Reference compound	$[Cu(CNMe)_4]ClO_4$ in MeCN	
Frequency MHz (^1H = 100 MHz)	26.515	28.404
Receptivity D^P relative to ^1H = 1.00	0.0650	0.0354
Receptivity D^C relative to ^{13}C = 1.00	371	202
Magnetogyric ratio, radT^{-1}s^{-1}	$7.1118 \cdot 10^7$	$7.6044 \cdot 10^7$
Nuclear quadropole moment, barn	–0.22	–0.204

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
28	Ni	7.461
29	Cu	8.028
30	Zn	8.616

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	52.1
17.37 keV ($MoK\alpha_2$)	49.7

Neutron absorption **Thermal neutron capture cross section** 3.8 barns

7.2
Copper in History

The name of the element copper is connected with Cyprus, the island in the Mediterranean Sea. The Greeks knew the island as Kypros. Did the island give its name to or receive its name from the metal? This question is discussed by Sir George Hill [7.1]. He suggests, with reference to the very old Sumerian word *zubar* for copper, that the answer would be in favor of the second possibility. An ore was mined there, the metal of which the Romans named *cyprium*, later *cuprum*. In antiquity, in the second millennium BC and thus long before the Roman period, copper was exported from Cyprus to different countries, for instance Syria and Egypt.

Silver and gold were highly prized metals but it was copper and iron that changed history. Copper could be found as native metal, as ores with oxide minerals such as malachite, cuprite, and azurite, and as ores with sulfide minerals such as chalcopyrite and copper glance, chalcocite. The oxide minerals could easily be reduced, starting with charcoal and open fires. When the ability to make copper hard by addition of tin developed, the Stone Age gradually changed to the Bronze Age. Later, but still before 1000 BC, the iron age began in the Mediterranean countries.

7.2.1
A Copper Age between the Stone and Bronze Ages?

Historians have defined a *Copper Age* between the ending of the Neolithic Stone Age and the beginning of the Bronze Age. For the Mediterranean region including Syria-Palestine the following scheme is adopted:

- 3000–2000 BC Early Bronze or Copper Age
- 2000–1550 BC Middle Bronze Age
- 1550–1100 BC Late Bronze Age

Thus the age of metals began with the *Copper Age*.

An early copper metallurgy developed when some craftsmen – who were surely considered to be in contact with the gods – acquired knowledge about what type of earth (containing a copper oxide mineral) should be mixed with charcoal to give the remarkable red metal in an open fire. Air blasts were also early used to obtain high temperatures and melting. Around 3500 BC a copper metallurgy, controlled by specialists, had been developed in Mesopotamia. Somewhat later the technique for winning and working of copper metal became known in the border district between Egypt and Israel and in Anatolia. From the Mediterranean countries, copper metal found its way north to the Neolithic cultures in Europe.

The metal could not really be used for tools and weapons. It could certainly be forged into knives and arrowheads, but it was too soft. Stone-Age man might see a copper sword as a curiosity and a symbol of a new time, but for hunting and fighting he relied on the good old flint tools.

7.2.2
A Clear Greeting From the Copper Age

The “iceman”, found in 1991 in southern Tyrol on the border between Austria and Italy, became a worldwide sensation. The man had been lying frozen in the ice for 5300 years and had thus been living round 3300 BC, in the Neolithic time in Central Europe. He might perchance have come into contact with the incipient Copper Age of the Mediterranean countries. And indeed so! In his equipment a copper ax was found, but also tools and weapons of reliable materials: a bow with arrows of flint stone and a dagger with a blade of the same material. The copper metal in the ax was analyzed and proved to be of surprising purity: 99.7% Cu, 0.2% As, 0.1% Ag.

7.2.3
Copper in Many Regions

The Copper Age was established when the supply of copper from reduction furnaces in different regions became regular. Native copper, however, was found earlier and hammered into components. Copper ornaments dated to 6000 BC are found in Persia and Anatolia. Excavations in Rudna Glavia (in the former Yugoslavia) show that copper was mined there in 4000 BC. The native peoples in the regions of the Great Lakes in North America used copper very early. There are indications that the native metal was exploited in the Upper Peninsula of Michigan, perhaps around 5000 BC. At Lake Superior, relics of copper extraction from malachite have been found, dated to perhaps 2000 BC. In Wisconsin and Illinois bracelets and other ornaments of copper, and even knives, axes and spearheads, have been discovered.

La Tolita’s occupants in the South American gold country Esmeralda also manufactured many objects of copper: sewing needles, small axes and pieces of filigree made of fine copper wire.

Edom was a country in ancient Palestine, situated between the Dead Sea and the Gulf of Aqaba. There the Edomites lived long before the Jewish tribes arrived in the country [7.2]. In 1934 an archaeological investigation of the region was made. The range of institutions sending scientists to the expedition, was notable: the American Council of Learned Societies, the American School of Oriental Research in Baghdad, Hebrew Union College in Jerusalem and the Trans-Jordanian Department of Antiquities. The expedition worked under the guidance of Nelson Glueck. The results were remarkable. In *Wadi el-Jarim* an immense sandstone, containing copper, was found and in *Umm el' Amad* a large copper mine with ores containing the minerals cuprite and malachite. In the *Timna Valley* Solomon's copper mines were rediscovered. The ores had been easy to work for copper, based as they were on copper oxide and not sulfide minerals. When the ores were technically and economically evaluated at the beginning of the 1950s they were found to be workable, starting with a sulfuric acid leaching. Today mining and copper extraction have ceased.

7.2.4
A Model for the Development of Mining and Metallurgy

The Egyptians mined copper in the Sinai Peninsula from the third millennium BC. They used oxide and carbonate minerals, malachite and azurite. The scale of mining reached a size that made it the first real industry in the ancient world. Ruins of the old mines can be found to this day in Sinai.

Copper became the base for knowledge of metallurgy and also of mining, especially underground working. When the supply of superficial ores ran out, digging for ore started. This can be followed in the Timna Valley, north of Eilat in the Negev desert. Copper shafts from the 4th millennium BC have been found there. After several centuries mining was ended for some reason. After an intermission of 1000 years it was recommenced. In the New Kingdom of Rameses II, Pharaoh at that time (1279–1213 BC), Timna was developed to a large-scale industry for copper mining and metallurgy. The furnaces were improved and bellows installed. In the middle of the 12th century BC, however, the activities were shut down. After another 200 years, Timna experienced a third time of prosperity. The reason for the irregular operation was not lack of ore. It was instead recurrent energy crises. Charcoal was needed for the furnace processes and it was manufactured from acacia trees and date palms. When the region round Timna was clear-felled copper production had to stop. When new forests had grown up the industrial activities could continue.

7.2.5
Copper in the Roman Empire

A broad exposition [7.3] about copper in the Roman Empire and other aspects of the "Red Metal" is given by Tom Lugaski at the University of Nevada. Rome explored all the regions around the Mediterranean for minerals. This was necessary for the growing empire. An immense mineral wealth, including great mines in Spain, was acquired round 200 BC when the Phoenician colony of Carthage was destroyed. A large copper deposit, also containing iron, was found in the southwestern corner of Spain. The minerals colored a nearby river red. The river was called "*Rio Tinto*". The mining district was also called Rio Tinto. 3000 years of mining have left a huge crater where the red mountain once stood. Remnants of Roman tunnels and shafts can be seen in the walls, and millions of tonnes of black slag remain from the Roman smelting operations. Total copper production in the Roman Empire was about 15 000 tonnes per year. Mines in Spain accounted for more than half of the world production at this time. After the fall of the Roman Empire, Rio Tinto became a ghost town.

7.2.6
Bronze – A Leap in Technology

The pure soft copper metal with its very good formability could well be used for various decorative wares but was less suitable for utility goods. It was discovered that alloying could result in hardness. The first alloy used by people was probably arsenic–copper with as much as 7% As. Bronze, the alloy of copper and tin, also appeared early in copper's history. The alloy was in fact known long before the metal tin had been discovered. In the long valley of the river Indus in India, in Mesopotamia and in Egypt, bronze was being manufactured by 3000 BC. The alloy seems to have been made even earlier in Thailand. It was observed that some copper ores, not pure but containing a certain foreign mineral, gave a much harder copper than an ordinary, good copper ore. We now know that the foreign mineral was cassiterite, tinstone, SnO_2.

> At the Royal School of Mines in London some experiments were made in the 1910s in order to rediscover the techniques of the early Bronze Age [7.4]. A very simple furnace, a hole in the ground, was charged with:
>
> - Copper ore (a carbonate), containing 30% Cu 15 lb (1 lb = 1 pound = 454 g)
> - Tin ore (cassiterite) with 29% Sn 10 lb
> - Limestone (slag former) 7.5 lb
> - Charcoal 10 lb
>
> Of the total metal content in the charge 39% was tin, 61% was copper. After reduction and melting a cast alloy with 22% tin was obtained. Thus the tin had shown a greater tendency to form slag than the copper, which might be expected. The experiment, repeated several times, proved, according to the metallurgists of the day, that ancient bronze manufacture using copper and tin ores had really been possible.

On Crete the metal tin was known by 2000 BC and was added to copper in order to decrease the melting point. It is easy to imagine the surprise of the Cretan metallurgists when they found that soft copper, alloyed with the still softer tin, gave hard bronze. It took a long time, almost 4000 years, before the explanation came, by means of metal microscopy and theories of physical metallurgy. But the experienced ancient metallurgists manufactured axes and spearheads from the new alloy and found them to be clearly superior to the corresponding tools and weapons of copper or flint.

With tin and copper available the way to bronze manufacture was straightforward. The casting of the bronze doors for the mighty Egyptian Amon temple is described in detail in Figure 7.1 [7.5]. The temple was the most important sacred edifice in the New Kingdom (1575–1087 BC). It was situated at El-Karnak.

The discovery – or invention – of bronze was a technological leap that was also of great political importance. A people with knowledge of the manufacture of bronze could control the neighboring nations. Bronze also opened international trade routes

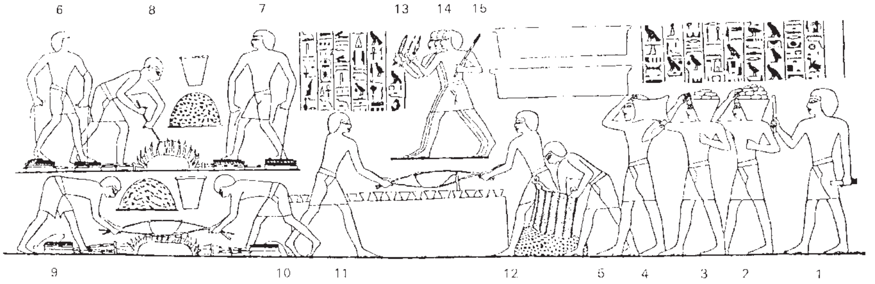

Figure 7.1 Making the bronze doors for the Amon temple in El-Karnak. Two workers (2 and 3) carry in tin while one (4) carries copper. A basket with charcoal for heating of the furnaces is emptied (5). Two men (6 and 7) are in charge of the treadle blowers. The workers 8–12 are busy with the casting. The "workshop drawing" is placed as pictures of the doors on the wall behind. The foreman (1) and armed guards (13, 14, 15) supervise the process.

and promoted communications between the nations. The old, highly cultured people in Mesopotamia, India, China and Central and South America owe a big debt of gratitude to the cast copper alloy with ca. 10% tin.

The native peoples of South America used copper tools and weapons long before the European invasion. As early as AD 700 the Chimu on the coast of Peru were making bronze. The great copper and tin deposits of Bolivia were available to the Inca Empire of Peru. Bronze tools were beginning to appear at the time of the invasion by the Spanish Conquistadors.

7.2.7
Brass – Copper and Zinc

Brass manufacture started before the essential alloying element zinc was discovered. Brass articles dated to 1000 BC have been discovered in Palestine. Aristotle wrote in the 4th century BC that there was a people at the Black Sea, "who can make a light, brilliant copper by melting the red copper metal with an earth they have found in their region". Around the beginning of our chronology, ores containing zinc spar were known as *cadmeia* (Greek) or *cadmia* (Latin). This was the linguistic model for the word *galmey* for zinc ores in Germanic languages. In the time of the Emperor Augustus these ores were used for manufacturing brass. Zinc ore powder and charcoal were mixed with copper granules in a crucible and heated to a temperature below the melting point of copper. Zinc vapor was formed and reacted with the copper. The temperature was increased until the alloy (brass) fused. The Romans called the alloy *aurichalchum* as it looked like gold (*aurum* is the Latin word for gold).

Central and Northern Europe developed its own brass manufacture concurrently with the increased knowledge of zinc and its ores (see Chapter 33 Zinc).

7.2.8
The Copper Mine in Falun

After the fall of the Roman Empire, copper production declined in Europe. During the Middle Ages, China was the largest copper producer, especially in the Northern Sung period during the 12th and 13th centuries. In Europe the situation changed with the discovery of the big copper deposit in Falun in central Sweden and the opening of the mine there. This mine became for centuries the largest in the world. The mine was most important in the 17th century and its glory days coincided with Sweden's period as a great power. In fact the export of copper from Falun constituted the economic base for the Swedish position of power. As is the case for many old mines, there are legends about the discovery of the copper treasure in Falun.

7.2.8.1 The Billy Goat Kåre Finds the Copper Hoard in Falun

> The white he-goat Kåre used to come back to the farm with reddish earth and clay on his horns. One day the farmer followed his goat and found the place where he had scraped his horns. He found the copper ore and country folk began to dig it up. It might have been in the 5th century – more probably, however, in the 9th. Geological and archaeological investigations have shown that mining had occurred by the end of the 9th century. Analysis of bronze objects from this period, found on the island of Gotland in the Baltic Sea, indicates that copper in the alloy originates from Falun. During the Viking Age around AD 1000 the mine was certainly active.

7.2.8.2 The Oldest Corporation in the World

> Local working by farmers changed to large-scale production, and the mining was organized in a form similar to a modern corporation. The formation of the company seems to originate from an agreement in 1288, confirmed with the seals of the King of Sweden and eight bishops. The owner of the mine, the company *Stora Kopparbergs Bergslags AB* (now *Stora Enso Inc.*), probably the oldest corporation in the world, considers this important transaction as its inception. In this connection an anecdote from a later time might be of interest. In one of the first decades of the 20th century the company had offered some product to a firm in the United States. The purchasing manager of this firm did not know the Swedish corporation. Perhaps it was risky to do business with it! He wrote back with thanks for the offer and asked if the corporation with the curious name *Stora Kopparbergs Bergslags AB* was perhaps only recently started. From Falun the answer arrived that the corporation was 200 years old when America was discovered by Europeans.

In the 17th century, mining was no longer an affair for local people and the province of Dalecarlia. The copper deposit concerned the whole of Europe. In the 1650s 90 000 tonnes of rock were mined annually and 3000 tonnes of raw copper were manufactured. Sweden then accounted for two-thirds of the world trade in copper. The intense working was dangerous at a time when mine mapping was defective. Mining occurred in big, open rooms, called stopes. The carrying capacity of partitions and pillars was incompletely known; sometimes they broke under the pressure and the roofs came down. A catastrophe of this type occurred in 1687 and the remains of it may be seen even today.

At the end of the 19th century new rich copper deposits were discovered in the world, starting in the Lake Superior region in the United States. The dominance of the mine in Falun ceased but production continued into the 1990s. During the last decades, large quantities of pyrite were mined for production of sulfuric acid and red ochre. Today the mine is a historical museum and a valued tourist attraction.

7.2.8.3 **Copper Production in Falun**

In the early years, copper was mainly obtained from ores containing copper oxides. The ore in the Falun deposit was sulfidic and more complex. Copper was present as chalcopyrite, $CuFeS_2$, in quartzite in impregnation zones. There the copper content was 4%. In other geological formations within the rock the copper content was low but the sulfur content high. Pyrite, FeS_2, dominated here. After breaking, the ore was separated by hand. In the mine zinc sulfide, lead sulfide and native gold were also present. During 1000 years of mining in Falun a total of 5000 kg gold was obtained.

It is difficult to extract copper from an ore of the type described. Typical copper metallurgy was developed by work over many generations. The processing of the ore from the Falun mine has been investigated by a study group[1]. The results can be concluded as follows:

- The ore with 2.5% Cu was partly roasted in order to decrease the sulfur content
- The ore was melted to a copper matte, a mixture of copper and iron sulfide, with a copper content of 10%
- The matte was roasted to remove sulfur
- The completely roasted matte was melted, using an air blast and with the addition of charcoal and slag-former. Raw copper or “blister-copper” with 90–95% Cu was obtained
- The raw copper was remelted and charcoal thrown on its surface. The melt was then “poled“, i.e. stirred with poles of green wood, birch or oak, pushed into the melt and kept submerged. Much gas evolved, improving the stirring, and carbon from the poles and from the charcoal reacted with the oxygen in the copper melt. The purified copper was tough and forgeable.

See further Figure 7.2.

Figure 7.3 gives details of the production quantities over the last 5000 years [7.6].

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[1] *Kopparhyttorna längs Rogsån* (About copper manufacturing in Dalecarlia) written by a study circle (E. Börje Bergsman editor).

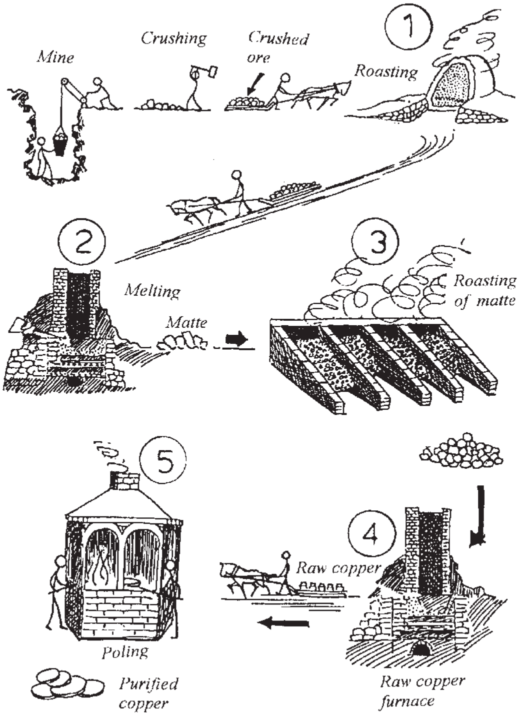

Figure 7.2 Copper manufacturing round 1700 in Dalecarlia, Sweden. (Reprinted from the former periodical Metallen 13 (1957):2, Svenska Metallverken Inc.)

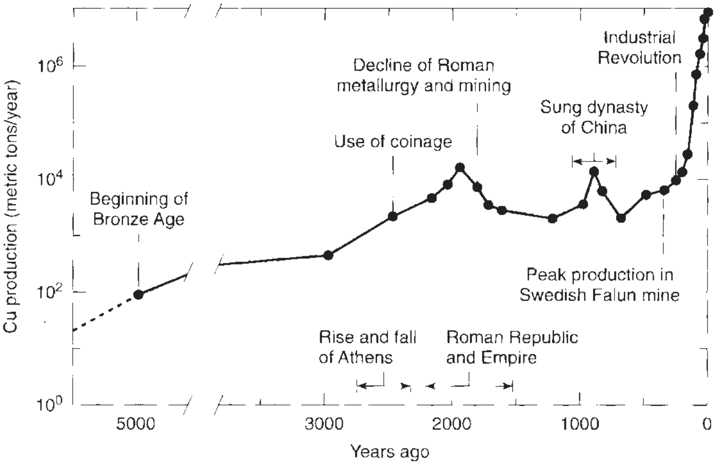

Figure 7.3 World production of copper during the last 5000 years [7.6]. (Reprinted from ref. [7.7].)

7.3
Copper Ores

Of economically workable copper deposits in the world, about 90% are sulfide ores, 9% are oxide ores and less than 1% is native copper. Considerable amounts of native copper were found on the Kewenaw Point peninsula in Lake Superior in Michigan. That copper was extracted economically from the 1840s. Nowadays mining has ended.

7.3.1
Copper Minerals

Important copper minerals are listed in Table 7.1. The minerals can themselves tell their own geological history. Chalcopyrite, $CuFeS_2$, has crystallized from high-temperature solutions, so-called hydrothermal solutions, in connection with volcanic activity. Chalcopyrite is found in veins in the solid earth's crust, where it is attacked by surface water, rich in oxygen. The oxygen-rich water reacts with the chalcopyrite and FeO(OH), *gossan*, is formed. Like an "iron hat", a ferruginous deposit, it fills the upper part of the mineral vein. In the oxidation zone, new copper oxide minerals may be formed, such as malachite $Cu(CO_3)_2 \cdot Cu(OH)_2$. Below the groundwater zone there is a lack of free oxygen and new, more copper-rich sulfide minerals can be formed, such as covellite, CuS, and bornite, Cu_5FeS_4, see Figure 7.4.

Table 7.1 Copper minerals

Mineral	Formula	Color	Comments
Chalcopyrite Figure M6	$CuFeS_2$	brass-yellow	The most common copper mineral. Large deposits in Chile, Zambia, US (Montana and Utah), Spain (Rio Tinto), England (Cornwall)
Covellite	CuS	indigo-blue	An indigo-blue secondary copper mineral
Chalcocite Copper glance	Cu_2S	black or dark lead-gray	An important ore of copper. Common in the zone of secondary enrichment
Cuprite	Cu_2O	red; metallic luster	In copper ores in Chile
Bornite	Cu_5FeS_4	reddish-brown; iridescent purple	"Peacock" copper ore
Malachite Figure M5	$Cu(CO_3)_2 \cdot Cu(OH)_2$	green	Considerable distribution in the Ural Mountains. Used for ornaments and jewelry
Azurite Figure M5	$(CuCO_3)_2 \cdot Cu(OH)_2$	deep blue; glassy luster	Mineral present in the oxidation zones of sulfide ores. Mostly used as a pigment; to some extent also an ore mineral

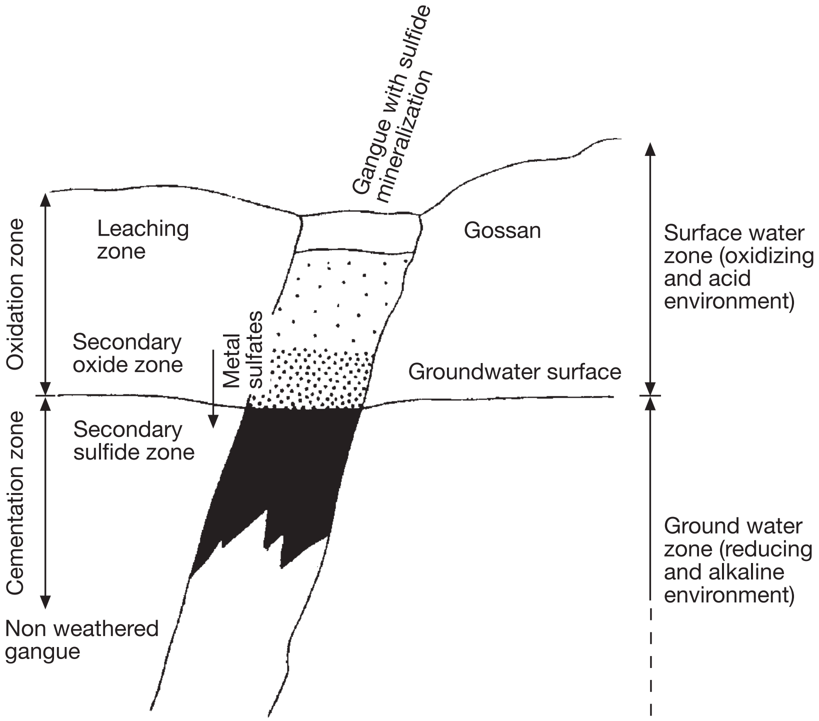

Figure 7.4 A vein of sulfide mineral is attacked by surface water and groundwater. (Reprinted from B. Loberg [7.8]. With permission.)

Thus concentration and ore dressing have occurred on a micro scale. The *bonanza*[2] deposits with high contents of copper, silver and gold were formed in this way.

7.3.2
Experimental Geology Discovers How Ores Were Formed

Some massive sulfide ores have a volcanic origin. It is astonishing that they have such varying ages although their properties and modes of occurrence are similar. They may be *archaean*, i.e. more than 2500 million years old, or very young, 10 million years. These volcanic deposits have been formed at the bottom of the sea and formation continues even in our own day. A sensational breakthrough in the knowledge of ore geology occurred on April 21st 1979 in the Pacific, on the East Pacific Ridge, southwest of California. From an underwater craft openings were observed in the sea

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[2] Bonanza is Spanish for "fair weather". A miner's phrase for "Good luck" or "a body of rich ore".

bottom with chimney-like formations[3], through which hot solutions at 275–350°C passed from subterranean volcanic eruptions, see Figure 7.5. Chimneys giving black solutions of suspended black metal sulfides were called "black smokers". The others, giving solutions with suspended barium sulfate and silicic acid, got the name "white smokers". The chimneys themselves are built up of minerals. When the hot hydrothermal solutions come in contact with the seawater their dissolved compounds are precipitated and form deposits together with the suspended particles.

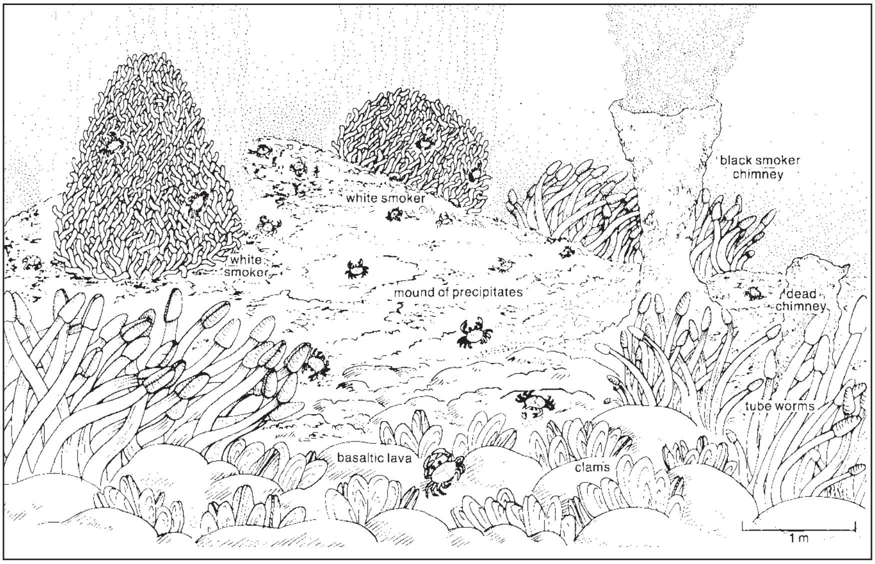

Figure 7.5 A region on the sea bottom with hydrothermal activity. (Reprinted from ref. [7.9] with permission of Robin M. Gowan/American Scientist, magazine of Sigma Xi, The Scientist Research Society.)

The discovery suddenly gave an explanation of the origins of many massive workable sulfide ores. The sulfide particles were baked into the sediments and preserved. The deposits may later have moved from sea to land in geological processes. Many of the ores we find in the earth's crust have been formed in this way, among others probably the famous ores in the Trudos mountains on the copper island of Cyprus.

[3] Hydrothermal solutions rise from deeper zones within the earth. At the existing high temperature and pressure the water may contain and transport high concentrations of metal and sulfide ions as well as suspended mineral particles.

A typical hydrothermal vent cluster includes an array of structures on top of a mound of mineral precipitates and organic debris. The mound rests on black basaltic lava. White smokers are encrusted with the tubes of polychaete worms (earthworms). The milky-white fluids emitted by white smokers have temperatures below 300 °C. Chimneys composed of calcium sulfate and sulfide minerals precipitate around the black smoker jets, which reach temperatures from 300 to above 400 °C.

7.3.3
Types of Copper Deposits

The Swedish copper ores in the Skellefte field have been formed in just the described way. Hydrothermal solutions streamed out over the sea bottom in a region with much volcanic activity round 2000 million years ago. A metamorphosis followed and created the deposits of our day, distinguished mainly by copper but also with gold and silver. The old mine in Falun has a similar origin.

Important copper deposits may also have been formed by conventional sedimentation on ancient sea bottoms without volcanic activity. In present times they appear *stratiform*, i.e. composed of layers in the rock. Large deposits of this type are characteristic of the so-called copper belt in Zambia and the Democratic Republic of Congo.

Other sedimentary ores are clay and carbonate-containing shales and sandstones, with 1.5–2.5% copper. They are mined in Central Africa with cobalt as an important by-product. Similar shales, yet with lower copper content, exist over wide areas in Germany and Poland and have been mined there for centuries. Mansfeld was such a center.

An important type of copper ore is found in a rock called porphyry (an igneous rock, in which larger crystals are distributed in a fine-grained matrix). *Porphyry copper* contains disseminated copper minerals, sulfide minerals, in a large body of porphyry. The average copper content is as a rule low. A deposit in Utah was of this type. In Bingham Canyon gold was mined from 1852, silver from 1873 and copper from the middle of the 1890s. The copper content was 1.4%. When prospectors looked for more porphyry deposits they found them in New Mexico, Arizona, Nevada and in several places in Chile.

Copper is also present in many nickel ores, from which it is won as a by-product. The largest and most famous is the deposit at Sudbury in Canada.

7.3.4
Copper Reserves

A great part of the global copper reserves is located on the American continents. Reserves and reserve bases, by country, are given in Table 7.2 according to an estimate in 2001 [7.10].

Table 7.2 Copper reserves and reserve base

Country	Reserves		Reserve base	
	Million tonnes	Percentage of total	Million tonnes	Percentage of total
Chile	88	25.8	160	24.6
United States	45	13.2	90	13.9
Poland	20	5.8	36	5.5
Russia	20	5.8	30	4.6
Indonesia	19	5.6	25	3.8
Peru	19	5.6	40	6.2
China	18	5.2	37	5.7
Mexico	15	4.4	27	4.2
Kazakhstan	14	4.1	20	3.1
Zambia	12	3.5	34	5.2
Canada	10	3.4	23	3.5
Australia	9	2.6	23	3.5
Other countries	51	15.0	105	16.2
Total	340	100	650	100

7.3.5
Copper Production in Mines

In the United States, Arizona is the largest producer of copper, followed by Utah, New Mexico, Nevada and Montana. Many of the deposits in North America are, however, of a high-cost type with low copper contents. Because of this, more interest has been devoted to deposits in South America, China and Indonesia, countries that have shown the greatest increases in copper mine production in recent years. Annual production in the United States has decreased by 25% since 1996 owing to high production costs, falling copper prices and a weak demand, but the country is still second among the producer countries.

The most important countries in the world for copper production in mines are listed in Table 7.3.

Table 7.3 World mine production by country in 2000

Country	Copper production 1000 tonnes	Percentage of total production	Country	Copper production 1000 tonnes	Percentage of total production
Chile	4 602	34.8	Papua New Guinea	201	1.5
United States	1 440	10.9	Argentina	145	1.1
Indonesia	1 012	7.7	Iran	145	1.1
Australia	829	6.3	South Africa	137	1.0
Canada	634	4.8	Mongolia	125	1.0
China	590	4.5	Turkey	76	0.6
Russia	570	4.3	Portugal	76	0.6
Peru	554	4.2	Sweden	76	0.6
Poland	456	3.4	Bulgaria	75	0.6
Kazakhstan	430	3.2	Uzbekistan	65	0.5
Mexico	365	2.8	Other countries	356	2.7
Zambia	241	1.8			
			Total	13 200	100

Source ref. [7.10].

Chile is the country with the greatest production, which is also increasing. In 1996, production was 3116 thousand tonnes and in 2000 it was 4600 thousand tonnes, an increase of 48%. The Chuquicamata mine was the biggest single copper mine in the world until 1997, when this role was taken over by an Indonesian mine.

Indonesia has been a great copper country through the development of one single deposit, Ertzberg/Grasberg (its name is a reminder of the Dutch colonial time). The mine was discovered on Irian Jaya in Indonesia and built as a copper–gold mine in the period 1985–95. In 1997 it was the mine with the biggest copper production in the world. There are, however, many environmental and political problems connected with this mine. The deposit is situated on an altitude of 3500 m. All mining waste has to be taken care of in a sensitive landscape with alpine valleys and local rivers.

In Europe, Poland, Portugal and Sweden are the most important producers.

Table 7.4 Changes in mined copper in two African countries between the years 1996 and 2000

Country	Copper production in mines. 1000 tonnes		Change %
	1996	2000	
Democratic Republic of Congo	50	21	–58
Zimbabwe	9	2	–78

The changes in annual copper production in the rich copper region in Central and South Africa reflect the unstable political situation, the lack of investments and health problems within the population, see Table 7.4.

The Democratic Republic of Congo has 10 million tonnes of copper in its rocks. This corresponds to 3% of the total copper reserves of the world. In the year 2000, production in its own mines was 21000 tonnes, i.e. less than 0.2% of the world production.

7.4
The Manufacture of Copper Metal

The manufacture of copper metal from ores is called the *primary production*. Ores worked may be of oxide or sulfide type. Only 9% of exploitable copper resources worldwide consist of oxide ores while 90% are sulfide ores. When copper metal is manufactured from scrap it is a *secondary production*.

7.4.1
Primary Production from Oxide Ores

Oxide ores are generally treated by hydrometallurgical processes. After concentration they are leached with sulfuric acid. The copper-rich solutions are then treated by solvent extraction (SX) and copper is finally obtained by an electrolytic process (EW). The combined process is designated SX/EW.

7.4.2
Primary Production from Sulfide Ores

7.4.2.1 Conventional Pyrometallurgical Processes

The copper contents in sulfide ores are as a rule low, sometimes below 1%. The first step after crushing and grinding of the ore is therefore mineral dressing by flotation. The complex manufacturing process thereafter is briefly described in Table 7.5.

Table 7.5 The process steps in the metallurgical manufacture of copper

Material	Production step	Reactions	Product from the step
Ore concentrate	Roasting at 700°C	The process occurs in a fluidized bed roaster. A part of the sulfur is oxidized to sulfur dioxide, SO_2, which is used to manufacture sulfuric acid.	Roasted stuff
Roasted stuff	Melting in an electric arc furnace at 1200°C. Addition of a slag former, for instance sand	At the reaction a copper matte is formed. It is copper and iron sulfides with a copper content of ca. 47%	Low-grade copper matte, high in Fe; containing also Zn, Pb, Ni, Se, and noble metals
Low grade copper matte	In a converter, air enriched with oxygen is blown throw the molten matte	In the converter the sulfur of the iron sulfide is oxidized to SO_2. Addition of silica sand forms slag that removes the iron	High-grade copper matte, consisting of copper sulfide. „ White metal“
High grade copper matte	Continued blowing in converter	Sulfur in copper sulfide is oxidized and removed. A raw-copper , blister copper is formed	Blister copper with 98–99% Cu
Blister copper	Melted blister copper is “poled” with ammonia gas (earlier fresh birch poles were used).	Poling reduces the oxygen content and the product has a copper content of ca. 99.8%. The copper is cast to plates, anode copper	The anode copper, with the total contents of noble metals, is used for further refining to electrolyte copper.

7.4.2.2 **Copper Production and the Environment**

Copper manufacture during the last part of the 20th century was influenced by an ever-increasing concern for the environment. The most significant release of pollutants in the pyrometallurgy of sulfide ores is related to atmospheric emissions of sulfur dioxide and particulate matter containing heavy metals. If not captured, some sulfur dioxide reacts with water vapor in the atmosphere to form sulfuric acid, which returns to earth in acid rain. All the effects of acidic deposition on soils, vegetation, wildlife and man-made structures are well documented. With new techniques sulfur dioxide is transformed to sulfuric acid. A “must” from the environmental viewpoint may thus – as is often the case – be profitable.

The smelter gases for production of sulfuric acid also contain particulate matter. In 1998, USEPA (US Environmental Protection Agency) in *The Clean Air Act* gave a rule to establish a numerical emissions standard of 23 mg/m^3 of total particulate matter as a maximum. In the production of sulfuric acid more than 99% of the particular matter is removed from the gases.

A typical example of the trend in emission level development at Outokumpu Harjavalta copper + nickel smelter in Finland is presented in Figure 7.6. As can been

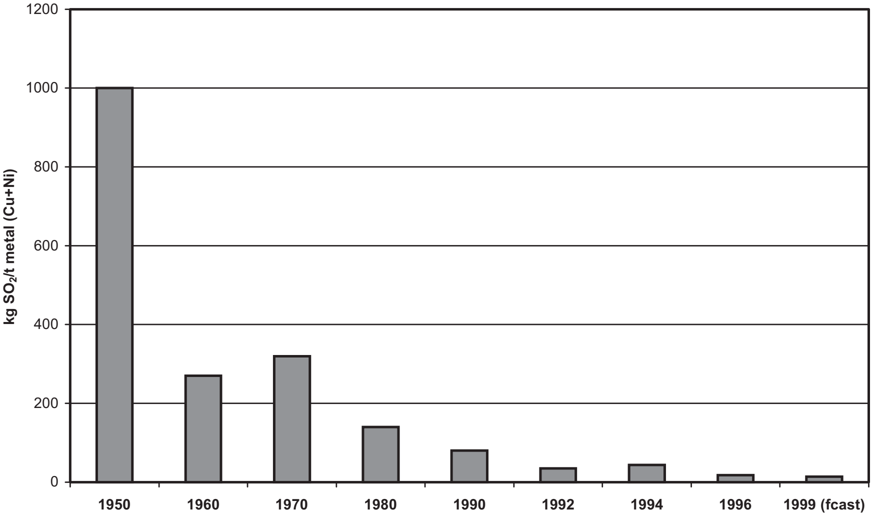

Figure 7.6 Emission level development at Outokumpu Harjavalta smelter [7.11].

seen, the present levels are only a fraction of the values that were acceptable some years ago.

7.4.2.3 The Flash Melting Technique

The environment has not been the sole problem for the copper smelting industry. In addition the falling real price level of the metal and the high investment costs have caused economic problems. These had to be compensated for by new, effective production techniques with high productivity and a low metal inventory. One of these new methods is the Outokumpu Flash Smelting Technology, with which more than 50% of the copper in the world is produced.

The characteristic of Outokumpu Flash Smelting technology is that powdered copper ore concentrate is suspended in oxygen-enriched air. Roasting and melting take place simultaneously. The reactions are strongly exothermic and the particles melt to form matte and slag. The temperature in the reaction shaft is about 1250–1300°C. If the oxygen enrichment in the air blast is lower than 50%, additional heat may be generated by oil combustion in the shaft. The flash melting technique produces copper matte with up to 65% copper with good economy and in a way acceptable for the environment.

7.4.3
Electrolytic Refining of Copper

Anode copper, produced in the metallurgical process, is used for electrolytic refining. The anodes are placed in an electrolyte containing copper sulfate and sulfuric acid. Between the anodes, thin start plates made of pure copper are inserted as cathodes. In the process the anodes are dissolved and the cathode plates grow by copper precipitation. After electrolysis for 10 days the weight of the cathodes has increased to 145 kg and their copper content is 99.95% or more. This copper is delivered as *refined copper*.

There are different commercial qualities within the group "refined copper":

- *Oxygen-free high conductivity*, Cu-OF, with 99.95% Cu. Oxygen uptake is avoided during refining;
- *High conductivity tough-pitch*, Cu-ETP, which contains traces of cuprite;
- *Deoxidized copper*, Cu-DLP; Cu-DHP, in which traces of oxygen are removed by addition of phosphorus, although the P-content is below 0.05%.

During electrolysis an anode slime is obtained that is processed for extraction of gold, silver, platinum metals and selenium.

7.4.4
Bacterial Leaching

An additional group of methods, also used for sulfide ores, is bacterial leaching. One microbe, *Thiobacillus ferroxidans*, can oxidize divalent iron to trivalent and metal sulfides to sulfates. Bacterial leaching is industrially applied to low-grade ores of copper, nickel, zinc and so on and also to complex ores containing conglomerates of different metals. Ores with high metal contents may also be leached bacterially. In a new Chilean method, the *thin layer leaching process*, the leaching of copper sulfide occurs over 3–6 months. A high copper yield and low energy consumption also characterize this environmentally friendly process.

7.4.5
Secondary Production – Recycling of Copper

Secondary production, where copper scrap is used as raw material, is important. It requires less than half the energy input of primary production from ore. Recovered or recyclable copper can have various origins, namely:

- *direct scrap* from melting and refining processes in copper manufacturing
- *new scrap* obtained from the transformation of copper materials into finished products
- *old scrap* from different used consumer products.

Of the total production of refined copper in the world in the year 2000, reported to be 15 million tonnes, 2 million tonnes or 13% originated from scrap.

7.5
Copper Production

Copper is heavily traded throughout the world. It is true that some refined copper is produced near the mines. However, in many cases the ore is exported from the mining country to industrial regions in other parts of the world. In ancient times the copper ore and metal was moved by caravans to trade routes on the rivers, the Tigris, Euphrates and Nile, and over the sea. Trading took place in the whole Mediterranean world. The situation is the same in our day but in a much bigger world.

World production of refinery copper totaled 15 million tonnes in the year 2000. Twenty-three countries made more than 100 000 tonnes each, as shown in Table 7. 6, which also shows a "*mined/refined*" ratio for each country. In those cases where producers of refined copper use their own mined copper the ratio has a value near 1. Other countries export much of the mined copper, giving a high ratio, as for Indonesia. Some industrialized countries with small, or no, copper mines import ore and are big producers of refined copper, like Japan and Germany. A low ratio or a value of 0 indicates this.

Table 7.6 The production of refined copper in 23 countries with more than 100 thousands ton each in the year 2000. For discussion of the ratio „mined/refinery" see the text. Production values from ref. [7.10]

Country	Refined copper production 1000 tonnes	Relation mined/ refinery	Country	Refined copper production 1000 tonnes	Relation mined/ refinery
Chile	2668	1.72	Kazakhstan	395	1.09
United States	1790	0.80	Spain	316	0.07
Japan	1437	0	India	243	0.15
China	1400	0.42	Zambia	225	1.07
Russia	840	0.68	Brazil	185	0.17
Germany	710	0	Indonesia	174	5.82
Canada	551	1.15	Iran	144	1.01
Australia	487	1.70	Philippines	135	0.24
Poland	486	0.94	Sweden	130	0.58
Korea South	475	0	Finland	114	0.10
Peru	452	1.23	South Africa	101	1.36
Belgium	423	0	Other countries	716	–
Mexico	403	0.91			
			Total	15 000	

7.6
Uses of Copper

7.6.1
Copper Metal

The properties of copper have made it a major industrial metal. It is ranked third, after iron and aluminum, in terms of quantity consumed.

Its formability makes copper a suitable metal for the manufacture of different components. It can be rolled to a foil with a thickness of 0.02 mm and drawn to a 0.02-mm wire but it is too soft for many applications. Its softness is its weakness, today as in history. In alloys, e.g. bronze and brass, the strength is increased considerably.

The corrosion resistance of copper is good, but in polluted, humid air, containing sulfur dioxide and/or chlorides, the copper surface is oxidized. A black film, mainly cuprite, Cu_2O, is formed. A green patina with varying formula is formed by secondary processes. Two common types are $Cu_4(OH)_6SO_4 \cdot H_2O$ and $Cu_2(OH)_3Cl$. These compounds have a decorative effect but serve also as protecting layers, reducing the rate of further corrosion.

Besides electrical ones there are many applications for copper, e.g.

- tubes for water and heat exchangers
- vessels and containers for breweries
- roofing on buildings
- component in alloys for coins
- component in brass and bronze (see below).

There are alternative materials with which copper has to compete. Aluminum substitutes for copper in electrical power cables and in refrigeration tubing. Titanium and steel are alternatives in heat exchangers. Plastics substitute for copper in water pipes, and optical fibers in telecommunication applications.

Some of the properties of copper are especially important for its utilization for electrical purposes. Among metals, only silver has better electrical and thermal conductivity. The electrical properties of copper, conductivity and resistivity, are highly influenced by low contents of some foreign elements while others are less harmful. This is shown in Figure 7.7.

The development of electric power for energy generation and transportation has largely contributed to the widespread use of copper. About 75% of copper is, at the present time, used for electrical and electronic products, including power generation, power transmission and telecommunications. In these applications, refined copper with a copper content of more than 99.95% is used. For other purposes, such as industrial machinery and consumer products, unrefined metal with 99.8% copper can be used. Its electrical conductivity is somewhat reduced.

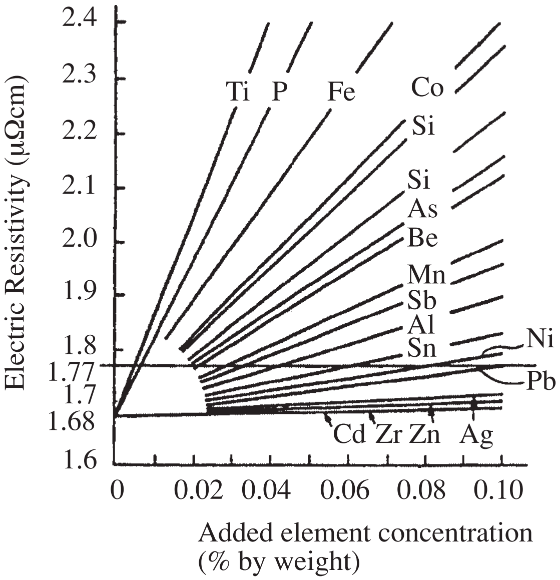

Figure 7.7 The influence of foreign elements on the electrical resistivity of copper.

7.6.2
Brass

7.6.2.1 Copper–Zinc Alloys

Brass is the most used alloy of copper metal. Normally brass is copper alloyed with zinc. There are two types of this alloy, α-brass and α/β-brass. At room temperature, copper can dissolve up to 38% zinc in solid solution. In physical metallurgy this phase is called the α-phase. An alloy with 37% zinc, the most common brass, thus consists entirely of the α-phase, and is also called α-brass. It is used as sheet metal and strip for all types of cold forming. For deep drawing, which is especially difficult for the material, the zinc content is decreased to 30%.

The color of the alloy depends on the zinc content. A brass with 10% zinc and 90% copper is golden yellow and is used for ornamental applications.

If the zinc content is increased above 38% a new structural component, the β-phase, appears. In the composition range 38–45% zinc there is a mixed structure and these alloys are called α/β-brass. They have improved strength but reduced corrosion resistance. For special purposes, for example cables in condensers and oil refrigerators, a brass with 40% zinc is used.

7.6.2.2 Nickel Brass – German Silver

An alloy with the composition 64% Cu, 24% Zn and 12% Ni is called nickel brass. The alloy has high strength and good corrosion resistance and is used as material for mechanical springs, e.g., contact springs. Nickel brass looks like silver and its usefulness as an alternative for silver in, for instance, cutlery is improved by final silver plating after component forming. The material is then called argentan, electroplated nickel silver (EPNS) or German silver.

7.6.3
Bronze

Bronzes are primarily cast alloys and constitute a very diversified group. The prototype is tin bronze, an alloy with 90% Cu and 10% Sn. When the molten alloy solidifies, a number of intermediate phases are precipitated and reinforce the copper matrix. That is the reason why the soft tin metal makes copper harder.

As well as tin, aluminum, beryllium, nickel and iron are also used in special bronzes. An overview of the bronze family is given in Table 7.7. Only one alloy of each type has been included as an example.

Table 7.7 Members in the bronze family

Bronze	Composition	Use
Tin bronze CuSn10[1]	90 % Cu, 10 % Sn	Pump housings, impellers, slide bearings
Tin bronze CuPb10Sn10	80 % Cu, 10 % Sn, 10 % Pb	Slide bearings
„Red metal“ CuSn5Pb5Zn5	85 % Cu, 5 % Sn, 5 % Pb, 5 % Zn	Very much used bronzes. Ranges of uses are slide bearings and pump housings
Beryllium bronze	98–99 % Cu, 1–2 % Be	Alloy for mechanical springs. Avoided as beryllium is poisonous
Aluminum bronze CuAl10Fe3	87 % Cu, 10 % Al, 3 % Fe	Aluminum bronzes have high strength (almost as steels) and good wear resistance.
Nickel-aluminum bronze CuAl10Fe5Ni5	80 % Cu, 10 % Al, 5 % Fe, 5 % Ni	The Ni-variant has very good corrosion resistance, especially in marine environment. It is sparkless and may be used as heavy duty mixers for dynamite

1) CuSn10 and so on are the material designations that are used by ISO, the International Standard Organization

7.7
Copper and the Environment

Copper is a component in many metalloenzymes and other proteins. Because of that it is an essential trace element for life [7.7] and [7.12]. Several copper-containing enzymes catalyze oxidation/reduction reactions. Its function is thus similar to that of iron but copper works primarily outside the cells, iron inside. This indicates that copper has been utilized for life relatively late in the evolutionary process and in connection with an increase of oxygen content in the atmosphere and the development of multicellular organisms. Copper deficiency is not unusual in grazing animals, especially sheep, and can be treated by dietary supplements. With regard to pigs it has been observed that copper is not only an essential trace element but also has a strong growth-promoting effect. Earlier common copper additions were 200 mg Cu/kg feed but the addition is now reduced and regulated.

In too high concentrations copper is toxic. The higher the organism is in the food chain, however, the bigger is its ability to regulate the copper uptake. A special protein, metallothionein, is synthesized in the liver just to protect the body against the intake of sulfide-forming metals such as copper, lead, cadmium and mercury. This reacts strongly with copper.

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8
Iron

8.1 Fe
Facts about Iron

8.1.1 Fe
The Element

Symbol:	Fe
Atomic number:	26
Atomic weight:	55.85
Ground state electron configuration:	$[Ar]3d^6 4s^2$
Crystal structure:	α-Fe cubic bcc with $a = 2.87$ Å. Up to 912 °C γ-Fe cubic fcc with $a = 3.65$ Å. Between 912 and 1394 °C δ-Fe cubic bcc with $a = 2.93$ Å. Between 1394 and m.p. 1538 °C

8.1.2 Fe
Discovery and Occurrence

Discovery: Metallic iron was known and used for ornamental purposes and weapons in ancient civilizations. Oxidized iron beads in Egypt are dated to about 4000 BC.

Most important mineral: Hematite Fe_2O_3 (Figure M10)
Magnetite Fe_3O_4 (Figure M9)
Siderite $FeCO_3$ (Figure M11)

Ranking in order of abundance in earth crust:	4
Mean content in earth crust:	$5.63 \cdot 10^4$ ppm (g/tonne); 5.63 %
Mean content in oceans:	0.002 ppm (g/tonne)
Residence time in oceans:	100 years
Mean content in an adult human body:	60 ppm
Content in a man's body (weight 70 kg):	4 g

Encyclopedia of the Elements. Per Enghag

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8.1.3 Fe
Chemical Characterization

Iron is a silvery, lustrous metal but chemically active. After a short time in moist air it changes from silvery to rusty as reddish-brown FeOOH is formed. Water and soluble electrolytes such as salt accelerate the reaction. Iron is the basic metal for the production of the steel family. This is very diversified and plays a crucial role in modern human life, from the load-bearing functions in large steel buildings and bridges to the small springs in precision mechanics; from material in cannons and tanks to peaceful tools in agriculture; from stainless steels for the corrosive environments in offshore equipment to stainless steels for implants in the equally corrosive milieu in the human body; from special steels for the surgeon's scalpels to all steel components in household and kitchen. Iron is also a vital constituent of plant and animal life, and is the key component of hemoglobin.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Fe^{II} as in FeO and $FeCl_2 \cdot 4H_2O$	$Fe(g) \rightarrow Fe^+(g) + e^-$	762.5	$Fe(g) + e^- \rightarrow Fe^-(g)$
Fe^{III} as in Fe_2O_3 and $FeCl_3 \cdot 6H_2O$	$Fe^+(g) \rightarrow Fe^{2+}(g) + e^-$	1562	–15.7
Fe^{II} and Fe^{III} in Fe_3O_4 that is $Fe^{II}[Fe^{III}]_2O_4$	$Fe^{2+}(g) \rightarrow Fe^{3+}(g) + e^-$	2957	
	$Fe^{3+}(g) \rightarrow Fe^{4+}(g) + e^-$	5290	

Standard reduction potential:
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^0 = +0.771$ V
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^0 = -0.440$ V

Electronegativity (Pauling): 1.83

Radii of atoms and ions: (WebElements™)		
	Atomic:	140 pm
	Covalent:	125 pm
	Fe^{2+} (4-coordinate, tetrahedral):	77 pm
	Fe^{2+} (4-coordinate, square-planar):	78 pm
	Fe^{2+} (6-coordinate, octahedral):	75 pm
	Fe^{2+} (6-coordinate, octahedral, high spin):	92.0 pm
	Fe^{2+} (8-coordinate):	106 pm
	Fe^{3+} (4-coordinate, tetrahedral):	63 pm
	Fe^{3+} (6-coordinate, octahedral):	69 pm
	Fe^{3+} (6-coordinate, octahedral, high spin):	78.5 pm
	Fe^{3+} (8-coordinate):	92 pm

8.1.4 Fe

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
7874 kg m^{-3} 7.87 g cm^{-3}	7.09 cm^3	1811 K 1538 °C	3134 K 2861 °C	449 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
99	83.5	72	56	34

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$5.6 \cdot 10^{-6}$	$11.8 \cdot 10^{-6}$	$14.4 \cdot 10^{-6}$	$16.2 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
7	89	147	315	855	1220

Mass magnetic susceptibility χ_{mass} at 293 K	–
Magnetic characterization	Ferromagnetic

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
211 GPa	82 GPa	165 GPa	0.29

8.1.5 Fe
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	13.8 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	349.5 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	416.3 $kJmol^{-1}$
Entropy S^0 at 298 K	27.28 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	12.1	25.10	32.0	54.4	46.0	46.0

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Fe + O_2 \rightarrow 2FeO$	−493	−465	−405	−350	−287
$3/2Fe + O_2 \rightarrow 1/2Fe_3O_4$	−508	−475	−397	−321	–

8.1.6 Fe
Nuclear Properties and X-ray

Isotope range, natural and artificial 46–69

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{54}Fe	Stable	5.8	0	–
^{56}Fe	Stable	91.72	0	–
^{57}Fe	Stable	2.2	–1/2	0.0906
^{58}Fe	Stable	0.28	0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{57}Fe
Reference compound	$Fe(CO)_5/C_6D_6$
Frequency MHz (^1H = 100 MHz)	3.2378
Receptivity D^P relative to ^1H = 1.00	$7.52 \cdot 10^{-7}$
Receptivity D^C relative to ^{13}C = 1.00	$4.30 \cdot 10^{-3}$
Magnetogyric ratio, $radT^{-1}s^{-1}$	$0.8681 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
25	Mn	5.888
26	Fe	6.391
27	Co	6.915

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	303
17.37 keV (MoKα_2)	38.1

Neutron absorption	**Thermal neutron capture cross section**	2.56 barns

8.2
Iron and Steel – Some Definitions

Steel is an alloy with iron as main component and a carbon content less than 2%. In modern technology all iron with low carbon content is steel if it has been molten during manufacture. Thus the material in an iron nail is steel and so is the automobile body sheet, although the carbon content is below 0.1%. A certain content of carbon makes it possible to harden the steel to a high strength by heating to about 850°C followed by rapid cooling. In older times steel was an iron with so high a carbon content, often at least 0.4%, that such a hardening gave an obvious result. Reading descriptions of the history of iron discovery we discover this way of looking at things: iron is almost pure iron and steel is iron with a certain carbon content.

The important and rather complicated equilibrium diagram for the iron-carbon system is shown in Figure 8.1.

It is obvious that pure iron (carbon content 0) has a melting point of 1538°C. The fact that increased carbon content decreases the melting point is important for an understanding of the development of iron manufacturing. Even those who do not have a deep knowledge about equilibrium diagrams may understand that if the carbon content is 4.3% the alloy has its lowest melting point, 1147°C (the eutectic point). Iron–carbon alloys with higher carbon contents than 2% are called cast iron, pig iron or raw iron. The designation is cast iron if the iron will be used to manufacture cast components, frames, housings, engine blocks, etc. The cast iron composition is modified to be suitable for the casting requirements. Different elements, silicon and phosphorus among others, are used. On the other hand, raw iron or pig iron is the designation if the iron is intended for further processing to forgeable iron and steel.

The greatest proportion of carbon steels has carbon contents below 0.8%. Spring steels have a carbon content of 0.60–0.85%. Alloyed steels are steels with intentionally added alloying elements, e.g. chromium, nickel, molybdenum, vanadium or tungsten. If the total content of alloying elements is below 6% the steels are *low alloy*, otherwise *high alloy*. Two types of high alloy steels, stainless steels and high-speed steels, are treated in Chapter 23 Chromium and Chapter 25 Tungsten respectively.

Iron containing carbon at a percentage of some tenths, is a forgeable alloy. Unlike pure iron it can also be *hardened by heating to a high temperature and quenching in water*. By an after-treatment, a *tempering*, it is possible to get a desired combination of

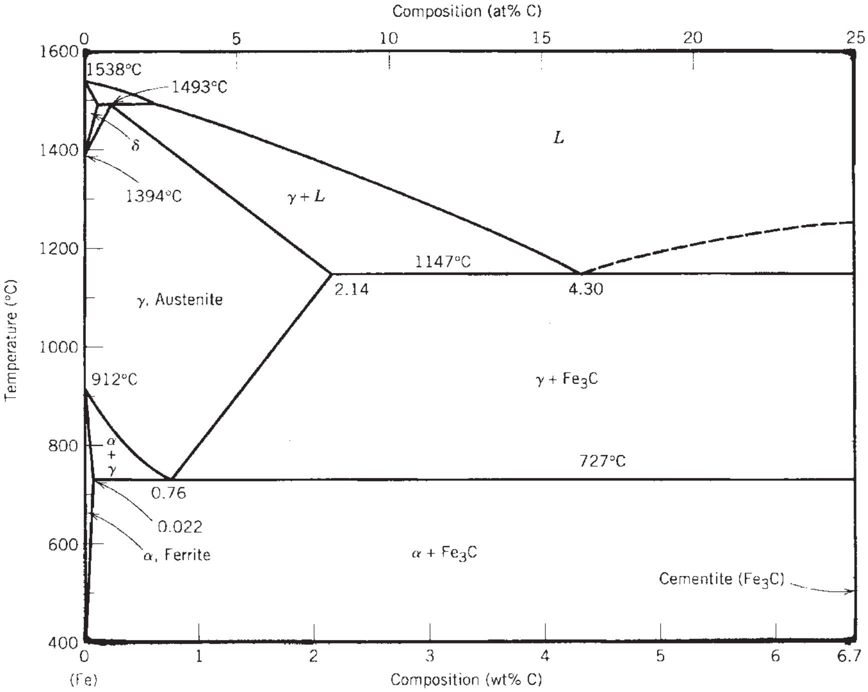

Figure 8.1 The iron-carbon equilibrium diagram up to 6.67 weight% C. (Reprinted from ref. [8.1].)

strength and toughness. This possibility to give iron a high and adjustable hardness has given the element a special value. This position has been further strengthened by its formability and its accessibility. No other metallic material has had such a great influence on human history as iron and its simple alloy with carbon, steel. But iron was in reality not an important metal until hardenable steel was known and could be managed. Only then could iron compete with bronze as a tool and weapon alloy.

8.3
Metallurgy – Chemistry at High Temperatures

In metallurgy the reactions are complicated and occur at high temperatures. This made a theoretical understanding difficult, and the fundamental processes became known empirically long before chemical science had developed to such a level that it could be of some use.

During the centuries around 2000 BC humans had a rather good knowledge of the metals copper, tin and lead, which can easily be reduced from oxides and sulfides. Alloy formation, e.g. bronze from copper and tin, was discovered and practically tested in a well-established casting technique. Cold forming as a method to give metal components intended form and increased hardness was well known, heat treatment, tempering, to restore softness and formability likewise [8.2]. It is easy to imagine how confused the early craftsmen might have been, confronted with different observations without having a background in theories or written textbooks. What is really happening within the metal when it hardens on forging and softens again on tempering? Why does the alloy of lead and tin have a lower melting point than either one separately?

Metallurgists and ceramicists used each other's products and skill. Metals and their oxides were coloring matter in glazing. The metallurgist had much to learn about the properties and reducibilities of different oxides. The craftsmen learned that reduction of an oxide to metal was a question not only of the temperature but also to a high degree of the composition of the furnace atmosphere. Further, pollutants in the ore were not desirable in the main metal or alloy. Instead a molten slag was created, in which the pollutants could be dissolved and thus be removed.

The manufacture of iron in all times – past and present – presupposes reduction by carbon of the iron oxides of the ores. If much carbon is absorbed into the iron, raw iron is formed, which melts at 1150°C. At lower temperatures, well below the melting point of raw iron and pure iron, almost carbon-free iron – spongy iron – is formed. It was thought that the possibility of reaching high temperatures determined which iron type – non-melted carbon-free iron or carbon-rich raw iron – was produced at a certain period. It has, however, been shown – in practical experiments during the 1970s – that blowing air into glowing carbon with a treadle blower creates such a high temperature that melting of raw iron is possible. That indicates that it perhaps was an intentional choice to carry through the iron manufacturing process at a low temperature and with a large excess of air to avoid the formation of raw iron. Early processes and products in the Middle East indicate this. In China the circumstances were different, and cast iron was manufactured at an early time.

During the metallurgical reduction processes silicate slags are formed from the gangue material of the ore. Added slag formers are also used. In the slags, calcium and magnesium oxides, silicon and aluminum oxides, manganese and iron oxides are present. From early iron manufacturing processes the produced iron has been removed and used for the purpose intended. Even if some iron products had been left they have as a rule rusted away and are not available for investigating. But the slags are still there. Their chemical composition is important for assessing the reactions that may have occurred in the furnaces.

8.4
Ancient History – A Global Outline

8.4.1
Early Incidence of Iron

In the first half of the third millennium BC pieces of man-made iron appear in Mesopotamia, Asia Minor and probably also in Egypt. H. H. Coghlan [8.3] reports that metallic iron was prepared as early as 2700, perhaps 3000 BC. It occurred in Tall Chagar in the north of Syria.

One of the oldest objects of iron, preserved to our time, is part of a sledgehammer that was discovered in the Cheops Pyramid. It was found in 1837 in a stone joint and was certainly left by a workman when the pyramid was built around 2000 BC. See Figure 8.2.

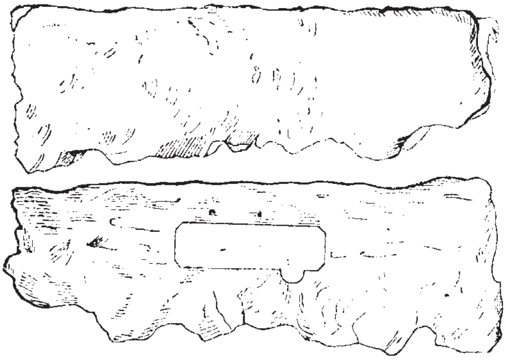

Figure 8.2 The sledgehammer of iron, found in the Cheops Pyramid, now kept in the British Museum in London.

8.4.2
A Heavenly Metal

Many old finds of iron have a meteoritic origin, shown by the nickel content. Meteorites are considered to be remainders of the material of which the planets were formed, 4.6 billion years ago. Most of them are stone meteorites consisting of silicate minerals, but some are iron meteorites built up of iron-nickel alloys with 4–20% nickel. The iron meteorites are forgeable and can be formed after heating. This metal from heaven has undoubtedly been used by humans for manufacturing different objects.

> The nickel-containing iron is austenitic at high temperature. On cooling it is normally transformed into ferrite. Under special cooling circumstances both phases can coexist down to room temperature. The ferrite with 6% Ni then forms laminae within the austenite with 15–20% Ni. A *Widmannstätten structure* has been formed, shown in Figure M7.

At Gerzeh in Egypt ca. 100 km south of Cairo, iron pieces, dated to 3500 BC, have been found. The nickel content 7.5% guarantees the origin. Another object, manufactured of an iron alloy with 11% nickel, was discovered during the investigation of a burial-place in Ur. Such findings, however, were rare and components of meteoritic iron very expensive. In Babylon the price of meteoritic iron was eight times higher than the price of silver.

Iron objects are depicted in the wall paintings of the Egyptian pyramids and always with a blue color. The butcher has a blue grinding tool hanging at his hip, the carpenter has blue tools for woodworking. The metal iron was called *benipe*, a word that probably has the meaning *metal from heaven*, a reason for the blue color [8.4].

For a long time iron was a curiosity and exclusively reserved for kings and great men. When the archaeologists in 1922 opened the tomb of the Egyptian Pharaoh Tutankhamen in the Valley of the Kings in Luxor they met a fabulous magnificence: furniture, weapons, vases, precious metals. The dead young king rested in a coffin made of solid gold. Many tools in miniature were with him, many of gold, some of exquisite glazed earthenware. In a gold belt around the waist, along his right thigh, one of the king's most esteemed treasures was found: his dagger with a rock-crystal knob on top of its hilt and a sheath of gold with decorations on both sides. The blade was made of the miraculous metal *iron*. Was it perhaps a piece of the metal from heaven? If so, a suitable companion for the last journey. With a less prominent placing there was also a dagger with a blade of gold, see Figure 8.3.

Terrestrial iron was of course also used in Egypt. But iron manufacture was not well developed there. The Sinai Peninsula and the mountainous country of Nubia are considered to be suppliers of the desirable metal for the Egyptians. Even black Africa is pointed out as a supplier. Tutankhamun died in 1343 BC. The Iron Age was near, but the technical development did not occur in conservative Egypt.

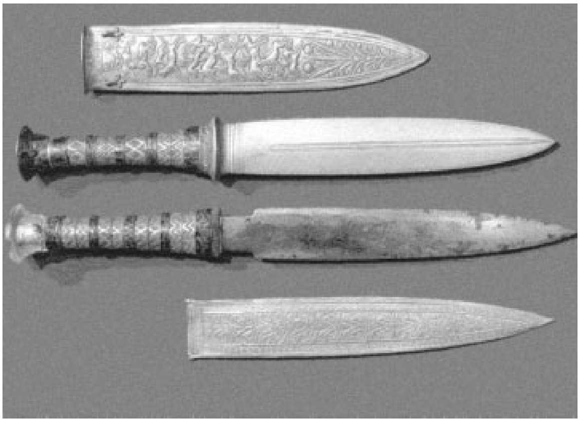

Figure 8.3 Pharaoh's two daggers, one with a blade of gold, one with a blade of iron [8.5]. Total length 320 mm (12.5 in.)

8.4.3
The Ores of Early Iron Manufacture

The present-day important iron ores *magnetite* (Figure M9) with the mineral Fe_3O_4 and *hematite* (Figure M10), Fe_2O_3, are easy to find but compact and difficult to mine. As they are also difficult to reduce they were not used in the early epochs of iron manufacture. Iron carbonate, $FeCO_3$, *siderite* (Figure M11) is easy to handle and is, after roasting (heating with air), easy to reduce and so was used. The most important ore type in olden times was, however, *hydrated ores* with varying water contents. Lake and bog iron ores (Figure M8) are of this type. They have been, and are, formed by oxidation of iron carbonate dissolved in water. The carbonate has a certain solubility if the carbon dioxide content of the water is high enough. Influenced by the air the iron is oxidized and precipitates as a brown slime of hydrous iron hydroxide oxide, FeO(OH). This ore has a low content of gangue and was easily won and reduced and was thus very suitable for early iron manufacture. That was also the case for red hematite, so called *red earth*, in many places used for the very first iron making.

8.4.4
Not Cast but Forged – While the Iron is Hot

Pyrometallurgy in combination with forging was developed in the Middle East in the 2nd century BC. From there the knowledge about the techniques followed the trade routes westward to Rome, Spain and England and eastward to Persia, India and China. But every region had, in addition, its own early development.

In the beginning it was well known to people that most metals, as for instance tin or lead, melt at the reduction temperature. If so they are easily separated from the gangue. On the other hand, a metal that is reduced at a temperature below its melting point, will be mixed up with gangue and molten silicate slag. The latter was the case for the early direct method of iron manufacture. In antiquity, iron was manufactured with direct reduction from ore to forgeable iron, see Figure 8.4.

When the iron ore was reduced at this "right" temperature non-molten, soft, forgeable metal was formed. If the furnaces had been forced up to much higher temperatures, iron development would have run the risk of missing the whole field of formability with the possibility of forging swords and plowshares. The natural product would have been – as in China – cast iron, totally impossible to forge. We should be grateful to the early metallurgists for their ability to see beyond the casting technique they had already mastered for bronze. The smiths stayed with a soft, solid and malleable iron and avoided falling into the trap with too much carbon uptake. And they found a very important way of increasing the carbon content and yet keep the formability.

In the first stage of the process the iron took up a considerable amount of carbon, which was removed spontaneously when the air blowing gave oxidizing conditions and brought iron back to the slag as iron oxide. The product, reduced iron, was solid and formed an iron sponge, a *lump*, containing molten slag inclusions, which had to be separated by hammering and a final forging. The slag separation was made more

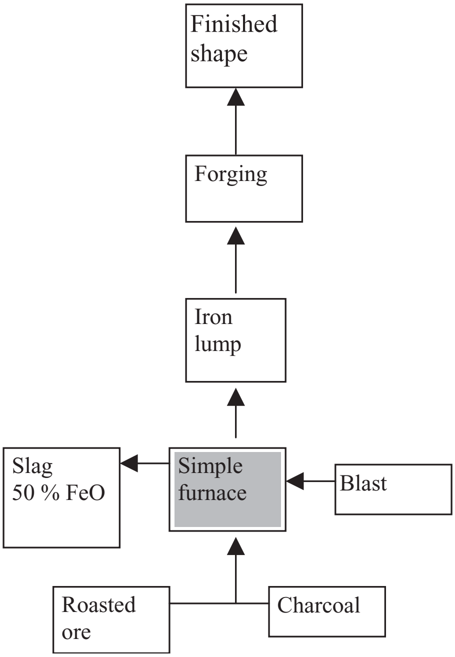

Figure 8.4 The start of iron manufacture: the direct method.

effective by a technique already used in early metallurgy: *fluorspar* was added and made the slag easily fusible. Thus, early iron manufacture was characterized by the following steps:

- burning of charcoal to get a high temperature
- reduction of the iron oxide in the ore to solid iron, an iron sponge
- air supply with a blast to increase the temperature and melt the slag
- tapping of molten slag through a special slag hole
- hammering of the iron lump to remove the remaining slag
- forging to final form.

In the iron manufacturing process in general the phosphorus of the ore is distributed between slag and iron. One part goes to the slag as phosphate while one part stays in the iron as harmful phosphides. Iron with a high phosphorus content tends to exhibit *blue brittleness*, which implies that brittle fracture may occur at a slightly increased temperature (when the iron is warmed to a blue but not a red color). In the process of making iron, phosphorus removal takes place if the furnace temperature is comparatively low and the furnace atmosphere oxidizing. The simple furnaces that produced iron in antiquity worked in this way. The produced iron got a passably low phosphorus content even if produced from an ore rich in phosphorus. Conditions in the blast furnace process are quite different. In the strongly reducing conditions there, phosphorus goes almost entirely into the iron.

Sulfur also is harmful to the iron. It gives so-called *red brittleness* or *hot shortness,* i.e., disposition towards crack formation in the red-hot state. The ores are *roasted* before processing. Roasting is heating with full air admission so that the sulfur in the ore is oxidized to sulfur dioxide, which disappears. The risk of red brittleness in the iron is decreased or eliminated.

The final step in the primitive iron manufacturing process was a difficult one. Forging is a complicated technology, the practicing of which presupposed special knowledge and good contact with the gods. The art of forging was already in pre-Greek times, in the religions of the Orient, associated with the god who in Athens got the name Hephaestus and in Rome Vulcan. He was often accompanied by dwarfs possessing technical skill at forging. In *The Iliad* Hephaestus is praised as creator of Achilles' shield and suit of armor.

As an everyday metal, iron became used comparatively late. Small-scale manufacturing was known but something prevented a general use. Coghlan [8.3] saw two reasons for the slow development. Firstly, it was difficult to forge without suitable tools, hammers, anvils and tongs. Secondly, and perhaps more important, the produced iron was soft and impossible to harden as the carbon content was so low. A good edge sharpness could certainly be obtained but not maintained, owing to the softness. As long as the metal with these properties had to compete with copper it was an interesting alternative. But, when bronze, about 2500 BC, came into general use people lost interest in iron as a tool and weapon material.

8.4.5

Steel – At Least on the Component Surface

The transition from the Bronze to the Iron Age was of course a lengthy process. For the eastern Mediterranean countries the year 1000 BC is stated. Hundreds of years before that date, iron manufacture was improved on the Sinai Peninsula, in Wadi Arabah in Palestine, in the desert regions in eastern Egypt, among many other places. Probably the common use of iron, however, began round 1500 BC, when iron manufacture became a developed technique in the *Hittite Empire* in present-day Turkey.

A region in Asia Minor, extending from the slopes of the Tauros mountains between present-day Turkey and Iran, and the Zagros mountains towards the central desert landscape in present-day Iran was suitable for an expansion of iron manufacture. Ore was available and in the dry regions pistachio nut trees grew on the mountainsides. These became the raw material for charcoal of the highest quality, suitable for metallurgical reduction processes.

> A revolutionary archaeological discovery was made in 1906, when excavations in Bogazköy in present-day Turkey revealed the town of Hatussa and its rich archives. An Indo-European people, the *Hittites*, migrated to central Asia Minor, probably during the centuries before 2000 BC. They captured the town of Hatussa, banished the domestic inhabitants and took over the Assyrian trading companies. Around 1600 BC, using horse-drawn combat wagons of iron, they made a military operation to distant Babylon and overthrew the Amorites and their Babylonian country. The Indo-Europeans introduced the

> horse into the old civilized countries and the horse was a reason for their military superiority, but not the horse alone. It must have been difficult for the ill-disciplined warriors of the old people to withstand the attack of an enemy with horse-drawn chariots in serried ranks. However, the remote occupation could not continue. The stress became to great, complications at home occurred and led to a period of political stagnation. But handicraft and industry developed. The country of the Hittites became a great metallurgical power, a center firstly for silver production but soon also for iron. The remarkable development of iron forging in the regions of Asia Minor, ruled by the Hittite kings, entailed a considerable improvement in the standard of living of the people. Even the image of the country as a military power was strengthened.

What was it then that happened regarding forging practice in the Hittite country? Two things.

In the first place, tools for handling of the hot iron-forging piece were developed. Forging could be carried out with greater safety, more regularly and with the same quality of forging each time. Secondly, and as a consequence of the improved handling technique, the smiths learned to manufacture steel, an iron with enhanced carbon content – at least in the surface region of the component – an iron that could be given surface hardness and edge sharpness.

Before this development the red-hot lump formed in the furnace had with difficulty been transferred to a flat rock serving as an anvil. As it was hammered with a stone the workpiece had been fixed with thin wooden poles. The Hittite forgers developed smiths' tongs of iron, although none have actually been found. After long use they were scrapped and reforged. Even if any had been left they would have rusted away. Other finds from the centuries BC, however, elucidate the development, see Figures 8.5 and 8.6.

With better tongs it became possible to forge, heat again and reforge, perhaps several times. The intention certainly was to perfect the shape. A most valuable side effect was, however, obtained. The repeated heating in charcoal resulted in carbon uptake and formation of steel in the surface region. Rapid cooling in water after this forging gave a pronounced hardness and a new type of tools and weapons. This process is parallel to modern case hardening, in which, before quenching in water or oil, the carbon content of the surface is increased by different means.

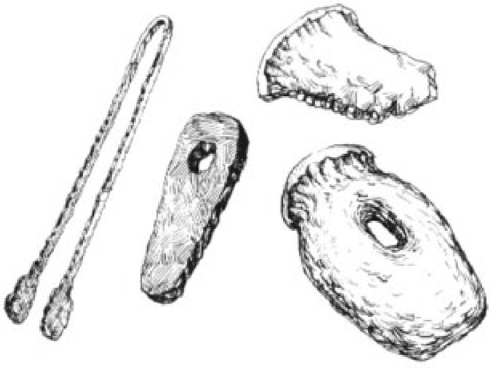

Figure 8.5 Examples of iron tools from finds in Eastern Europe from around 500 BC. A pair of tongs, two hammers and (at the top) an anvil. (Reprinted with permission from Tomas Johansson, Östersund, Sweden.)

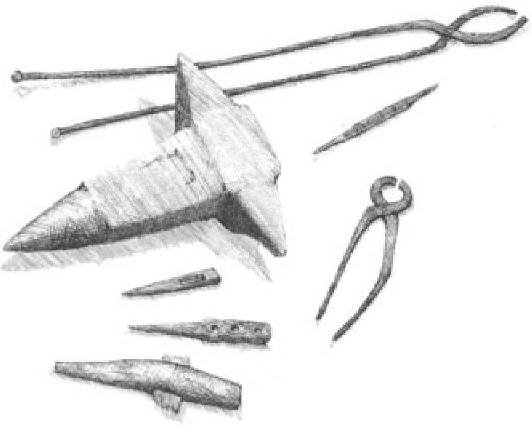

Figure 8.6 Forging tools from central Europe dated to the centuries BC. The large object is an anvil that has been carved from a stump. As well as hammers and tongs there are tools for making nails. (Reprinted with permission from Tomas Johansson, Östersund, Sweden.)

Through the achievements of the Hittites, the ground was prepared for the Iron Age and an everyday use of iron. Their technique is illustrated in Figure 8.7.

That hardening of tools and weapons was known in Anatolia, Asia Minor, is apparent from the Greek heroic poems from ca. 700 BC. In *The Iliad* the Greek heroes do not have iron but they know that this metal is available in Troy. An expansive metal! On their way home, described in *The Odyssey*, it is evident that they have seen the hardening of steel and they use this fact in the tales. It is quite clear from the description of how Odysseus twists a hot wooden pole in the sole eye of the giant Polyphemus:

> "Just as a smith plunges into cold water some great axe-head or adze and it hisses angrily – for that is the treatment, and the strength of iron lies in its temper – just so his eye sizzled about the olive-spike."
>
> (Homer, *The Odyssey*, trans. T. E. Shaw, Wordworth Classics **1992**, p. 99.)

Supported by their own technical development, the Hittites took up top-level military activities again. Around 1250 BC they fought against the Egyptian Pharaoh Rameses II over Syria. According to peace terms, formulated and recovered in both an Egyptian and a Hittite version, the battle ended in a draw and Syria was divided between the two rivals. For the Hittites the eastern Mediterranean became a natural living space and it was to be of the greatest importance in the hard times that drew near.

During the 13th century BC Egypt was invaded by the "sea-people". Coming from the sea they fell upon the Egyptian possessions on Cyprus and the coasts of Syria. In Egyptian documents from this time the name *Philistine* has been found as a designation for the warlike and seafaring tribes. This invasion from the north also affected Asia Minor. The crowd of people who broke in there had probably met with misfortune due to a sudden deterioration in the climate. This resulted in the disorganization about 1200 BC of the Hittite nation and a significant migration southeastward, towards Syria. A generic term for the refugees from Anatolia was "Philistines". They settled in the Palestinian coastal area and formed city-states, see Figure 8.8. Following this group the Hittites brought knowledge about forging and steel hardening with them. That made them superior in war.

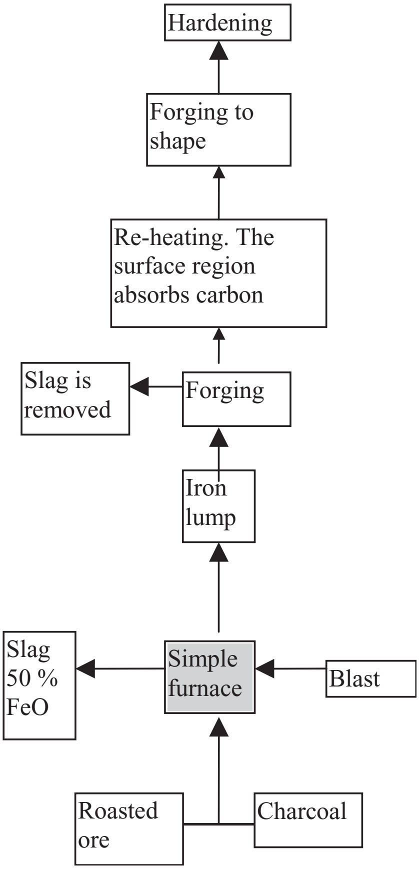

Figure 8.7 The Hittite method for manufacturing forgeable iron with a hardened steel surface.

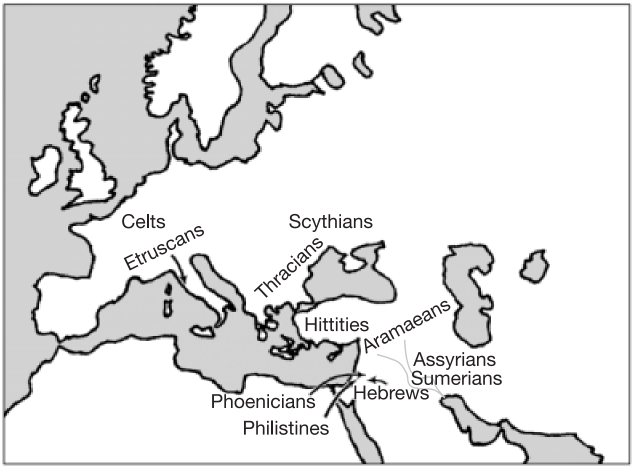

Figure 8.8 Ancient cultures in Europe and the Middle East [8.6]

8.4.6
No Blacksmith in All Israel

During the first Israelite kingdom the Philistines were dangerous antagonists. King Saul's three sons fell in a battle against the Philistines on Mount Gilboa and he took his own life by using his sword. Saul had a sword of iron, a privilege that was denied to the Israelite soldiers. The Philistines carefully guarded their knowledge of forging and for a long time they retained control over iron and its fabrication for both agricultural and martial purposes. This is clearly described in the Old Testament.

> Not a blacksmith could be found in the whole land of Israel, because the Philistines had said: "Otherwise the Hebrews will make swords and spears!" So all Israel went down to the Philistines to have their plowshares, mattocks, axes and sickles sharpened. The price was two thirds of a shekel for sharpening plowshares and mattocks, and a third of a shekel for sharpening forks and axes and for repointing goads. So on the day of the battle not a soldier with Saul and Jonathan had a sword or spear in his hand; only Saul and his son Jonathan had them. (1 Samuel 13:19–22)

8.4.7
China – Persia – India

When iron ore is reduced at the "right" temperature a soft, malleable iron is formed, as already mentioned. If the temperature is increased very much during the reduction process an iron product with a high carbon content is obtained, brittle and impossible to forge. In our day it is called cast iron, pig iron or raw iron. In China this "mistake" was used for the manufacture of cast iron in the period 500–300 BC, thus long before the technique was known in Europe. It is probable that the use of anthracite and coke instead of charcoal increased the temperature and also the carbon content of the iron, with molten cast iron as a consequence. Chinese metallurgists became clever founders [8.7].

In *Avesta (Zend-Avesta)*, the Holy Scripture of Persia, early iron manufacture is reported. The Persian weapon-smiths also had a very good reputation.

India has a special position in the history of iron. The evolution of the ancient Indian civilizations is described in *Rig-Veda*, perhaps the oldest document in human history. A people of high culture, living in the Indus valley, are described. They manufactured bronze but iron is not clearly mentioned. In another poem, *Atharva-Veda*, iron is described. In Sanskrit the word *Ayas* (meaning "luminous") is used for this metal. Words for iron in different Indo-European languages are derived from *Ayas*, as for instance "iron" in English, "Eisen" in German and "järn" in Swedish. Later, it became typical of iron making among the Hindus to manufacture heavy forgings of a size not made in Europe until a thousand years later. The Kuwat-ul-Islam Mosque in Delhi has a forged pillar with a diameter of 400 mm and a total height of 7.5 m, of which 1 m is below the ground. The weight is about 6000 kg. Originally it was placed at a Hindu temple in Mathura and was made in the period 330–380 AD. The manufacturing technique was welding together small iron lumps, from a simple reduction process, before the final forging, see Figure 8.9. Investigation of the pillar has revealed a very pure iron with low content of slag inclusions.

Figure 8.9 The forged Kutub iron pillar in Delhi. The pillar is shown to the right in the picture.
(Reprinted from R. Hadfield, Journal of the Iron and Steel Institute, 1912, 85.)

The pillar has been standing for more than 1600 years. Why has it not rusted away? One reason may be that air in the actual region has a very low humidity and consequently electrochemical corrosion processes in adsorbed moisture films cannot occur. The low carbon content of the iron may be another reason. Few microgalvanic elements are formed, and these are necessary for the general corrosion of iron surfaces in the atmosphere.

Emigration from the slopes of the Himalayas to settlements south of the Caspian Sea brought knowledge of iron manufacture to the people in Armenia and the Caucasus. From about 1200 BC they themselves became exporters of iron products.

The art of making steel, iron with increased carbon content, is also old in India. During the Middle Ages Indian steel was counted as luxury. The Church Father Clement of Alexandria requested his fellow Christians to live moderately and not always use knives of Indian steel to carve the steaks at th meals. The Indian steel *wutz* was a *crucible steel*. The crucible was first charged with a piece of glass and then with a mixture of iron ore and charcoal. It was heated strongly in an air blast. A molten *regulus* weighing 0.75 kg was obtained. Another, and more usual alternative, was to use soft iron with a low carbon content and heat it together with a plant rich in sap or resin. The iron was carbonized to steel. It was delivered to Damascus and forged by experienced masters. The sword was hardened by quenching “in a strong northerly wind” and etched with a solution containing ferrous sulfate and acetic acid. Layers with different carbon content were etched differently and the *damask steel* got its typical, distinctive appearance1).

1) This pattern is called genuine damask. Artificial damask is received when welded strips with different carbon contents are etched (see page 199).

8.4.8
Nineveh Tests the Forgeability

Iron was used early in Assyria. In King Sargon's palace, which was built in Nineveh around 710 BC, a big iron find was made. It weighs 160 tonnes and consists mainly of iron pieces, forged at both ends (Figure 8.10). Heating and forging without cracks was a proof of good formability and quality. In one end also a hole was made through which a rope could be threaded for transport. In the Nineveh treasure manufactured iron components were also found, a saw among other things.

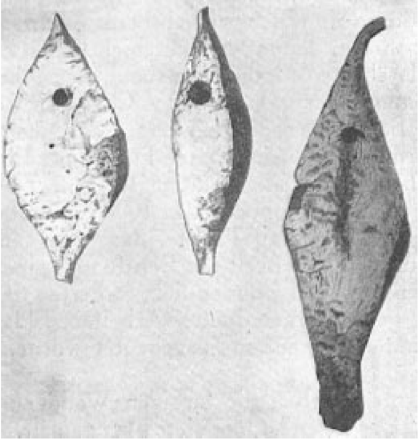

Figure 8.10 Iron pieces from Nineveh with forged ends for quality control.

8.4.9
Africa

In the African development of metallurgy the Bronze Age was "left out" even if there is some evidence of copper manufacture in the Niger area. Iron became the first dominant metal [8.8]. Obviously there are no pictures of the oldest iron manufacture. And yet they are available! When the European colonizers and missionaries reached the interior of Africa they found iron manufacturing methods that in all probability resembled the ancient techniques. *Kurdufan* is a province in present-day Sudan, rich in superficially situated bog ores. In 1840 an active iron-manufacturing locality was found. The furnace was a pit in the sand, about 30 cm deep. In the furnace charcoal and ore were put in layers and the charge was covered with charcoal, see Figure 8.11.

H. M. Stanley found Livingstone at Lake Tanganyika during his expedition in 1871. His expression at that moment is famous: "*Dr. Livingstone, I presume....*" Stanley described iron manufacturing in the region and used sketches, obviously made by Livingstone himself (Figure 8.12). The description could have been valid for an ancient process:

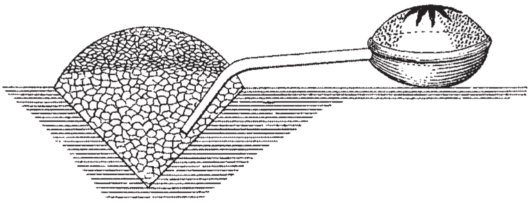

Figure 8.11 Reduction furnace with blast in Kurdufan, Sudan (1840). (Reprinted from ref. [8.9].)

> ... Four men who produce a strong current of air by rapidly moving the handles up and down drive the four bellows, with two handles each. ... The furnace is made of stamped clay and forms a four feet high mound. In this a hollow is made, two feet deep and two feet in diameter. In the walls are four holes, in which clay tubes are adapted and through which the blast is introduced into the hearth. Near the reduction furnace a smaller furnace is situated, in which the produced iron is heated up again and forged to hammers, battle-axes, knives, nails, rings, and so on.

Figure 8.12 A village inhabitant in Simarianjo operates two bellows at the iron furnace. (A drawing by David Livingstone, reprinted from ref. [8.9].)

8.4.10
Iron in Old Europe

8.4.10.1 The Celts

The Celtic people reached a leading position in culture and politics in central Europe during the four last pre-Christian centuries. Long wanderings resulted in settlement in France, England, Scotland and Ireland. In fact, in 387 BC they also conquered Rome. When Caesar incorporated Gaul – Gauls was a Roman name for Celts – to the Roman Empire in 50 BC the strong Celtic influence came to an end.

The Celts were first in Western Europe with underground mining. They were also able metallurgists and smiths and invented the horseshoe. Their knowledge of applied physics was demonstrated in a method to make the wooden wheels of barrows iron-shod. An iron ring, formed from a strip, was heated up and put round the wheel. As it cooled it shrank onto the wheel. This iron protection of the horses' hooves and carts' wheels increased their mobility and endurance, important for a nation of horsemen.

8.4.10.2 The Etruscans

In antiquity the Etruscans dominated Central Italy. They founded their society around 800 BC in Etruria, present-day Tuscany, on the western coast of Italy. They never brought their autonomous city states together to form a country. Etruscan warriors had the best armor of their day, battle-axes, lances, shields and helmets, and they fought from horse-drawn chariots. Remains of Etruscan cities and graves reveal a wealth that certainly had its origin in the export of iron. The ore was mined on Elba and was reduced by charcoal in a lot of small furnaces in Tuscany. The total iron quantity was small but large amounts of charcoal were needed. The forests were cleared of trees and massive soil erosion started. The consequences – the bare mountains in Italy – are visible even today. Without forests there could be no iron-making, but iron-making *had* to continue to guarantee the welfare of the people. The Etruscans moved their furnaces and forges northwards. Marzabotto, a town on the way to Bologna, became a new industrial center in the 5th century BC. From there the iron was transported to the Po valley and exported to Athens. There was a real reason for the Etruscans to export iron to Athens in the 5th century BC. Greek felt a constant threat of war from Persia, and real battles – Marathon, Thermopylae – have gone down in history. The smoke from the armourers' workshops laid thick over Athens.

8.4.10.3 The Romans

When the Romans built their empire the important regions for mining and metallurgy in Anatolia, Syria, North Africa, Gaul and Spain were incorporated. The Iberian short sword became the principal weapon of the Roman legionaries. These famous Spanish swords were made with soft iron in the blade core, while the surface was made of a carburized and hardened steel. In the fourth century AD, when the Roman Empire was most militarized, eight large armourers' workshops were situated in Gaul to supply the Roman legions at the Rhine border [8.10]. The workshops were very specialized. Swords were made in Reims, spears in Trier, shields in Amiens. The armies on the Danube boundary were provided with weapons from workshops in Swabia, Franconia and Noricum. Weapons were also transported to the seaport of Aquileia on the Adriatic and shipped out to the legions in Greek. The most important workshops for weapons in the Palestinian region were built in Syria (Damascus and Bosra).

8.4.10.4 The Germanic Peoples

Germanic smiths did not imitate the large-scale Roman methods for iron manufacture, but used a technique of their own, based on intensive forging of the red-hot iron lumps from small furnaces. Slag inclusions in the iron were removed and weapons and tools gained their shapes. The Germanic smiths could not manufacture swords like the Spanish, and for a Viking a Spanish sword was a dream. If fulfilled, he gave the sword an individual name.

Leaders and kings were very anxious to develop the important technique and the smiths were held in esteem among the Germanic people. The murder of a smith was punished more severely than the murder of other craftsmen.

8.5
Pig Iron – Impossible to Forge – But Forged to Bar Iron

8.5.1
More Iron!

During the 11th and 12th centuries new social and economic circumstances led to the growth of societies. Castles and new towns with houses and cathedrals were built. All this resulted in the need for more iron. An army of crusaders had to be equipped to march through Syria and capture Jerusalem or set the Holy City free. The knights had to wear coats of mail and be armed with heavy swords. Their horses should be iron-clad and be provided with stirrups and horseshoes of iron. In addition, more effective agricultural production called for large quantities of iron for sickles, scythes, leaf knives and plows. This peaceful iron use is often underestimated but certainly used more of the total iron production than did the martial campaigns.

8.5.2
The Blast Furnace

In Europe, iron had been manufactured in many small and very dispersed furnaces. There was a big demand for a more effective manufacturing process. The answer was *the blast furnace*, and the production became a multi-stage process:

- Manufacture of raw iron (pig iron) in the blast furnace
- Reduction of carbon content. Transformation of the pig iron into wrought iron by different hearth processes
- Manufacture of bar iron with low or medium-high carbon content.

The big advantage of the blast furnace was that it could be continuously charged with ore and charcoal and tapped intermittently for liquid pig iron and liquid slag. A concentration now occurred on those deposits of ores suitable for the blast furnace process. The need of charcoal for the reduction presupposed good access to adjacent forests. The new technique also needed a more effective and persistent blast heating than had been possible with the older muscle-driven bellows. A decisive step was taken during the 12th century when waterpower began to be used for both blasts and hammers. Remains of small blast furnaces from the 13th century have been found in Jubachthal in Westphalia, Germany, and in Lapphyttan, Norberg, Sweden.

Using larger furnaces and increased air supply mainly achieved an increase of the produced iron quantity. In Germany the volume of the blast furnaces, *Stücköfen,* increased from ca. 1.5 m^3 to ca. 4 m^3 in the period 1500–1700 and the daily output grew from 1200 to 2000 kg. Around 1830 a blast furnace produced 3000–4000 kg of pig iron a day. For each tonne of iron 1500–2000 kg charcoal was needed.

Figure 8.13 shows how the blast furnace was built from the Middle Ages right up to the beginning of the 19th century.

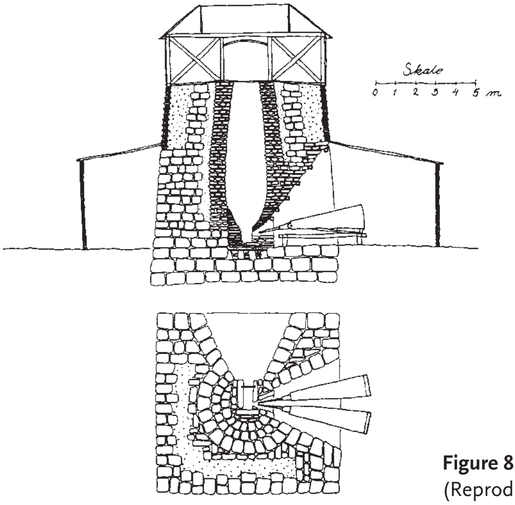

Figure 8.13 An old timber-clad blast furnace. (Reproduced from ref. [8.12]. With permission.)

The furnace was fed from above with iron ore, limestone and charcoal. Air was blown into the lower parts of the furnace. Then carbon monoxide CO was formed, which reduced iron oxide to solid iron sponge in the middle of the furnace. In the lower part the iron absorbed carbon and melted as pig iron with 4% carbon.

The principle and terminology of a modern blast furnace is shown in Figure 8.14.

The high-carbon iron from the blast furnace could in fact be directly used for *one* type of final product: cast components. Castings were made either directly from the blast furnace or from iron remelted in special low *cupola furnaces*, sometimes placed far from the blast furnace, even within the cities.

The consumption of cast iron rose considerably with the frequency of wars and the mechanization of the armies. It is said that during the Thirty Years' War the Catholic army under Tilly sent about 15 000 cannon balls of cast iron every day into Magdeburg at the siege of this town in 1631. Iron cannons were cast directly from the blast furnace. These pieces were inexpensive – compared to bronze cannons – but very heavy. They were not used for light field artillery but for permanent installations in forts and on ships.

Techniques for casting components for civilian use – garden furniture, equipment for stoves, water tubes, weights, coffee-grinders, and many other things – were especially developed in England.

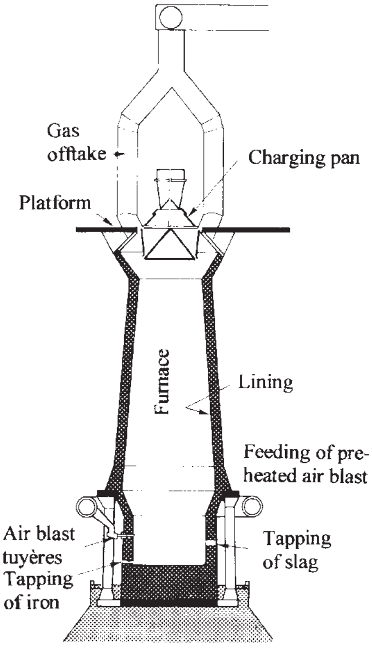

Figure 8.14 The principle of a modern blast furnace.

8.5.3
To Make Pig Iron Forgeable

The blast furnace had a large productive capacity but the product, if not used for cast components, was initially of limited value. Because of its high carbon content, 3–4%, it was brittle and impossible to forge. Iron wire, sheets or needles could not be made of it. At the end of the Middle Ages people said, "it was better in earlier years". Then it was possible to make armor, chain mail and helmets of the soft iron that was produced in the small furnaces by direct reduction. From the blast furnace product it was, however, impossible.

But a technique – involving different *hearth processes* – became available to convert the brittle pig iron to malleable, soft iron. The solidified "pigs" of high-carbon iron were placed on a layer of charcoal in the hearth and an air blast was directed from the side. The pig iron melted and droplets passed through the carbon layer and were collected on the bottom of the hearth. There the air from the blast created an oxidizing atmosphere and a slag, rich in iron oxide, was formed. This oxide reacted with the carbon in the pig iron and carbon oxides boiled away. The iron, the melting temperature of which now increased, was "puddled" to a pasty mass – a very tough work for the people.

During this long period from the first blast furnaces to the ingot steel processes in the middle of the 19th century, the "smith" worked as both metallurgist and smith. He melted the pig iron in his hearth, reduced the carbon content by air blasting and got a lump of wrought iron. That was work for a metallurgist. As a smith he then forged several lumps together and stretched the combined material out by different hammers, driven by water wheels (Figure 8.15).

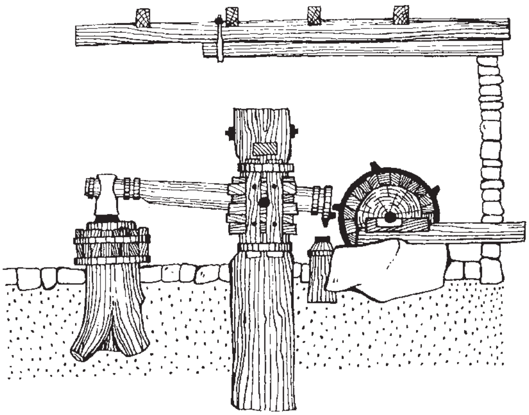

Figure 8.15 The presumably oldest and most used hammer type, the tail hammer. Made of wood but iron-shod on hammer and anvil. (Reproduced from ref. [8.12], with permission. See also [8.11].)

Different hearth methods – German, Walloon, Franche-Comté and Lancashire – were used, all in accordance with the above principle, but with differences in the practical performance. The main product, *bar iron* or similar, was processed to scythes, horseshoes, plows, chains, gratings, nails, wire, swords and so on in specialized workshops [8.10].

8.5.4
Steel Manufacture from Wrought Iron

For many purposes it was necessary to make steel from the soft wrought iron. In the 17th century the number of inventions in this field increased considerably. In one type of process, a cementation process, wrought iron rods were heated with charcoal in boxes. This method was particularly developed in England, and that country became the leader in steel-making by carburization from the 17th century. In other processes, wrought iron bars were immersed in a bath of molten pig iron, so that their carbon content was increased and the iron was converted into steel. The inventiveness of these methods is greater than we are inclined to think, as the people of that time did not have any knowledge of the real role of carbon in steel metallurgy.

For watch springs, a steel with better evenness than produced by cementation was needed. A *crucible steel technique*, a remelting process, was developed. The small crucibles, holding 30–40 kg, were placed in a furnace heated by coke.

8.6
Sweden and England – Cooperation and Competition

8.6.1
Iron Ores With and Without Phosphorus

Unlike the older, simple iron manufacturing processes, pig iron takes up the total phosphorus content from the ore. Iron made from a high-phosphorus pig iron will have a high content of phosphorus and suffer from blue brittleness. Thus, only iron ores with low phosphorus contents could be used in the blast furnace process for production of a high-quality iron. In the new situation in Europe the production units had to be located in regions with a large supply of ore with low phosphorus – and high iron – contents. Some examples are shown in Table 8.1.

Table 8.1 European iron ores with low P contents, suitable for early pig iron manufacturing in blast furnaces

Mine	Fe %	P %
Sweden		
– Striberg, Kärrgruvan	52,5	0,015
– Stripa	52,0	0,008
– Norberg	49,4	0,021
– Norberg, Kallmora	60,7	0,007
– Dannemora	52,0	0,002
– Persberg, Storgruvan	53,2	0,003
Spain		
– Bilbao	48	0,02
Austria		
– Erzberg	32	0,04
Germany		
– Mark, Westfalen	46	0,09

As can be seen, the iron country of Sweden had a favored situation. O. Johannsen [8.4] describes how the Swedish authorities and metallurgists clearly saw and used these possibilities. In the 16th century, king Gustavus Vasa prohibited the export of simple, inexpensive iron products and supported pig iron manufacture, making use of the good Swedish ores and production of bar iron. His son Charles IX and grandson Gustavus Adolphus continued the development, and invited Protestants and Huguenots, with a difficult religious situation in their homelands, to Protestant Sweden. Clever craftsmen, metallurgists and industrialists from Germany and the Netherlands settled and soon supported the growing Swedish iron industry. Improved methods for building blast furnaces were introduced. Metallurgists from Germany came with bellows made of timber instead of the earlier, less effective leather. From the Netherlands the industrialist Lois de Geer arrived (in 1627) and

> took an active part in the development of the whole Swedish iron industry. Together with the engineer Willem de Besche he developed the big Swedish cannon exports. A large number of forgers who had emigrated to Holland from Spanish-controlled Wallonia were recruited for work in de Geer's various iron factories. They brought new techniques with them, especially the Walloon process for making forgeable iron from pig iron. It was not least owing to the modernized iron industry that Sweden gained her position as the most important great power in Continental Europe – after France – in the 17th century.

In Stockholm the famous Jernkontoret, an organization of the Swedish ironworks owners, was founded in 1747 "to keep the price of iron at its correct level in these dangerous trading circumstances". Since then it has worked also as an institute for education, research and technical development.

8.6.2
England–Sweden in Cooperation

The iron manufacturers in Uppland in Central Sweden became famous for the Walloon iron they delivered as bar iron to England. During the 18th century, Sweden's iron production was doubled owing to the increased demand for bar iron. In particular, England had a large need for the so-called "Oregrund iron", a quality iron manufactured in Österby, Loefsta, Forsmark, and other works in Uppland, all shipped from the Öregrund harbor on the Baltic Sea. All manufacturers used ore mined in Dannemora.

Swedish Walloon iron is considered to have been a prerequisite of the quality reputation of Sheffield steel and of its dominance in Europe. The English steel had edge sharpness, polishability and formability. These qualities were essential for manufacturing razors, scissors, drills, instrument components and watch springs. The English steel manufacturing process was a cementation method in which the iron bars were placed in chests with charcoal and heated for a long time. Carbon diffused into the iron, which was converted into steel. The product was sorted into hardness groups according to the appearance of the fracture surfaces. The cemented steel could be used directly for manufacturing steel components but was also often remelted to crucible steel.

What made the Swedish Walloon iron so special? In Sheffield it was expressed by saying that the iron was characterized by better *soundness* and better *body* than iron from other suppliers. Wilhelm Ekman [8.13] has shown that *soundness* implies a low content of slag inclusions.

> A Walloon iron from a supplier got a bad reputation if slag inclusions led to scrapping of instruments after polishing and razors after grinding. When the pig iron is hit by the air blast in the Walloon process, a slag is formed that takes an active part in the decarburization process. On completing the process, slag droplets remain in the iron. They are removed during forging if they have not already solidified. If they have, they stay as slag inclusions in the iron. The composition of the slag is critical for the melting point. It is low,

1200°C, if the FeO content is 70% and the SiO_2 content 30%. If the composition is changed by 5% more or less, new solid particles are formed that are difficult to remove during forging. Too high a content of SiO_2 was especially dangerous, as it not only solidified the slag but also gave inclusions with harmful effects on the grinding and polishing properties. And now we can see the advantage of the Dannemora ore. It had a high content of manganese, so the slag in the Walloon process had a content of 10% MnO. The slag inclusions were not completely eliminated but the risk of the dangerous silica-rich slag was considerably reduced. The Walloon iron from Uppland had *soundness*.

The meaning of the word *body* is not quite clear. Perhaps it expresses a low disposition towards grain growth and brittleness at the long heat-treatment times in the carburization processes. Even in the Walloon process itself, an iron with a good *body* is an advantage. The iron can, without damage, be given an extra high temperature and thus make the slag very liquid and easy to remove during forging. But why should Walloon iron withstand grain growth during heat-treatment processes better than other qualities of iron? Could it be because the Dannemora ore contained some components, Al, V, Nb, that made the product similar to a modern micro-alloyed steel, designed to resist grain growth and brittleness after prolonged heating?

8.6.3
The Puddling Process – An English Threat to Swedish Hegemony

The technique for manufacturing wrought iron from pig iron presupposed access to charcoal for heating the hearths. Sweden (and Russia) had dominated the European market owing to their immense supply of timber from which charcoal could be made. In Great Britain, deforestation became a big problem, leading to a decline of the iron industry in some parts of the country. A powerful incentive was provided for the discovery of a method of melting with pit coal or coke, to increase domestic iron production and to reduce the large and expensive imports from Sweden. Several ineffective patents were taken out in the 17th century. It was not the smelting itself that was the problem. That functioned. It was the high sulfur content of the coal that destroyed the produced iron. Iron rich in sulfur suffers from *hot shortness* or embrittlement in the red-hot state.

In 1784 Henry Cort (1740–1800) invented the so-called puddling process that made it possible to decarburize pig iron with coal. What was new in the technique was that the pig iron was not allowed to come into direct contact with the solid fuel. The coal was burned in a special fireplace (Figure 8.16) and the hot flame had to pass over the iron and heat it to melting. The sulfur content of the coal passed as sulfur dioxide to the chimney and the iron absorbed only a small part of it. The wrought iron produced in the new process therefore did not show hot shortness. The bottom of the hearth and its walls were lined with a slag rich in iron oxide. Its oxygen reacted with the carbon of the pig iron to form volatile carbon oxides. At last the whole heavy mass came to a violent boil. The iron, now low in carbon and with a high melting point, became

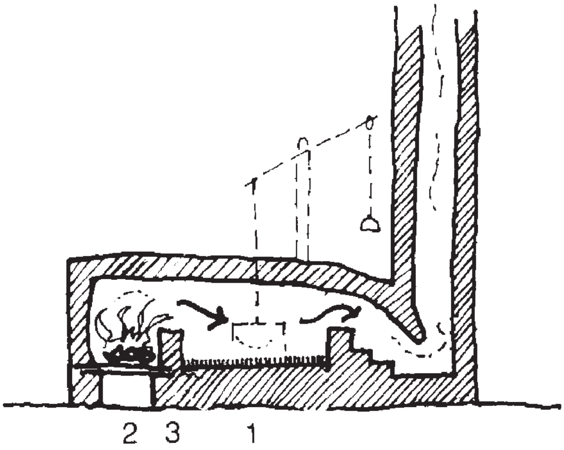

Figure 8.16 Furnace for the puddling process. The decarburization occurred on the hearth in the reverberatory furnace (1) that was heated up by the flames from the fire (2). Hearth and fireplace were separated by a wall (3). (Reprinted from A. Attman, Jernkontoret, Stockholm. With permission.)

viscous and pasty. The smith held it in constant movement by hooks. He "puddled" the iron – thus the name.

With this new method a bar iron could be manufactured with a quality good enough for ordinary needs and to a price far lower than what had to be paid for Swedish or Russian iron. The breakthrough of the puddling process at the beginning of the 19th century led to a considerable decrease of Swedish exports. But for England and its industrial development it was of tremendous importance. To that it must be added that Cort also made a big change in the treatment of the wrought iron after the puddling. Instead of forging he finished the iron by passing it through grooved rollers. This became of very great importance, not only for England but also for the whole industrial world. Henry Cort was a brilliant engineer and inventor but not so successful as a businessman. In spite of his very big contributions to the development of his country's industry he had to live the last years of his life in poverty.

Puddling was a hearth process in which the chimney was not above the hearth but at the end of the furnace. The hearth itself was covered with an arched roof that reflected the heat. Because of this the process had a good fuel economy. A separate furnace was used to weld the iron pieces together before forging to bar iron. This idea was adopted by the Swedish iron industry but the technique was modified by using charcoal in order to keep the top quality of the produced iron. The method became known as the Lancashire process and was installed from about 1830 in several works in Central Sweden. The product was characterized by a very good evenness, so good that the final forming could be done by rolling. And the charcoal consumption was reduced to the half. Yet, the days were numbered also for this modern process. At the end of the century the Bessemer process and other ingot steel processes took over.

8.7
Metallurgy Becomes a Science

In our time it seems obvious to regard iron ore minerals as oxides, from which the metal is liberated when oxygen is removed. It is easily forgotten that there is a passage of time of 3000 years between the pioneer work of the Hittites and the discovery of oxygen by Scheele and Priestley. The discoveries made during this long period and the practical documentation were a part of the base that Lavoisier used when at the end of the 18th century he was able to explain the role of oxygen in oxidation and reduction. But even if the role of oxygen was understood, the role of carbon was obscure and the difference between cast iron, wrought iron and steel indistinct.

8.7.1
Early Opinions and Methods

Early in history, steel, unlike iron, was regarded as a material capable of being given a considerable hardness by quenching. In these days the main question was: *How can we make and handle this marvelous material steel*? and not: *What happens within the material when we change iron to steel or quench a red-hot sword or ax in water*? During the long technical development the science derived more from technology than did technology from science. From the 17th century some very detailed descriptions of steelmaking appear and also attempts at explanations, the latter naturally not all so easy to accept. In his book *De la Pirotechnia* [8.14], referred to by Smith [8.15] Biringuccio makes a good description of steel preparation: Into a bath of molten cast iron lumps of wrought iron are immersed. After four to six hours steel has been formed.

> When the masters observe this they make sure of it by testing, taking out one of the masses and bringing it under a forge hammer to beat it out, and then throwing it into the water while it is as hot as possible they harden it; and when it has been hardened it they break it and look to see whether every little part has changed its nature and become entirely free inside from every layer of iron.

Biringuccio summed this up by saying “steel is nothing other than iron, well purified by means of art and given a more perfect elemental mixture and quality by the great decoction of the fire”.

The first book devoted entirely to iron was *L’Art de convert le fer forgé en acier*…by R. A. F. de Réaumur, published in Paris in 1722. The author’s terminology was highly influenced by alchemy, which makes his explanations difficult to follow. Nevertheless, he clearly recognizes that steel is intermediate in nature between wrought iron and cast iron and could be made, starting with either.

The German chemist J. A. Cramer, a staunch phlogistonist, wrote in 1739 a book in Latin, *Elements of the art of assaying*, in which he tried to supply a framework of theory in connection with iron and steel. He regards steel to be nothing but pure iron impregnated with phlogiston.

In his important work *Dictionnaire de Chymie* P. J. Maquer wrote in 1776 that "steel is … impregnated with a larger quantity of the inflammable principle (phlogiston), and hardened by the temper."

The following simple diagram (Figure 8.17) characterizes the knowledge round about 1770.

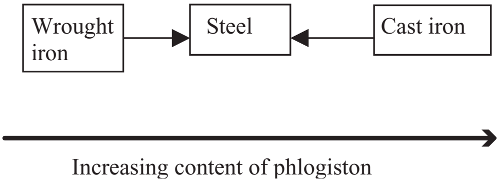

Figure 8.17 The knowledge of iron, cast iron and steel around 1770.

8.7.2
Carbon an Alloying Element?

It was a long time before the metallurgists became aware that steel and cast iron are alloys. And that is in fact not so remarkable. Carbon has two other easily observable functions in the iron manufacturing process. Firstly, it is the fuel for the furnace and creates temperatures high enough for the chemical and metallurgical reactions to occur. Secondly, it is – in modern terms – the reducing agent that takes care of the ore oxygen, so that the metal is set free. Carbon also had these two functions in relation to oxides of, for instance, copper, lead and tin. For just one of the metals – iron – carbon had a third function: the alloying element. This was difficult to grasp.

With the great excess of carbon present in the small furnace it was unlikely that the small amount absorbed by the iron should be seen as of importance. Aristotle and many of his successors even up to the Middle Ages looked on steel as a purer sort of iron. It had come nearer the typically metallic state. Cast iron had arrived at this state, yet it was brittle and non-formable. But it had the properties most typical of a metal: fusibility and castability. Even as late as 1783 Georges Louis Leclerc de Buffon (1707–1788) in France wrote that

> … steel should be regarded as iron, even more pure than the best iron; the one and the other are only the same metal in two different states, and steel is, so to say, an iron more metallic than simple iron; it is certainly denser, more magnetic, less dark in color, and of a finer and more compact structure.

De Buffon ought perhaps to have known better. He was both an ironmaster and a naturalist. He contributed very much to the strong position of French science from the middle of the 18th century. Together with L.Daubenton and B. G. E. de Lacépède he edited a monumental work in 44 volumes, *Histoire naturelle, générale et particulière*. In his treatment of steel it is clear that he heavily criticized the concept of phlogiston. In France, at the end of the 18th century, phlogiston was on the way out. But he seemed not to be able to imagine that carbon had something to do with the formation of steel.

8.7.3
Swedish 18th-Century Chemistry – Again

Sven Rinman (1720–1792) in Sweden lived at the same time as de Buffon. He, however, refused the guesses and speculations of his contemporaries. Instead he performed experiments, which were evaluated in the circle of active and famous scientists, Carl Wilhelm Scheele, Gottlieb Gahn and Torbern Bergman, with whom he shared a great interest in the chemistry of metallurgical processes and their theoretical conditions.

> At the age of eighteen he was attached to the *Bergskollegium*, The Royal Swedish Board for Mining and Metallurgy, and he devoted all his life to his country's industry. He also became an authority abroad. Many new Swedish establishments were designed and built up under the direction of Rinman. He was a practical man and active over the whole area, mining, metallurgy and manufacturing, from the drilling of cannons to the making of thimbles. He was both a clever experimentalist and a theorist. He summarized his own knowledge and that of his time in *Bergwerks Lexicon*, two volumes with beautiful and very instructive drawings (Figure 8.18).

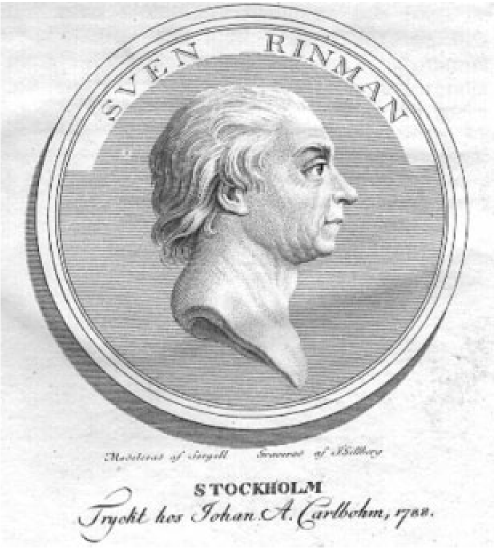

Figure 8.18 Engraving of Sven Rinman on the title page of his Bergwerks Lexicon 1788. Below the picture is written: Modeled by Sergell. Engraved by J. Gillberg.

In 1773 Rinman was given a somewhat peculiar assignment. A factory to make Damascus guns from forged interlaminated plates of iron and plates of steel was established (to compete with Turkish guns). The steel and iron components in these guns had different colors, beautiful and impressive. The question was put to Rinman:

How can we etch to get the same appearance on our new Swedish guns? Rinman studied the attack of nitric acid on iron, steel and (at the same time) gray cast iron. He observed clear differences and like his forerunners in Europe he considered phlogiston responsible for the differences. His experiments, however, gave the phenomenon an immediacy that it had previously lacked. What was called phlogiston suddenly became a tangible and separable material, especially in the case of extremely phlogisticated cast iron. He found that the attack of nitric acid left a black, insoluble sediment, small amounts in the experiments with steel and large amounts in the beakers with cast iron.

Rinman's practical experiments awakened Torbern Bergman's interest. He was professor of chemistry in Uppsala and had good laboratory resources. He was also a convinced phlogistonist and did not abandon this main idea. He verified Rinman's results that the nitric acid after reaction with cast iron contained a considerable insoluble residue. He preferred the designation *plumbago* for this residue and thought that this substance was the carrier of the high phlogiston content of cast iron. He carried out a serious scientific investigation, many hundreds of experiments with different iron alloys. Results and discussions were published in *Dissertatio chemica de analysi ferri*, 1781. A few results are collected in Table 8.2.

Table 8.2 Percentage composition of iron, steel and cast iron, according to Bergman

	Cast iron	Steel	Wrought iron
Silicon	1.0–3.4	0.3–0.9	0.05–0.3
Plumbago	1.0–3.3	0.2–0.8	0.05–0.2
Manganese	0.5–3.0	0.5–3.0	0.5–3.0

If "plumbago" is replaced by "carbon" a first quantitative analysis of iron and steel is presented. The work of Bergman was very much appreciated in his time and his descriptions of analytical methods were translated into French, German and English.

8.7.4
A Modern Version of Damascus Steel

The technique for manufacturing the steel that got the name *damask* has been used in our day for decorative purposes. Several layers, often seven layers, of different strip steels are welded together. Originally steel layers with low and high carbon content were combined. In modern applications one strip can be made of nickel, others of steel. In industrial applications stainless steels and tool steels are also used. The strip package is heated to a high temperature and forged to double its length. After reheating the bar is folded double so that the number of layers becomes fourteen. It is again forged to double the length. After repeated folding and forging the number of layers can be 28, 56, 112, etc. If the bar is now twisted and forged to a flat strip a very ingenious pattern can be created by etching. Sulfuric acid in different concentrations is especially suitable for the etching operation. For the blade of a knife the effect is best if the etching is made after hardening. The steel stripes then appear dark gray, the soft iron pale gray. Nickel is not attacked by the acid and appears light and shining, see Figure 8.19.

Figure 8.19 Blade of a knife made from a twisted bar of damask and etched. (Reprinted with permission from P. and M. Billgren, *Damasteel Handbook*, Söderfors, Sweden, 1998.)

8.7.5
Two Revolutions Take Over

C. S. Smith [8.15] says that history and geology had combined to give Sweden by far the strongest school of mineralogical chemistry in the 18th century. The phlogiston idea was, however, a hindrance. The Swedish chemists were wedded to it and at the end of the century the leadership was taken over by France. The chemical revolution of Lavoisier and his co-workers changed the basis for understanding oxidation and reduction processes. Phlogiston did not exist any more. But then – what about the phlogiston-rich *plumbago* in steel and cast iron? It was simply carbon, from now on accepted as an element. Cast iron was no longer rich in phlogiston, it was rich in carbon. This new way of looking at the matter was of enormous importance for the metallurgy of iron. Everything became so simple – but yet – not *so* simple. The question of *how* carbon actually exists in steel and in gray/white cast iron remained to be answered. And why should the soft carbon make the iron harder? And what happens within the material when a red-hot sword gets very hard when quenched in water – if carbon is present? All this was not cleared up until the metal microscope was developed in the 19th century and revealed the structural components in iron and steel.

A paper presented to the French Academy of Sciences in May 1786, *Mémoire sur le fer considéré dans ce difference états métallique, (On the different metallic states of iron)* became a landmark in metallurgical literature. C. A. Vandermonde, C. L. Berthollet and G. Monge wrote it. The French scientists used their dephlogisticated theory to explain processes and observations in connection with iron, steel and cast iron. In the introduction they say, with reference to Bergman and other writers, that the variations of the properties of iron come only from foreign substances alloyed with the iron. The degree of difficulty of the field was demonstrated by a remarkable initial mistake in the description of cast iron: “The quantity of carbon in white cast iron is less than in steel." This mistake was soon corrected. They saw that the solubility of carbon in cast iron changes with temperature. During slow cooling the dissolved carbon will form "plumbago" but quick cooling will "surprise" the graphite before it separates so it stays scattered and dispersed in the metal. In fact white cast iron contains just as much carbon as gray. It is, however, not present as graphite but as cementite, Fe_3C. Regarding steel, they found that conversion of iron into steel by cementation resulted in an increase in weight. After different investigations they concluded that steel is a completely reduced iron combined with a certain amount of carbon. Commercial soft iron, wrought iron, also always has a certain carbon content, although sometimes it is very low. It also contains some oxygen. When the carbon content is increased by cementation, this oxygen reacts to carbon monoxide that bubbles away.

These discoveries were made in a time of revolutions, one scientific and one political. The report from Vandermonde *et al.* was edited in 1786, the Bastille was stormed in 1789, the French king was executed in 1793 and Lavoisier guillotined in 1794.

All three authors of the famous paper were distinguished scientists. Vandermonde, best known as a mathematician, became interested in steel, as from 1782 he was director of the *Conservatoire pour les Arts et Métiers*. Berthollet made many contributions to industrial chemistry but is best known for his powerful fight against the phlogiston theory. Monge had synthesized water from its elements independently of Cavendish and Priestley. Berthollet and Monge became important public figures in the Revolutionary and Napoleonic periods. They followed Bonaparte on the Egyptian campaign and were among his favorites.

The Academy paper on iron was rewritten in a shorter, more popular version and published in a large edition by the Committee of Public Safety in the War Department.

8.7.6
Modern Metallurgy – A Diversified Science

The great achievements of Swedish and French scientists during the 18th century constituted the basis for the exceptional development of technical iron metallurgy during the 19th and 20th centuries. According to the new knowledge, the product from the blast furnace, cast iron, was an iron with 3–4% carbon. This fact made it possible for Henry Bessemer in England to invent a new technique for transforming cast iron to wrought iron. He saw that there is something wrong with the old method of removing this carbon: *To deforest the landscape and produce charcoal to heat the cast iron/pig iron up to such a high temperature that the air blast could remove – the carbon.* His own idea was brilliant and simple. Just blow air through the molten cast iron. The carbon should react with oxygen and go away as carbon monoxide. And the energy needed for the process? No additional energy should be necessary. The oxidation of the carbon in the cast iron should give energy enough to increase the temperature so that the carbon-free iron formed would be kept molten in spite of its high melting point. If possible and true, this indeed might be designated as another scientific and technical revolution. The method was protected by patent and the inventiveness was considerable. Many experienced metallurgists, however, shook their heads at such madness. And they seemed to be right. In practice many obstacles arose. A Swedish industrialist, G. F. Göransson, however, bought the patent and started production of Bessemer steel in 1862. This became the basis for Sandvik Inc., today a steel supplier with employees all over the world. When this technique had been developed, as shown in Figure 8.20, steel production could increase considerably. This process came at the right time and made possible the expansion of the railroad network in the world. Today the Bessemer process is obsolete. The principle of the transformation of cast iron into steel in converter processes is, however, still used, but the air blast is exchanged for a stream of pure oxygen.

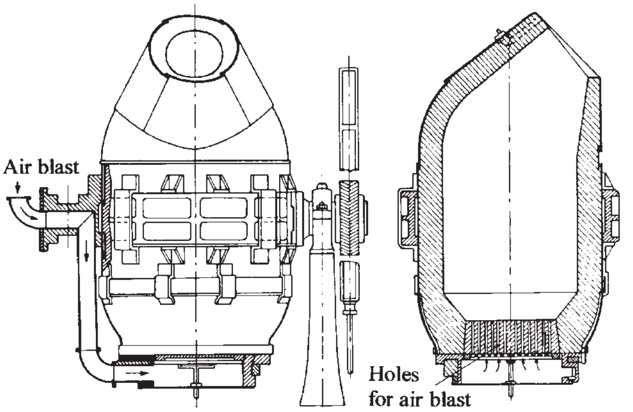

Figure 8.20 A Bessemer converter.

The new steel age required new control methods and equipment. Chemical analysis proved to be immensely helpful in controlling the smelting and refining, and new methods were developed. Spectral analysis was developed and adapted to the need for rapid process control. In 1865, H. C. Sorby in England began to use a microscope to study metals. In polished and etched samples the internal steel structure was revealed and *metallography* was developed to a science within metallurgy. With this equipment and this investigation technique it became possible to give an answer to the question: *How is carbon present in steel*? It is there not as elemental carbon but as iron carbide, *cementite*, Fe_3C.

Metallurgical research in the new centuries, the 19th and 20th, did not principally attract interest from and work by "pure" chemists and physicists. Metallurgy built up its own research and education and published its own scientific journals. The metallurgical literature became extensive.

Organizations were formed in different countries on the pattern of Jernkontoret in Stockholm, which, among other duties, had to support technical and scientific research and development.

During the 20th century a rapprochement occurred between metallurgy/metallography and the "pure" sciences physics and chemistry. It became possible to study the atomic arrangement in metals and alloys by X-ray diffractometry. Dislocation theory, developed in solid-state physics, has been of extraordinary importance for understanding the plastic forming of metals and alloys.

Chemical thermodynamics within metallurgical chemistry was applied to and even stimulated by the empirical knowledge of reactions in complicated systems at high temperatures. It resulted in several advanced metallurgical techniques, utilizing oxygen instead of air for carbon removal.

8.8
Iron Ores

Figure 8.21 is an outline of the Kirunavaara iron ore in northern Sweden. The ore consists of magnetite and is made up of a plate, sharply inclining eastwards, having a length of about 6 km and a width varying between 20 and 200 m. The ore is known down to a depth of 1500 m and the ore quantity exceeds 1800 millions tonnes. Yearly 18 millions tonnes are mined, which makes Kirunavaara one of the biggest underground mines in the world.

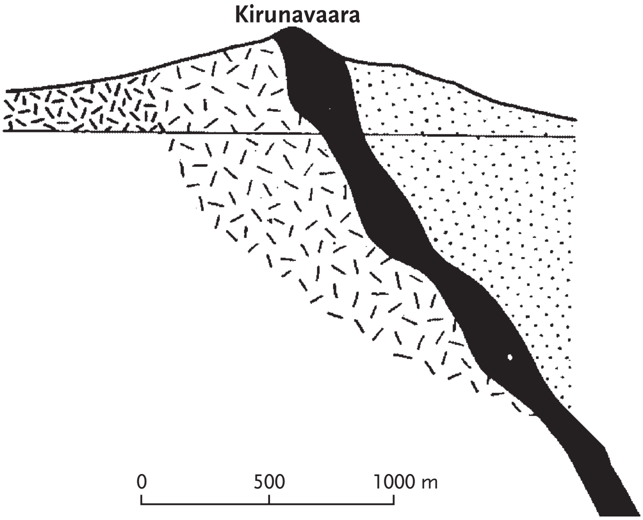

Figure 8. 21 The iron ore deposit in Kirunavaara.

8.8.1
Minerals

The two dominating minerals in iron ores are hematite (Figure M10) and magnetite (Figure M9). Siderite (Figure M11), goethite and limonite are other, less common, iron minerals. Formulas, properties and comments on their occurrence in iron ores are given in Table 8.3.

Table 8.3 Minerals in iron ores

Mineral name	Formula	Appearance		Fe-content in the pure mineral %	Occurrence
		Color	Luster		
Hematite. Bloodstone	Fe_2O_3	Steel gray to black. Brick-red as powder	Metallic	69,9	The principal ore of iron in the world, e.g. in the big deposits at Lake Superior in the USA
Magnetite Magnetic iron ore	Fe_30_4 $FeO·Fe_2O_3$ A spinel	Black	Metallic to dull	72,4	An important ore of iron, e.g. in the big deposit at Kiruna in the far north of Sweden
Taconite	–	Variously tinted jaspery rock	–	> 25	A low-grade iron formation, containing magnetite, hematite, siderite, hydrous iron silicates, suitable for concentration and manufacturing of pellets with 62–65% Fe
Siderite. Chalybite	$FeCO_3$	Gray, yellow, brown	Vitreous, pearly, silky	48,2	Important mineral in sedimentary iron ores all over the world. In Europe for instance in Erzberg, Austria and Bilbao, Spain
Goethite	FeO(OH)	Reddish, brownish-black	Earthy. Crystals metallic	62,8	Goethite is a constituent of natural rust and also of limonite. Occurs as a weathering product in the gossans of sulfide-bearing ore deposits. The mineral type dominates in the minette ores as in Alsace-Lorraine in France
Limonite	Several iron hydroxides, including goethite	Yellowish brown	Earthy to dull	–	A secondary mineral formed by weathering of iron-bearing minerals. Also formed as a precipitate in bogs or lakes

8.8.2
Iron Ore Resources and Production

Reserves and the reserve base for iron ore are collected in Table 8.4.

Table 8.4 Reserves and reserve base for iron ore

Country	Iron ore, million tonnes		Iron content, million tonnes	
	Reserves	**Reserve base**	**Reserves**	**Reserve base**
China	25 000	50 000	7 800	15 000
Brazil	7 600	19 000	4 800	12 000
Australia	18 000	40 000	11 000	25 000
Russia	25 000	56 000	14 000	31 000
India	2 800	6 200	1 800	3 900
United States	6 900	15 000	2 100	4 600
Ukraine	22 000	50 000	12 000	28 000
Canada	1 700	3 900	1 100	2 500
South Africa	1 000	2 300	650	1 500
Sweden	3 500	7 800	2 200	5 000
Kazakhstan	8 300	19 000	4 500	10 000
Mauritania	700	1 500	400	1 000
Other countries	17 000	38 000	10 000	23 000
World total	140 000	310 000	72 000	160 000

Data from ref. [8.16].

Annual iron ore production figures for the year 2000 are shown in Table 8.5.

Table 8.5 World mine production of iron ore in the year 2000

Country	Mine production million tonnes	Country	Mine production million tonnes
China	224	Canada	35
Brazil	195	South Africa	34
Australia	168	Sweden	21
Russia	87	Kazakhstan	16
India	75	Mauritania	12
United States	63	Other countries	77
Ukraine	56		
		World total	1 060

Data from ref. [8.16].

8.9
Modern Manufacture of Steel

8.9.1
Two Production Methods – From Iron Ore and Iron Scrap

Modern steel-making is characterized by two different material flows. In one of them raw iron (pig iron) is made from iron ore and then used to manufacture raw steel. In the other technique raw steel is made by melting scrap. As a matter of fact, steel scrap is an important raw material for steel-making. Utilizing scrap is also an important component in modern environmental thinking and in the efforts currently being made to re-use industrial products, see Figure 8.22.

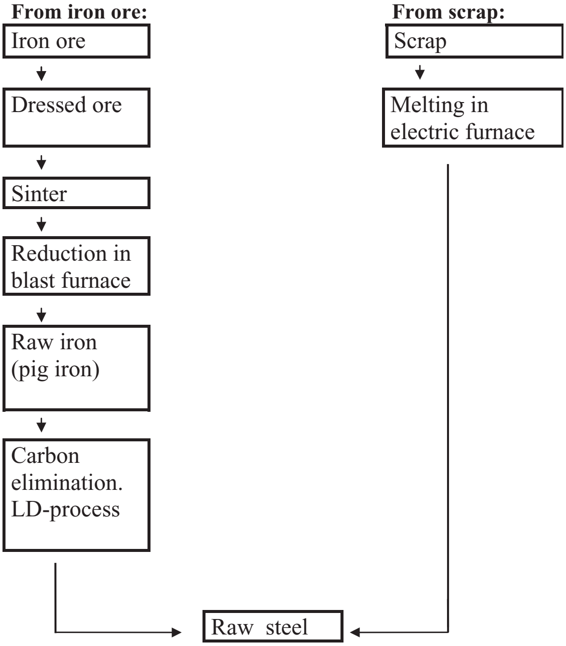

Figure 8.22 Two ways of making raw steel.

Raw steel is refined by ladle processes to final steel, which is then cast by continuous casting into work pieces for final steel production by rolling or forging (billets, blooms and slabs).

8.9.2
Ore-Based Steel Production

The concentrated (dressed) iron ore is formed into sintered pellets at the mine, which are then reduced to iron in a blast furnace by carbon (coke). A modern integrated steel production process based on ore is shown in Figure 8.23.

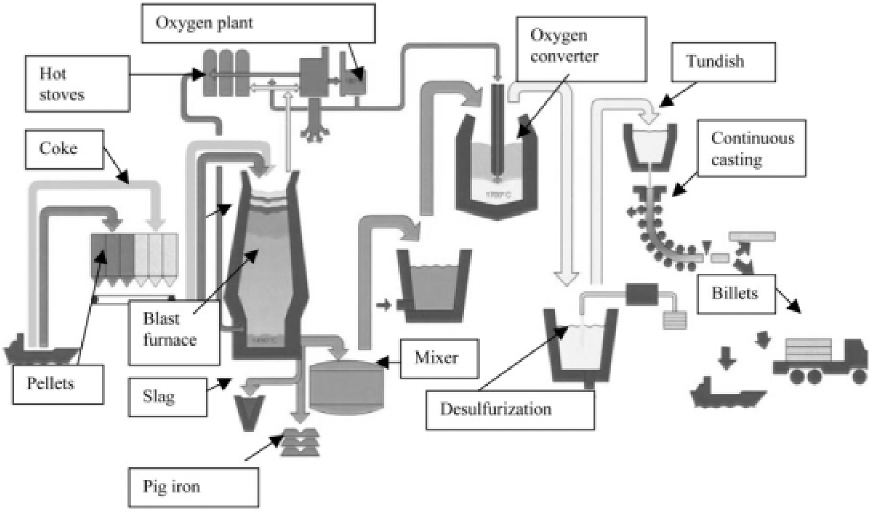

Figure 8.23 An integrated steel production process based on ore. (Reprinted with permission of Fundia Wire Oy AB Dalsbruk Finland.)

The raw iron produced in the blast furnace is not cooled to solidifying but processed further in decarburization processes, nowadays not using air but with oxygen in a converter. That is shown in the figure. In exceptional cases “pigs” of solidified iron may be produced.

8.9.3
Raw Steel from Scrap

Electric steel furnaces are “melting machines” for the production of raw steel from scrap (Figure 8.24). The raw steel produced in this way can be directly used for some purposes but is, as a rule, refined to give steels of a higher quality.

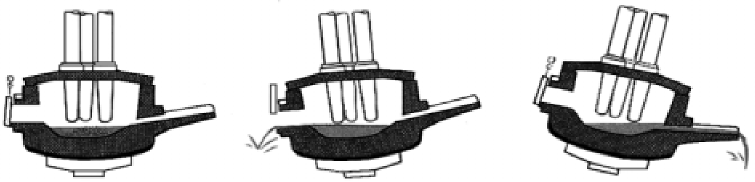

Figure 8.24 Electric furnace for the production of raw steel from scrap. (Reprinted from the booklet *Steel* with permission from Employers Association of the Swedish Steel and Metal Industry, Stockholm.)

8.9.4
Refining of Steel

8.9.4.1 Deoxidation

Oxygen is highly soluble in molten steel. However, in solid steel the solubility is almost zero. Thus, at solidification, the oxygen combines with carbon to form a carbon oxide that is released. A small part of the gas remains in the steel as blowholes. In traditional steel-making the molten steel is then cast into ingots in moulds, see Figure 8.25.

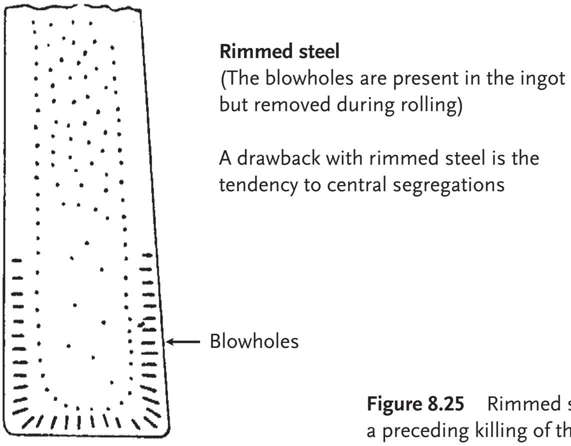

Figure 8.25 Rimmed steel ingot, cast without a preceding killing of the steel.

Blowholes are prevented from forming if the oxygen is removed before solidification in a process known as *deoxidation*. Silicon (as ferrosilicon) or aluminum is added and the steel is said to be *killed* as shown in Figure 8.26.

$$Si + 2O \rightarrow SiO_2 \qquad 2Al + 3O \rightarrow Al_2O_3$$

The oxides formed during the killing leave the steel melt and rise into the slag. Some oxide particles, however, remain in the solid steel as slag inclusions.

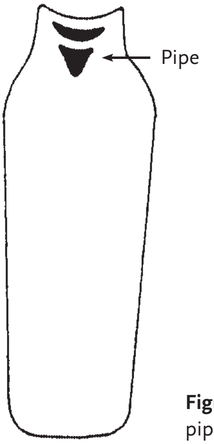

Figure 8.26 Steel ingot without blowholes but with pipe, cast after killing of the steel.

Rimmed steel products are rarely available nowadays. Because of the tendency to form central segregations (concentration differencies) in this type of ingot, and due to the dominance of continuous casting, killed steel is used instead.

8.9.4.2 **Injection Metallurgy**

Originally injection metallurgy was used to remove sulfur. Nowadays, however, this technique is also used for deoxidation and slag modification. Argon is used as a carrier gas to transport the powder into the melt and the powder, e.g. aluminum or ferrosilicon, is so fine that it is fluidized in the gas stream, see Figure 8.27.

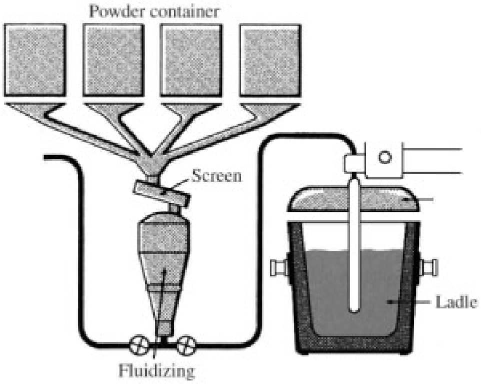

Figure 8.27 Injection metallurgy for deoxidation and slag modification. (Reprinted from the booklet *Steel* with permission from Employers Association of the Swedish Steel and Metal Industry, Stockholm.)

8.9.4.3 **Vacuum Treatment**

Vacuum treatment according to Figure 8.28 reduces the content of contaminants, nitrogen, oxygen and hydrogen. This gives the steel better fatigue properties.

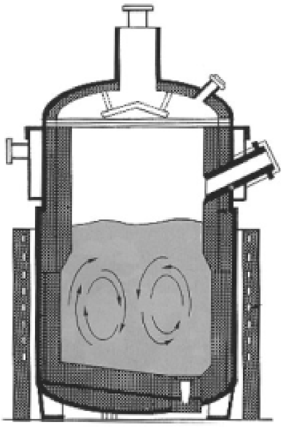

Figure 8.28 Vacuum treatment of molten steel. (Reprinted from the booklet *Steel* with permission from Employers Association of the Swedish Steel and Metal Industry, Stockholm.)

8.9.5
Production of Stainless Steel

Stainless steels are manufactured in two steps. Firstly, stainless scrap is melted in an electric furnace and, secondly, adding oxygen and argon in an *A*rgon-*O*xygen-*D*ecarburization (AOD) converter reduces the carbon content of the melt. An alternative process is the *C*reusot-*L*oire and *U*ddeholm (CLU) process, which was developed by the French company Creusot-Loire in conjunction with the Swedish firm Uddeholm. In this latter process, a mixture of oxygen and water vapor is added to the converter. Once in contact with the molten steel, the water vapor is decomposed into hydrogen and oxygen in order to treat the steel with oxygen. The hydrogen acts as an “inert” gas. The process ends with a short argon blow to remove the hydrogen. The final treatment for deoxidation and slag modification is shown in Figure 8.27.

8.9.6
Techniques in Modern Steel Manufacture – A Summary

An attempt to visualize modern steel manufacture “the ore way” is shown in Figure 8.29. The manufacturing process is in the highest degree a living technique in progress and development.

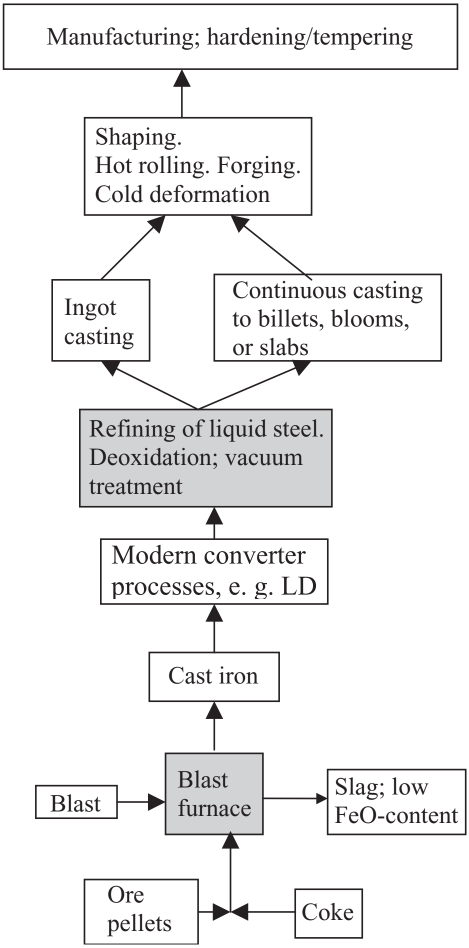

Figure 8.29 The principle of modern steel manufacture.

8.10
Steel for Many Purposes

The product family is very diversified and plays a crucial role in modern human life: from the load-bearing functions in large steel buildings and bridges to the small springs in precision mechanics; from material in cannons and tanks to peaceful tools in agriculture; from stainless steels for the corrosive environments in offshore equipment to stainless steels for implants in the likewise corrosive milieu in the human body; from special steels for the surgeon's scalpels to all-steel components in household and kitchen. A comprehensive list cannot be given but some general comments will be made:

General constructional steels that will be welded are used for machinery and buildings, e.g. houses, cranes, ships and equipment in the manufacturing industry. Good weldability is obtained by a low carbon content (0.2% maximum) and often an enhanced manganese content (1.5%). Steel for car bodies and sheets for refrigerators and so on has a very low carbon content. The formability is good but the strength low. The new so-called *dual phase steels* (DP) with higher tensile strength but retained formability are important in the automotive industry. The body sheet steel can be made thinner and the car lighter, resulting in decreased petrol consumption.

The carbon content of *machine steels* is increased to 0.35–0.45%. Addition of sulfur (0.2%) gives so called *free cutting steels* with very good qualities for drilling, turning and milling.

Heat treatment steels, intended for hardening and induction hardening, are usually alloyed with chromium, nickel and molybdenum, which improve the deep hardening.

Spring steels are made with high carbon content, 0.6–0.8%. The spring hardness is created by hardening and tempering or by cold deformation. Spring steels are also used in strings for guitars and pianos.

For metal cutting, *tool steels,* which require hardness, edge sharpness and wear resistance, are used. Tool steels in general have a high carbon content (0.5–1%) and are alloyed with chromium (e.g. 5%), molybdenum (e.g. 1.5%), and vanadium (e.g. 1%). The hard carbides formed within the steel create the wear resistance. High-speed steels are special highly alloyed tool steels. It is characteristic of these steels that they keep their hardness and edge sharpness up to a temperature of 600°C. These steels will be treated in Chapter 26 Tungsten.

Stainless steels are described in connection with the element chromium in Chapter 24.

8.11
Large Volumes of Steel in a Modern Society

Some years after Word War II, the USA, the Soviet Union and Western Europe accounted for 90% of the world steel production. In 1981, the total for these three regions had decreased to 50%. Asian countries had become big producers. During the period 1990–93, Japan was the biggest steel producer in the world and China was third. In the year 2000 China and Japan were second and third, after the European Union as shown in Table 8.6.

The iron country of Sweden, which in the 18th century (along with Russia) was the leading exporter of iron, is nowadays not an important country in relation to the total quantity of steel produced. Sweden has, however, kept its position as a significant manufacturer of special steels. Important Swedish products are tool steels, especially high-speed steels, and stainless steels. Highly alloyed types of the latter have been developed for very severe, corrosive situations as in offshore applications.

Table 8.6 World steel production in the year 2000

Country/Region	Raw steel production, million tonnes
European Union	158
China	127
Japan	106
United States	102
Russia	59
Korea, Republic of	43
Ukraine	32
Brazil	28
Other countries	190
World total	845

Data from ref. [8.16].

8.12
Iron at the Center of Life – A Positive Biological Role for a Heavy Metal

Iron has been described as the metal of war. Nature has, however, used this element also for life. The different oxidation states of iron atoms and their disposition to co-ordinate both oxygen, nitrogen and sulfur atoms constitute the background. The presence of iron in all forms of life, even primitive ones, shows that iron must have been present very early in the development of life. In fact iron is an essential element for almost all organisms.

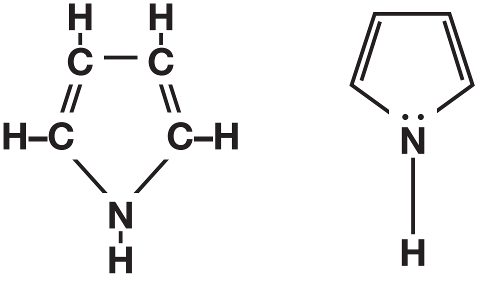

Figure 8.30 Pyrrole.

Organisms bind iron into organic molecules suitable for the vital functions. One molecule that iron cooperates with is the heterocyclic compound pyrrole, Figure 8.30.

The most important pyrrole derivatives are macrocyclic rings with four pyrrole molecules, known as *porphyrins*. There are numerous groups, such as methyl, vinyl or acetic acid, attached to the peripheral carbon atoms. In the center – between the four nitrogen atoms – a vacant space arises, which an iron atom can occupy, bonded to all four nitrogen atoms. This is an example of *chelation*. The complex formed is called a *chelate* (from the Greek *chele*, meaning "crab's claw"). Chelates are important in nature and include, for instance, *hemoglobin* with iron and *chlorophyll* with magnesium.

It is iron-*porphyrin,* with the name heme (after Greek haima, blood), which actually binds oxygen, see Figure 8.31. It may be said that iron in the heme-group can alternate between Fe^{2+} and Fe^{3+} and thus give an oxygen-binding and an oxygen-releasing effect. The situation is, however, more complicated. The porphyrin traps the iron so that there is no equilibrium with free iron. The metal does not dissociate from heme and is almost a new element, distinct from iron. The heme as a whole endows the proteins, in which it is a constituent, with the ability to transport and store oxygen.

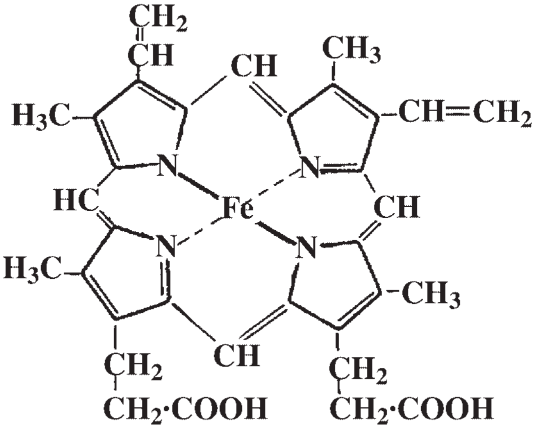

Figure 8.31 Iron-porphyrin, heme, the functional part of myoglobin, hemoglobin, cytochrome, etc.

Myoglobin contains a heme group that binds oxygen in muscle cells. The amount of myoglobin in an animal muscle varies and influences the color of the meat. Beef has a high content of myoglobin (0.50%) and is dark red, while pork, with 0.06% myoglobin, is paler.

Cytochromes are other proteins that are red owing to their content of heme. They take part in oxidation reactions and in electron transfer and are included in the respiratory structures of mitochondria, the "power stations" of the cells.

Best known and perhaps most important is *hemoglobin*. It is present in large amounts in red blood cells and give the red color to blood. The hemoglobin molecule has developed according to the different needs of nature. The hemoglobin in animals living in thin air, e.g. the llamas in the Andes, has an especially high capacity for oxygen uptake.

In human blood the hemoglobin content is normally 135–160 g/l (men) and 115–140 g/l (women). Newborn children have a considerably higher content, 150–250 g/l, during the first day of life.

The efficiency of an athlete is increased if the ability to absorb oxygen increases. Blood transfusion in order to increase the body's transport capacity for oxygen is among the forbidden doping methods. *Erythropoietin,* a peptide hormone that stimulates the formation of red blood cells and thus has the same effect as blood transfusion, is also forbidden.

An adult man has in his body ca. 4 g iron, dispersed with 3 g in hemoglobin, 0.15 g in myoglobin and the rest in different iron deposits. Iron is brought into the body through the diet. Bread and meat are important iron-rich foodstuffs.

Iron enrichment of food is becoming more and more usual. To sifted flour 65 mg iron per kg meal is added. The enrichment material may be *ferrum reductum,* a fine dispersed, porous, metallic iron. A different type of bonded iron, which is more easily absorbed by the body, is also used.

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9
Hydrogen

9.1 H
Facts about Hydrogen

9.1.1 H
The Element

Symbol:	H
Atomic number:	1
Atomic weight:	1.008
Ground state electron configuration:	$1s^1$
Crystal structure:	Solid hydrogen is hexagonal hcp with $a = 3.76$ Å, $c = 6.13$ Å

9.1.2 H
Discovery and Occurrence

Discovery: Henry Cavendish identified hydrogen as an element in 1766, but he considered the new element to be *phlogiston*. He also discovered that water is formed when hydrogen and oxygen are combined. Thus, water is not an element, as was previously believed. In 1783, Lavoisier gave the name *hydrogène*, water former, to the inflammable gas.

Most important raw materials: Natural gas and oil are the dominant raw materials. Electrolytic decomposition of water is an alternative.

Ranking in order of abundance in earth crust:	10
Mean content in earth crust:	1400 ppm (g/tonne)
Mean content in oceans:	10.8%
Residence time in oceans:	–
Mean content in an adult human body:	10%
Content in a man’s body (weight 70 kg):	7 kg

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9.1.3 H
Chemical Characterization

Hydrogen is a diatomic gas but dissociates into free atoms at high temperatures. Liquid hydrogen is colorless. When evaporated rapidly it freezes into a colorless solid with a crystal structure similar to metals. Free hydrogen is abundant in the sun and other stars and makes up about 90% of the universe by weight. On earth free hydrogen is rare but in combination with other elements it is widely distributed. It is an essential part of all hydrocarbons and a vast variety of other organic substances. The most important and abundant compound of hydrogen is water, H_2O. It is a component of all living matter as well as of many minerals. Acids (mineral acids and organic acids) form hydrogen ions in water solutions. The concentration of hydrogen ions in a water solution is expressed by its pH value. Three isotopes of hydrogen exist: the predominant ^1H, ^2H *deuterium*, and ^3H *tritium*. The latter is an unstable, radioactive isotope.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
H^I as in H_2O, HCl	$H(g) \rightarrow H^+(g) + e^-$	1312	$H(g) + e^- \rightarrow H^-(g)$
H^{-I}, ionic as in LiH			−72.8
and covalent as in CH_4			

In addition: Hydrogen bonds, responsible for the unique and extremely important properties of water.

Standard reduction potential: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^0 = 0$ V

Electronegativity (Pauling): 2.20

Radii of atoms and ions: (WebElements™)		
	Covalent:	37 pm
	Ionic:	–

9.1.4 H

Physical Properties

Density (at 273 K)	**Relative density (air = 1)**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
0.0899 kg m^{-3} 0.090 g/l	0.069	13.81 K –259.34 °C	20.28 K –252.87 °C	$14.3 \cdot 10^3$ J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

73 K	**173 K**	**273 K**	**373 K**	**1273 K**
0.0509	0.1124	0.1682	0.2118	–

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K)

a	**b**	**c**
27.28	$3.26 \cdot 10^{-3}$	$-0.50 \cdot 10^5$

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.407 (277–290 K)

Solubility in water m^3 gas at STP per m^3 water

273 K	**293 K**	**313 K**	**333 K**	**353 K**	**373 K**
0.0214	0.0178	0.0153	0.0125	0.0085	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-25.0 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	diamagnetic (as susceptibility is negative)
Critical point:	T_c 33.2 K P_c 1.297 MPa

9.1.5 H

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	0.117 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	0.916 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	216 $kJmol^{-1}$
Entropy ΔS^0 at 298 K	130.6 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	28.16	28.82	29.33	30.20	34.28	35.84

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2H_2 + O_2 \rightarrow 2H_2O(g)$	–457	–438	–385	–328	–269

9.1.6 H

Nuclear Properties and X-ray

Isotope range, natural and artificial	1–3

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^1H	Stable	99.985	+1/2	2.7928	–	–	–
^2H	Stable	0.015	+1	0.8574	–	–	–
^3H	Active	0.000	+1/2	2.9790	12.33 y	β^-	0.0186 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^1H	^2H	^3H
Reference compound	$Si(CH_3)_4/C_6D_6$ for ^1H, $Si(C^2H_3)_4$ for ^2H, and $Si(C^3H_3)_4/C_6D_6$ for ^3H		
Frequency MHz (^1H = 100 MHz)	100.000	15.351	106.664
Receptivity D^P relative to ^1H = 1.00	1.000	$1.45 \cdot 10^{-6}$	–
Receptivity D^C relative to ^{13}C = 1.00	5710	$8.27 \cdot 10^{-3}$	–
Magnetogyric ratio, $radT^{-1}s^{-1}$	$26.752 \cdot 10^7$	$4.1066 \cdot 10^7$	$28.535 \cdot 10^7$
Nuclear quadropole moment, barn	–	$2.86 \cdot 10^{-3}$	–

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV	X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
–	–	–	**8.028 keV ($CuK\alpha_2$)**	0.391

Neutron absorption	Thermal neutron capture cross section	0.332 barns

9.2
Discovery

9.2.1
The Combustible Gas in Mars!

"The combustible gas in Mars" was an expression that Robert Boyle used in 1671. The symbol for the planet Mars was also was the symbol for the metal iron. Obviously the word Mars was used as a synonym for the metal. Boyle had observed that when he dissolved iron in hydrochloric acid or sulfuric acid an inflammable gas was produced. But it had to be pure iron! Not the metal that could be bought in the pharmacy – that was too rusty. Instead he used filings of iron. Reacting with these, the acid developed a gas, smelling unpleasantly of sulfur. Could it be a smell from sulfur in the iron? When a flame was placed at the orifice of the tube through which the gas streamed out, the gas ignited and burned with a blue flame, giving very little light. Boyle's results became well known as he described his experiments in a booklet: *New experiments touching the relation between flame and air.*

At the beginning of the 17th century, Paracelsus in Basel and J. B. van Helmont in Flanders had both noticed gas bubbles on iron in contact with sulfuric acid but they did not continue their investigations. In this connection van Helmont, however, began to use the term "gases", thus abandoning the earlier designation "elastic fluids".

9.2.2
Lomonosov – The Founder of Russian Science

> *Mikhail Vasilyevich Lomonosov* was born in 1711 in the small town of Denisovka, near Archangel in Siberia. His home town now bears his name, *Lomonosov*. He studied in St Petersburg and in Germany, in Marburg and Freiberg. In 1745 he applied for a professorship of chemistry at the University of St Petersburg. For qualifying he presented a work, *De tincturis metallorum* (*On the Luster of Metals)* in which he argued that the luster and ductility of metals depend on their content of phlogiston. He also claimed – as one of the very first – that he could prepare the mysterious substance: *When iron is dissolved in acid a combustible gas is evolved that is nothing but phlogiston*. Like Cavendish, he identified the unknown hydrogen with phlogiston – but he did it qualitatively while Cavendish, in fact, "weighed phlogiston". With this

> background it is interesting to note that Lomonosov was one of the first to discard the phlogiston theory.

In his scientific works after 1750 he gives a remarkably modern impression. In fact before the discovery of oxygen he made clear – by weighing experiments – that some component of air combines with metals in combustion. This is recounted in Chapter 47 Oxygen of this book. He regarded heat as a sort of movement, suggested a wave theory for light and formulated a law about the indestructibility of matter.

Mikhail Vasilyevich was a versatile and talented man. During the 1750s he became a scientist of good international repute and became known as the founder of Russian science. He took an active part in the foundation of the university in Moscow in 1755, which today is named after him: *The Lomonosov Moscow State University*. In 1760 he was the first Russian to be elected as a member of the Royal Swedish Academy of Science. The well-known chemist Georg Brandt was Academy President at this time and could welcome his Russian colleague.

9.2.3
Henry Cavendish

9.2.3.1 "... most learned among the rich and richest among the learned"

The substance water has a unique position in science and in human life. *Henry Cavendish* revealed that water is not an element but a compound of hydrogen and oxygen.

> In science we meet many odd persons with special characters. It is no exaggeration to say that Henry Cavendish was one of the most striking. He was born in 1731 in Nice in France, the place in which his mother stayed for the sake of her health. But his mother died when Henry was only two years of age. He had to grow up without a mother's care and perhaps this was responsible for his development into a shy and morbidly unsociable person, an eccentric. To him all men were strangers and women were so in the highest degree. Henry had been born into a highly aristocratic family, raised to the nobility in 1366. Between the ages of 18 and 22 he studied at Cambridge but left the university some days too early and did not obtain a degree. Instead he started intensive experimental work in chemistry and physics. When his father died, Henry, who was then 52, inherited a very large property. Shortly afterwards an aunt passed away and she also left a fortune to her nephew. Henry Cavendish was now one of the richest men in England. But he did not use his large income from interest for a life of luxury. Far from it! He lived a spartan life and always wore the same old-fashioned clothes. By his contemporaries he was considered to be a real character. He was laughed at, but that he endured, so long as he was able to work within the disciplines of science that– in his own way – he had displayed a keen interest in. In one respect his wealth, however, was noticeable. He had three big houses in London. One – near the British Museum – was filled with equipment for experiments and books; the second – in Soho – was a library, open to all who needed it. The third – *Cavendish House* – was situated in the suburb of Clapham. It was his

home but had almost entirely been arranged as a laboratory. In this house he worked, very much alone, and there his days also ended – in loneliness. When one day he felt he was at death's door he called his manservant and instructed him to leave the room and return at a given moment. He did so and found his master dead. Henry Cavendish passed away in 1810, at the age of 79.

The Cavendish family saw in young Henry a coming leader in the political or economic life of the country. These expectations were not fulfilled. Had he not made important contributions to the knowledge of the chemistry of water, the composition of air and the weight of the earth, he would have remained unknown to posterity. In the family chronicles he might have been remembered for his eccentricity and his lack of leadership.

With Joseph Priestley, the discoverer of oxygen (sharing priority with Carl Wilhelm Scheele), Cavendish had a certain contact. Yet they were so unlike! Cavendish, aristocrat, recluse, stranger to all, without any interest in social life, even less in religion and the church. Priestley, a man of the common people, a believer, pastor and preacher in the Free Church, leader in the liberal currents of his time. On just one front they fought together: the chemistry and physics of gases. Cavendish's contributions will be described here, Priestley's in Chapter 47 Oxygen.

9.2.3.2 **Hunting for Phlogiston**

Henry Cavendish was energetically interested in science from an early age. One of the big mysteries at this time was *phlogiston*, a phenomenon difficult to get hold of and, in fact, only a word. At university institutions and in private laboratories in Europe and America evidence of its existence was sought – this mysterious substance, which was set free on the combustion of matter. Metals were said to be rich in phlogiston. When Priestley in 1772 was awarded a medal for a method to manufacture synthetic mineral water, the president of the Royal Society said:

> I will indeed request you to continue these valuable investigations. But you must remember the fire, this important tool, of which not even the chemists have a particularly good knowledge. A questions remains whether it is a special fluid that is the cause of this phenomenon.

Fire and the nature of combustion were the largest separate problem within chemistry. The phlogiston theory would not be able to give an answer until somebody could catch phlogiston in their test tube and examine its properties. In his private laboratory in Clapham, Cavendish started his investigations. He introduced acid and metal filings into a bottle and the bottle was rapidly closed by a cork, provided with a glass tube. The tube was connected to an empty urinary bladder. Bubbles of a colorless gas evolved on the metal, left the flask and started to fill the bladder. When filled it was shut tight. Six experiments were made in 1766. In the first three sulfuric acid was used and the three metals zinc, iron and tin. Experiments 4–6 were made with hydrochloric acid and the same three metals. Cavendish now had six bladders filled with gas. Each one was opened and the gas was ignited by a candle-flame. All six samples showed the same behavior, burning with a faint blue color.

Could it be that all the metal samples had emitted their phlogiston in the acid treatment? Had he caught phlogiston in the urinary bladders? Cavendish knew his chemistry from the University of Cambridge. It was a well-established fact and a linchpin in chemical science. At the beginning of his investigations Cavendish also was convinced that the gas came from the metal and not from the acid.

He repeated the experiments but dried the gas samples before they were introduced into the bladders. He also weighed the bladders empty and filled. In every case he noted a weight increase, although very small. This gave reason for reflection. Had he weighed phlogiston? Now, at the age of 35, he published the results in *Transactions of the Royal Society* in a paper with the title *Factitious Airs*. Priestley in Birmingham reported these results to the *Lunar Society* (see p. 000)and they were received with enthusiasm. One of the members of the society remarked [9.1] that "we have long talked of phlogiston without knowing what we talked about, but now that Dr. Priestley brought the matter to light we can pour that element out of one vessel into another. This Goddess of levity can be measured and weighed like other matter".

9.2.3.3 **No – It Was Not Phlogiston**

The matter Cavendish had collected in his bladders was not phlogiston but hydrogen, and this was not the first time that the gas had been observed. Paracelsus, van Helmont, Boyle and Lomonosov all did it earlier. The systematic investigation of 1766, the very first attempt at quantification, and the subsequent careful experiments over two decades, placed Cavendish in a unique position and became the reason for giving Cavendish the priority in the discovery of hydrogen. The element name *hydrogen, the generator of water* is also connected with another of Cavendish's very important discoveries: *Water is not an element. It may be synthesized by the reaction of hydrogen with oxygen.*

Cavendish discovered hydrogen but he kept the old terminology. The gas was phlogiston or at least very rich in phlogiston. And many of the great chemists in Europe were of the same opinion. As late as the 1780s Scheele was arguing in favor of phlogiston. He pointed out that some metals develop gas when they react with acids, some with pure water and some with alkalis. Therefore it seems most reasonable that the gas in all these cases has the same origin, the metal, and that it is rich in phlogiston.

The days of phlogiston were, however, numbered. Lavoisier in Paris soon taught the world of chemistry that when metals are dissolved in acid the gas does not come from the metal but from the acid. In 1783 he also gave this gas, "inflammable air" the name *hydrogène* and in 1784 he demonstrated the splitting of water into hydrogen and oxygen in a glowing iron tube. Lavoisier was one of the first making careful quantitative analyses. When he wanted to know what happened during combustion he acted on a definite principle: *Let us weigh and let us make use of common sense*. The conclusion was: *When metals and other matter burns it is not some mysterious substance, phlogiston, that is given off. It is instead the element oxygen that is taken up.*

Knowledge of oxygen was a condition for the new model. It is remarkable that it was the two phlogiston spokesmen, Scheele and Priestley, who independently delivered the ammunition that was needed to shoot to pieces the way of thinking based on phlogiston.

In 1766, the year after the experiments with hydrogen, Cavendish still had very much left to do in chemistry. He continued, resolutely and carefully.

9.2.3.4 … The Sparks Flew

Cavendish did not contact people for conversation but he studied hard what they had written about experiments they had made. A characteristic feature of his own experimental work was that he carefully repeated the investigations of others, made them with better accuracy and used a more penetrating analysis to interpret the results. It was now the time when electricity began to be used for many things, possible and impossible. In a bottle filled with gas it was possible to emit sparks from one electrode to another.

An Englishman, John Warltire, who had assisted Priestley in his work on the discovery of oxygen, reported an experiment. He was trying to determine whether heat had weight or not. In a closed bottle he mixed some common air and hydrogen and set fire to the mixture by an electric spark. An explosion took place and Warltire detected the formation of some dew on the bottle walls. As he was interested in the weights, he paid no attention to that. But Cavendish did.

Another experiment was reported from France. Everybody knows that a porcelain spoon is blackened when it is placed in a candle-flame. The French scientist Pierre Joseph Macquer had set fire to hydrogen in common air. As the gas burned he placed a piece of white porcelain in the flame. The white piece remained white, “only it was wetted by drops of a liquid like water”.

From his friend Priestley, Cavendish orally got the following information: “On April 18th in 1781 I used my electric machine and fired a mixture of common air and hydrogen in a closed thick-glass vessel. It functioned but I don’t think that common air and hydrogen can be a substitute for gunpowder.” Priestley at this time was obviously working on another problem than studying chemical reactions [9.1].

This information caused sparks to flow through Cavendish’s head. Something of fundamental significance happened when a spark ignited the mixture between common air and inflammable air (hydrogen). He started a major attempt to repeat the experiments of Priestley, Macquer and Warltire. In a special series of experiments, he also replaced common air by the newly discovered oxygen. It was necessary to make many determinations of gas volumes before and after combustion. For improved accuracy he introduced mercury instead of water as the liquid in the volume measuring equipment. He learned that the volume of a gas was dependent on pressure and temperature and that all comparisons had to be made at some standard state. He worked year after year and the picture became more and more clear. *Water is not an element; it is formed when hydrogen reacts with oxygen*. Or, as he himself expressed it: “*Water consists of dephlogisticated air united with phlogiston.*”

At the beginning of 1783 he told Priestley about the results and in June the same year Lavoisier was informed. Not until January next year did he present a report, *Experiments on Air,* to the Royal Society.

9.2.3.5 An Amazed Royal Society

At the January meeting of 1784 the Royal Society met Cavendish's report with great surprise and skepticism. Could it be possible that water consists of dephlogisticated air and phlogiston? Water a compound of two gases – incredible!

In terms of modern chemical terminology, Cavendish asserted that:

- Water is not an element but a chemical compound between the two elements hydrogen and oxygen
- Water is formed at the reaction between two volumes of hydrogen and one volume of oxygen.
- In common air it is only oxygen that can combine with hydrogen to form water.
- When the oxygen is used for water formation, another gas is left over. In this residue wood cannot burn and mice die. This gas constitutes four-fifths of the air volume.

At the meeting Cavendish gave experimental demonstrations. He sparked a mixture in a glass vessel, a mixture of 42.3 volumes of hydrogen and 100 volumes of common air. After sparking, all the hydrogen and one-fifth of the air had "disappeared". The result of the reaction was visible as a dew, which lined the glass. In several other demonstrations the result was repeated: Two volumes of hydrogen always united with one volume of oxygen to form a weight of water equal to the weights of the gases. He had proved his theories conclusively and he had convinced the learned gentlemen of the Royal Society.

9.2.3.6 A Stranger in the Atmosphere

One of the best proofs of Cavendish's experimental ability and great accuracy is his discovery of a noble gas in the air, 100 years before the noble gas discoveries. In 1785 he made advanced experiments with electric discharges in a mixture of oxygen and common air. The nitrogen was oxidized to nitrogen oxide. It was absorbed in lye, present in the reaction vessel. The oxygen in excess became a residue. Cavendish found that the residue volume was too big. He had found, he said, that a part of the phlogiston-rich air (the nitrogen) had not been dephlogisticated (oxidized). He estimated that the gas amount that acted in this mysterious way represented 1/120, thus 0.83% of the air taking part in the experiment. Today we know that the air contains 0.93% noble gases, mainly argon, and that they are not oxidized by oxygen. Cavendish in fact observed noble gases in his reaction bottle in 1785. The experiment was forgotten. How it was observed again and resulted in the discovery of argon will be treated in Chapter 51.

9.2.3.7 Struggles Over Priority

Cavendish's way of working, experimenting over many years with few publications, prepared the ground for discussions on priority. Soon after the Royal Society's meeting in January 1784, James Watt, the inventor of the steam engine, asserted that he had elucidated the composition of water before Cavendish. From France its was claimed that Lavoisier had given an account of the same thing to the French Academy in June 1783, thus just over half a year before the meeting of the Royal Society. The eccentric Cavendish seemed to take no notice of these disputes. He continued with his experiments. Today the scientific world gives Cavendish priority for the discovery of the composition of water and for the discovery of the element hydrogen.

Cavendish lived and worked long enough to experience the new chemistry and the new opinions about the nature of combustion. But he did not bother too much about it. He changed the aim and direction of his research and carried out careful determinations of the forces acting between two large leaden balls. He amazed the world by calculating – from these results – the total weight of the planet earth.

9.2.3.8 **The Cavendish Laboratory**

A relative of Henry Cavendish, the duke of Devonshire, donated means which made it possible to establish a laboratory, the *Cavendish Laboratory*, in 1871. The first holder of the highly esteemed Cavendish professorship was James Clerk Maxwell, the second was Lord Rayleigh, who discovered the noble gas argon in the laboratory. In 1934 the heavy hydrogen isotope tritium was synthesized in the laboratory.

9.2.3.9 **Further Important Events in Hydrogen History**

W. Nicholson and A. Carlisle carried out the first electrolytic decomposition of water to hydrogen and oxygen in 1800. Between 1815 and 1820 Humphry Davy showed that hydrogen is the functional element in all acids. He thus corrected Lavoisier, who had thought that oxygen was the essential component. In the sun's spectrum, hydrogen was discovered by N. Lockyer in 1878. Hydrogen, with its very low boiling point (–253°C), was first liquefied in 1895 by J. Dewar. The discoveries of the heavy hydrogen isotopes deuterium and tritium are treated at the end of this chapter.

9.3
The Occurrence of Hydrogen

9.3.1
A Universe of Hydrogen and Helium

Hydrogen is overwhelmingly the most common element in the cosmos. In the observable part of the universe 90% of all atoms are hydrogen atoms. Practically all the remainder is helium. Calculated on weight, about 75% is hydrogen and 25% helium. All other elements together make up less than 1%. The hydrogen atom emits electromagnetic radiation and gives information about the structure of the universe. More than 70% of the sun is hydrogen and the giant planets Jupiter and Saturn consist mainly of hydrogen and helium. In the inner cores of these planets the pressure is so high that hydrogen is present as solid metal.

9.3.2
Hydrogen on Earth

When the earth was formed 4.6 billion years ago, the conditions were not favorable for keeping this most common element. The earth's gravitation is insufficient to hold the light hydrogen gas in the atmosphere. The hydrogen content is in reality also very low, about 0.5 ppm at the earth's surface. Water in the oceans, covering two-thirds of the earth's surface, contains 11% hydrogen.

The earth's crust has a mean hydrogen content of 0.14%, mainly as crystal water in minerals but also in compounds as oils and other hydrocarbons. Free hydrogen gas is present in locally high concentrations in volcanic gases and in natural gas.

On earth, hydrogen occurs in more compounds than does any other element. As a constituent of water and of all biochemical molecules, hydrogen is a component of vital importance in the biosphere. In organisms, hydrogen is bound in fats, carbohydrates and proteins. Muscular energy is to a large extent created by oxidation of the hydrogen in fats and carbohydrates. In a human the hydrogen content is 10% by weight.

9.4
Manufacture

The annual world production of hydrogen gas is about 40 million tonnes. The dominating raw material is natural gas but other feedstocks, such as liquefied petroleum and naphtha fractions, may also be used [9.2].

During the *reforming process* natural gas is heated together with water vapor at 800°C with a nickel catalyst. Water then reacts with for example methane in the natural gas:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

A mixture of carbon monoxide and hydrogen can also be obtained by burning petroleum products with insufficient oxygen:

$$C_8H_{18} + 4O_2 \rightarrow 8CO + 9H_2$$

The carbon monoxide is converted to carbon dioxide by a further reaction with water vapor, at first with a chromium-activated iron catalyst at 500°C and finally at 220°C with a copper–zinc catalyst:

$$CO + H_2O \rightarrow CO_2 + H_2$$

To remove the carbon dioxide, the gas mixture is led in counter-flow through a water solution of methyldiethanolamine, MDEA. Carbon dioxide is absorbed and is afterwards removed from the MDEA-solution, which is recycled. The carbon dioxide is passed to the atmosphere.

The reaction between glowing coke and water vapor was earlier used to produce so called *water gas*:

$$C + H_2O \rightarrow CO + H_2$$

from which the carbon monoxide could be removed.

Coal gas or *town gas*, with high contents of carbon monoxide and hydrogen, was earlier produced from water vapor and glowing pit coal. This was of great importance for heating household gas stoves, especially before electricity (and natural gas) took over.

From the environmental point of view, the drawback with the hydrogen manufacturing methods just described is that carbon dioxide is formed and passed to the atmosphere, where it contributes to the greenhouse effect. Hydrogen gas manufacture by electrolysis of water is expensive but causes no carbon dioxide formation.

Jules Verne wrote in his book *The Mysterious Island* (1870) that electrolytic decomposition of water would be the final solution of the energy problems of the earth.

However – here again we meet the problem of environmental thinking. Electrical energy is necessary for the electrolytic process. How should this energy be produced? If steam power stations are selected, carbon dioxide will be formed there. With nuclear power stations we get rid of the carbon dioxide but instead get radioactive waste. A method recently developed in Norway uses high-temperature decomposition of methane or natural gas into hydrogen and elementary carbon. This method, and also high-temperature decomposition of water into hydrogen and oxygen, may be "pure" techniques in a future society. In hot parts of the world perhaps large solar cells may be used to generate electricity for decomposing water.

9.5
Uses

9.5.1
Chemical and Metallurgical Industry

Hydrogen is used on a very large scale for manufacturing ammonia in the *Haber–Bosch* process, described in Chapter 44 Nitrogen, and for production of hydrochloric acid. It is also used for *hydrocracking*, *hydro-desulfurization* and *hydrogenation*. The latter is a reaction in which unsaturated organic compounds are treated with hydrogen at a suitable temperature and in the presence of a catalyst, such as finely divided nickel, platinum or palladium. For example, ethylene C_2H_4 may be hydrogenated to ethane C_2H_6. The hydrogenation reaction is applied on a large industrial scale in a number of processes. One important example is the hydrogenation of vegetable oils to produce fats for food, such as margarine.

In the metallurgical industry, hydrogen is used as a reducing agent for manufacturing metal powders, such as tungsten and molybdenum. More hydrogen is used, pure or mixed with nitrogen, as a protective gas during the heat treatment of alloys that are sensitive to oxidation.

9.5.2
Hydrogen – The Energy Carrier of the Future

Our society is highly dependent on power. The energy comes to a large extent from fossil fuels such as coal, oil and natural gas, causing well-known environmental problems. For a changed situation hydrogen and electricity are considered to be the dominant energy carriers for the future. The burning of hydrogen with air in combustion engines or gas turbines results in very low emissions. Nitrous oxide is, however, formed from the nitrogen in air and emissions of this type increase exponentially with the combustion temperature. Therefore appropriate process control is necessary.

For the success of future large-scale utilization of hydrogen as an energy carrier, systems for transport, storage and distribution must be built up. Pipelines for pressurized gas have, in fact, been built, containers for liquid hydrogen transport exist and large spherical tanks and underground caverns for storage are in development. Still, however, an infrastructure for large-scale distribution of hydrogen is lacking.

The low temperatures cause great risk of embrittlement of the container materials. Experiences from the use of hydrogen in spacecraft show, however, that problems of this type can be solved. A fairly recent possibility is to use the unique ability of rare earth metals to absorb and store hydrogen as metal hydride. This is described in Chapter 17 Rare Earth Metals.

An overview of hydrogen in the energy sector is given in ref. [9.3]. A hydrogen-powered hybrid electric bus in the city of Augusta, Georgia, USA has been described by L. K. Heung in *On-board Hydrogen Storage System Using Metal Hydride*, pp. 251–256 in ref. [9.4].

9.5.3
Rocket Fuel

For the new space technology liquid hydrogen mixed with liquid oxygen was the ideal fuel. Hydrogen has a combustion energy of 120 J/g while the corresponding value for aviation gasoline is 46 J/g. It was liquid hydrogen that took the first men to the moon. However, the first rocket stage was – for volume reasons – fuelled by aviation gasoline; stages 2 and 3 were fuelled by hydrogen. And this is the way it has continued. The European rocket Ariadne 5 has a store of 120 tonnes of liquid hydrogen.

9.5.4
Fuel Cells

In a *fuel cell,* Figure 9.1, the chemical energy present in hydrogen and oxygen can be converted into electrical energy. Hydrogen is oxidized at the anode of the cell and oxygen reduced at the cathode. By a catalytic (platinum catalyst) action on the anode hydrogen molecules are oxidized:

$$H_2 \rightarrow 2H^+ + 2e^-$$

The electrons flow as a current through the outer connection and the hydrogen ions migrate through the electrolyte to the cathode, where the following reaction occurs:

$$2H^+ + 2e^- + O_2 \rightarrow H_2O$$

It is the chemical energy liberated at the oxidation of hydrogen to water that generates the current.

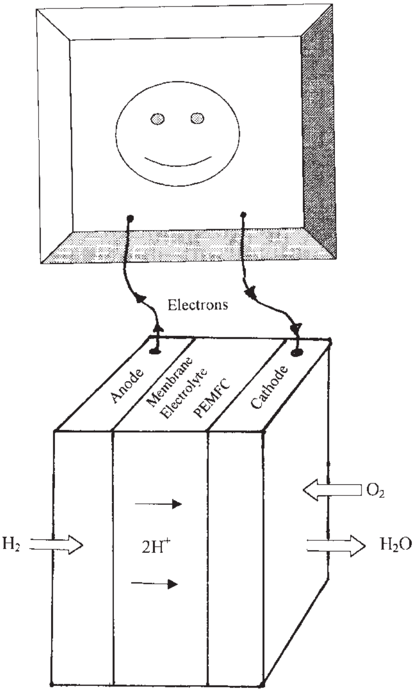

Figure 9.1 The fuel cell generates energy for a TV set

The electrolyte can be an aqueous solution, alkaline or acid. It was alkaline fuel cells that generated the necessary electricity on Apollo 11, the first manned spacecraft to the moon. In modern fuel cells a membrane may act as a solid electrolyte. A polymer PEMFC (Proton Exchange Membrane Fuel Cell) is often used.

The voltage over a loaded cell is about 0.7–1 V. Demands for increased voltage is met by combining a number of single cells in series into a *Fuel Cell Stack*.

Either a battery or a fuel cell powers an electric vehicle (EV). Both alternatives are very good from the environmental point of view. Cars powered by electricity, generated from hydrogen fuel cells, will have no emissions other than water. In the fuel cell case the car has to have a hydrogen "tank", liquid hydrogen or metal hydride storage. Oxygen is supplied from the air by a turbo-compressor. In the automotive industry, cars with hydrogen engines are being developed and testing of prototypes is going on [9.4].

9.5.5
Lifting Gas for Balloons and Airships

Jacques Alexandre Charles (1746–1823) was a pioneer spaceman in the lowest atmosphere. In 1783 he built a hydrogen gas balloon, the first in history. He produced the hydrogen by dissolving iron in sulfuric acid. In 1804, Louis-Joseph Gay-Lussac and J.-B. Biot made a famous and bold balloon ascent over Paris with the aim of studying the composition of the atmosphere and the behavior of the magnetic needle at high altitudes.

A dramatic occurrence in 1937 emphatically showed the importance of combining safety and lifting capacity. The German airship *Hindenburg*, built by Zeppelin Luftschiff AG and filled with hydrogen, burst into flames at the Lakehurst aerodrome outside New York. Thirty-six people out of a total of 97 were killed. Because of the explosion risk, hydrogen is nowadays replaced by helium as the lifting gas for balloons.

9.6
Hydrogen Isotopes – Deuterium and Tritium

9.6.1
The Three Isotopes of Hydrogen

Hydrogen occurs in nature as a mixture of three isotopes *protium* ^{1}H, *deuterium* ^{2}H or D and *tritium* ^{3}H or T. The last is radioactive. Some properties of nuclides of the three isotopes are collected in Table 9.1.

Table 9.1 The three isotopes of hydrogen

Isotope	Nuclide	Atomic mass	Part of total hydrogen in nature %	Half life
Hydrogen (Protium) H	^1H 1 proton	1,007825	99,985	Stable
Deuterium D	^2H 1 proton + 1 neutron	2,0140	0,015	Stable
Tritium T	^3H 1 proton + 2 neutrons	3,01605	0	12.33 years

9.6.2
Deuterium

Deuterium is a stable isotope of hydrogen and is present with a low concentration in all hydrogen. It was isolated for the first time in 1931 by H. C. Urey and his co-workers at the University of Columbia in the USA. He was awarded a Nobel Prize in 1934. The name deuterium was chosen from the Greek word *deuteros*, meaning the second. Shortly after this, G. N. Lewis prepared heavy water, D_2O, through the electrolysis of water. At the cathode the hydrogen ion H^+ is discharged faster than the deuterium ion D^+. After prolonged electrolysis heavy water is enriched in the electrolyte.

When the atomic bomb principle became known in different countries in 1939 and the search for a functioning nuclear weapon began, scientists also became aware that heavy water could be used as a moderator in nuclear reactors for the production of nuclear fuel. Heavy water then changed from a scientific curiosity to a strategic material of top-level political importance. The Norwegian company Norsk Hydro A/S started production of heavy water, using low-cost electrical energy from the Rjukan power station. In World War II it became important for both sides to have access to the heavy water from Rjukan. The physicist Frèdéric Joliot-Curie (1900–1958) got permission to transfer the whole Norwegian store, 180 liters, to France. This operation occurred just before the German occupation of Norway. From France it was transferred to England in a cat-and-mouse game with the invading German soldiers. German attempts to develop an atomic bomb were rendered very difficult owing to the lack of heavy water, and production in Rjukan was restarted. The works were, however, destroyed twice, first by a British commando unit and members of the Norwegian resistance movement, and later again by a British air raid.

The differences between the usual hydrogen isotope ^1H and deuterium D – as regards chemical and above all physical properties – are bigger than between isotopes of heavier elements. The same is true between compounds of hydrogen and those of deuterium. Some properties for common water and heavy water are listed in Table 9.2.

Table 9.2 Some properties of water and heavy water

Property	H_2O	D_2O
Molecular weight	18.015	20.028
Melting point at 1 atm, °C	0.00	3.81
Boiling point at 1 atm, °C	100.00	101.42
Vapor pressure at 25°C, kPa	3.166	2.734

In the study of reaction mechanisms in chemical research, compounds may be used in which one or several deuterium atoms have been substituted for hydrogen.

9.6.3
Tritium

Tritium is the third hydrogen isotope. It was prepared for the first time in 1934 by Ernest Rutherford. The isotope takes its name from the Greek word *tritos,* the third. The tritium nuclide is unstable and emits β-radiation. It is formed during nuclear reactions in the upper atmosphere by a reaction between nitrogen and neutrons in the cosmic radiation:

$$^{14}N + {}^{1}n \rightarrow {}^{3}T + {}^{12}C$$

Tritium arrives at the earth's surface in rain and is present as HTO in the hydrological cycle. The natural tritium content is, however, very low, 1 atom T in 10^{18} atoms of hydrogen. The atmospheric testing of nuclear weapons during the 1950s and 1960s made the contents considerably higher. Tritium is itself an important constituent of nuclear weapons as mentioned below.

Tritium has some peaceful use for research purposes. Organic compounds can be marked with tritium, which is the basis for a method of studying the course of chemical reactions.

9.7
Fusion Energy – „Energy From Water“

Fusion, unlike fission, is a process in which nuclei of light atoms are combined to heavier elements. That is what happens as energy is generated in the stars:

$$4\,{}^{1}H \rightarrow {}^{4}He + \text{energy}$$

The amount of energy set free is enormous, millions of times greater than during a conventional chemical reaction. Would it not be possible to use reactions of this type for energy production on earth? A controlled fusion reaction might provide humanity with an unlimited source of energy. But it is difficult – in fact one of the most difficult problems in technology up to now. Between nuclides with the same electrical charge very large energy barriers exist due to the electrostatic repulsion. If nuclides are to be brought together in order to achieve fusion, these barriers must be overcome. At first the nuclides must be forced into close proximity, and that in spite of the great repulsion forces. This is only possible if the nuclei are given a high thermal energy and a high temperature, so high that gases are completely ionized into a mixture of nuclei and electrons – a *plasma*. A reaction between heavy hydrogen isotopes, the DT-reaction, has the best prospects of success:

$$^{2}H + {}^{3}H \rightarrow {}^{4}He + {}^{1}n$$

The plasma must also have a high density for a sufficient time to permit the fusion reaction to occur. Laser heating of frozen deuterium–tritium pellets confined in a magnetic field is a method that has been tested. The neutrons formed react with lithium in an outer mantle, a reaction in which new tritium is formed. This reactor type is called *Tokamak* and is used in research projects in the USA and England. Similar reactors are used in France, Russia and Japan.

In the hydrogen bomb the DT-reaction is also essential. In practice lithium deuteride, LiD, and some tritium are used. Very high temperature and pressure are necessary for the fusion reaction to start. It is obtained by letting a conventional atomic bomb (a fission bomb), combined with the thermonuclear fuel, explode. At this fission reaction tritium is also generated.

9.8
The Biological Role of Hydrogen

Hydrogen is one of the elements that dominate living systems. It is present there free as hydrogen ion, or bound in water and in complex organic molecules. The binding may be conventionally covalent or with special *hydrogen bonds*.

In substances that are composed of non-polar molecules such as dimethyl ether $CH_3–O–CH_3$ and dipropyl ether $C_3H_7–O–C_3H_7$, strong covalent bonds act between the atoms in the molecules. An individual molecule is, however, loosely bound to another by very weak so-called van der Waals forces. These cannot keep the molecular aggregates together when the material is heated. Melting and boiling points are relatively low but increase with the molecular weight as is exemplified in Table 9.3.

Table 9.3 Some properties of water and heavier carbon analogues

Substance	Formula	Molecular weight	Melting point °C	Boiling point °C
Dimethyl ether	$CH_3–O–CH_3$	46	–139	+24
Methanol	$CH_3–OH$	32	–98	+65
Ethanol	$CH_3–CH_2–OH$	46	–114	+78
Dipropyl ether	$C_3H_7–O–C_3H_7$	102	–122	+91
Water	H_2O	18	0	+100

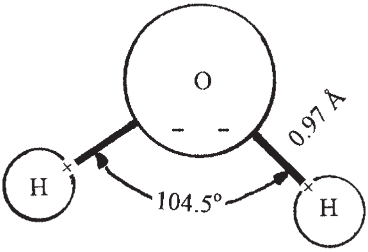

Figure 9.2 A water molecule – a dipole

Water is a common substance with uncommon properties. The last row of Table 9.3 shows values for water. Its melting point is 0°C, its boiling point 100°C. They are considerably higher than would be expected for a substance with a molecular weight as low as 18. Why? The answer is that the water molecule is highly polar and forms hydrogen bonds. This fact is of the utmost importance for life on earth.

The water molecule is a dipole with a concentration of negative charge on the oxygen atom and positive on the hydrogen atoms. The angle between the two OH-directions is 104.5°. An attraction occurs between different water molecules, and aggregates are formed with molecular weight apparently higher than 18. If no hydrogen bonds were acting between the water molecules, water might be expected to freeze to ice at about –100°C and boil at –80°C.

The hydrogen bond is a type of dipole–dipole interaction, stronger than other dipole interactions owing to the small size of the hydrogen atom and the absence of core electrons. When hydrogen bonding occurs it strongly affects bulk properties. One water molecule is bound to four neighboring molecules by hydrogen bonds in a tetrahedral arrangement. In ice a rigid structure, also tetrahedral, is formed. Each oxygen is surrounded by four nearest neighbors and the oxygen atoms are bound together by hydrogen bonds, leading to a very open structure. Because of this, ice is a low-density substance, so light that it floats on water. If it did not, the ice would sink, the lakes freeze solid, and the summer heat would not be sufficient to melt the ice.

Living matter contains proteins, DNA and other molecules with complex structures. In their reactions some bonds must be easily broken and reformed. The energy of hydrogen bonds is of a magnitude that allows this [9.5].

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10
Blowpipe and Spectroscope – Important Tools for Discovering Elements

10.1
Analysis With the Blowpipe

10.1.1
Introduction

A blowpipe is a narrow tube, about 200 mm long, bent or straight, equipped with a mouthpiece (Figure 10.1).

Figure 10.1 A simple blowpipe.

The operator blows a powerful stream of air through a flame against the sample to heat and melt glass or metals. The use of blowpipes was known in antiquity. Depictions of goldsmiths using blowpipes are found on tomb walls from old Egypt at Sakkara near Memphis. These paintings are dated to 2400 years BC. In later times, exemplified by the description in this book (page 106) the indigenous workers of Esmeralda in South America used blowpipes to make alloys of platinum and gold in the period AD 100–400, long before the Spanish conquest.

Johann Kunckel (1613–1703) seems to have been one of the first to use the blowpipe for analytical purposes. Using charcoal as a support for the sample, placed in a cavity, he could obtain valuable information about the sample composition by blowing on it with a pipe through the flame of a strong lamp. This technique was developed and used by chemists, mineralogists and metallurgists in the 18th century, especially in Sweden.

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U. Burchard [10.1] has described the whole history of the blowpipe. In his paper he also presents a comprehensive publications list and beautiful color photos of blowpipes and portable laboratories.

10.1.2
Mineral Analysis With a Blowpipe

It became possible for a skilled blowpipe analyst to interpret the behavior of the sample and get information about its composition. In the reducing environment in the charcoal cavity, oxides of many metals are reduced to molten metal droplets (Pb, Bi, Sn, Sb) or to a non-molten but sintered metal piece (Cu) or to sparkling metal fragments (Fe, Ni, Co). The oxides of cadmium, arsenic and zinc are easily reduced but the metals are volatile and evaporate. When the metal vapor is blown away and comes into the outer oxidizing part of the flame, the oxides are formed again and deposit as coatings on the charcoal, outside the cavity. A zinc oxide coating is yellow when warm and white when cold. An arsenic coating is also white but with a smell of onion in contrast to zinc oxide. A cadmium coating is brown. Characteristic coatings were also obtained from the somewhat volatile metals lead, bismuth and antimony.

Oxides of calcium, barium, strontium, magnesium and aluminum are not reduced but they glow intensively under strong heating.

Probably *Anton von Swab* (1702–1768) was the first to use the technique, but it was *Axel Fredrik Cronstedt* (1722–1765) who first used the blowpipe for systematic mineral investigations. He also had an own shape of pipe. It was provided with a bulb for collection of saliva that otherwise disturbed reactions and observations (Figure 10.2).

Figure 10.2 Cronstedt's blowpipe.

In his translation of Cronstedt's mineralogy von Engeström had an appendix, "Description of a mineralogical pocket laboratory; and especially of the use of the blowpipe in mineralogy".

According to von Engeström, Cronstedt was a pioneer in using portable laboratories for mineral analysis in the field. Figure 10.3 shows Torbern Bergman's portable laboratory with a silver blowpipe.

Cronstedt's students further developed blowpipe analysis. One of them was *Johan Gottlieb Gahn* (1745–1818), who lived and worked in Falun. He was looked upon as the most able blowpipe analyst in the 18th century. His own blowpipe (Figure 10.4) was used by and further developed at the Bergakademie Freiberg in Germany.

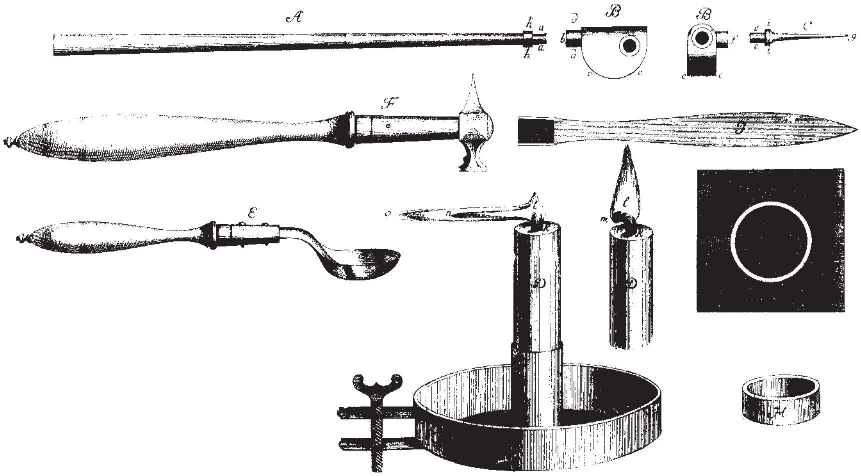

Figure 10.3 Components in Torbern Bergman's portable laboratory.

It was also Gahn who introduced the method of melting a borax bead or a phosphate to form a clear bead in a loop of a platinum wire to study the color effects when a very small sample quantity is dissolved in the bead. Two examples:

- In an oxidizing flame, copper compounds dissolve in a borax bead with a green color that changes to red on cooling. If the flame is reducing the bead is colorless when hot but red after cooling.

Cobalt compounds give a blue color to the borax bead, whether hot or cold.

Gahn was a mentor for young *Jöns Jacob Berzelius* (1779–1848) and deeply interested Berzelius in mineralogy and blowpipe analysis. In 1821 Berzelius published an important book, *Employment of the Blowpipe in Chemistry*, a work that became a classic.

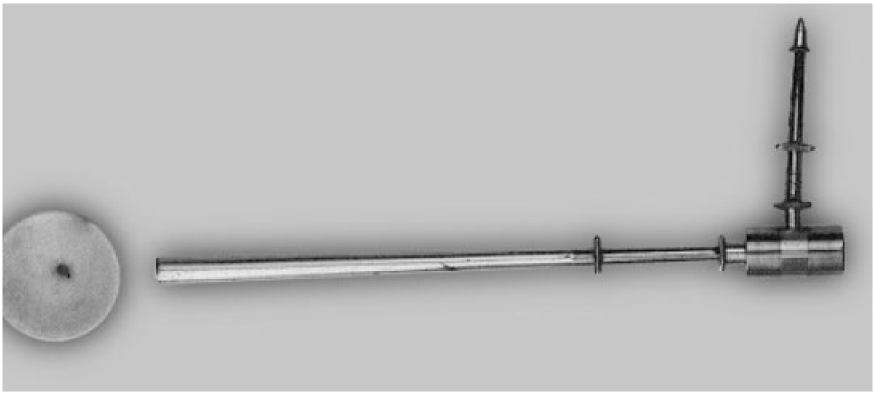

Figure 10.4 Gahn's blowpipe.

> One day in Karlsbad in Austria, where Berzelius spent some time in 1821 to improve his health at the spa, he met *Johann Wolfgang von Goethe* (1749–1832), famous poet but also amateur mineralogist. The blowpipe analysis was quite unfamiliar to Goethe. Berzelius showed him and identified some of Goethe's unknown minerals. The poet was very impressed and complained bitterly that he now was too old to learn the handling of this equipment. Goethe was 72 years at that occasion.

Blowpipe development continued strongly at the Bergakademie Freiberg (Freiberg Mining Academy) in Germany in the first half of the 19th century. When the Bunsen burner and the spectroscope were introduced in the second half of the century blowpipe analysis began to decline.

10.2
The Fundamentals of Spectral Analysis

The element gold occurs in nature as the free metal, and silver likewise, to some extent. The discovery of these metals has, because of that, been uncomplicated. It occurred in prehistoric times. Observant people saw and collected the remarkable metals and were surprised at their properties. Archaeologists today find them as jewelry, god statuettes, crowns for kings and queens, created in remote cultures. Most of the elements, however, are bound in chemical compounds, very often in minerals of complicated composition. The discovery of these elements presupposed chemical analysis. Several methods of analysis were developed in the 18th century, which explains the large number of element discoveries in this period. At first the blowpipe was used but gradually conventional quantitative analysis with *gravimetric analysis* (weighing methods) and *volumetric analysis* (titration methods) was introduced. In 1787 a black mineral was discovered that later got the name *gadolinite*. This started the long period of element discoveries dealing with the *rare earth metals* (REM). The great chemical similarity between the different RE elements made their separation very difficult and time consuming, and this is described in Chapter 17 Rare Earth Metals. Identifying on the basis of conventional chemical analysis became almost impossible, particularly as the elements occurred in minerals with very complicated compositions. In the middle of the 19th century, however, spectral analysis was developed into an effective tool for element identification.

When the radiation from a glowing, not gaseous, body passes through a prism of glass or quartz a spectrum is formed. It is well known how the light from a white-hot tungsten wire in a light bulb is split up into different colors by a prism. This spectrum will be continuous. From a glowing gas the spectra will be discontinuous, consisting of distinct lines. The red light (long waves) is diffracted least, the violet (short waves) most, see Figure 10.5.

Another way to split up the components of a light ray is to use a grating. A transmission grating is made by scribing parallel tracks in a thin metal coating that has been vaporized onto a glass plate. The distance between the scribed lines, the grating constant d, may be a few microns (μm), see Figure 10.6.

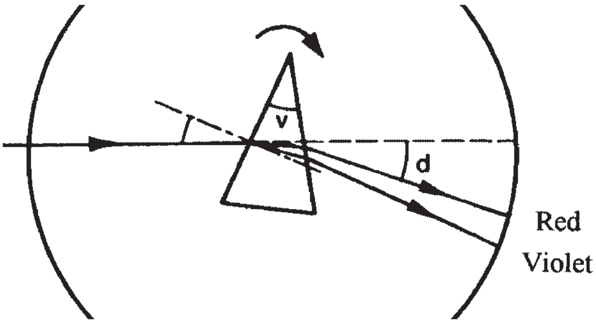

Figure 10.5 Dispersing the radiation according to its wavelength in a prism.

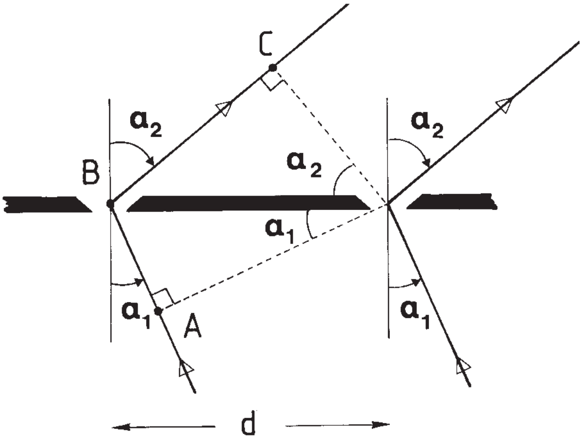

Figure 10.6 The principle of a transmission grating. (Reprinted from ref. [10.2] with permission.)

An incoming beam of light (from below in the figure) emits its radiation in all directions from the scribed lines in the grating. Two scribed lines are shown in the figure. In a direction in which AB+BC equals an integral number of wavelengths, the two rays come in phase and the intensity is strengthened. For intermediate directions the radiation is extinguished. Thus the grating, like a prism, splits the radiation according to wavelength, but in the grating the long waves are diffracted more than the short waves. Diffraction in prisms and gratings became the basis of spectral analysis according to the principles shown in Figure 10.7.

The slit in the so-called collimator is depicted as a line on the photographic plate or film, different lines for different wavelengths. Nowadays special plates, CCD-plates, are used in order to avoid the need to develop photographic plates. In these, the surface is covered with square picture elements, the number of which per surface unit is expressed as pixels of the CCD unit.

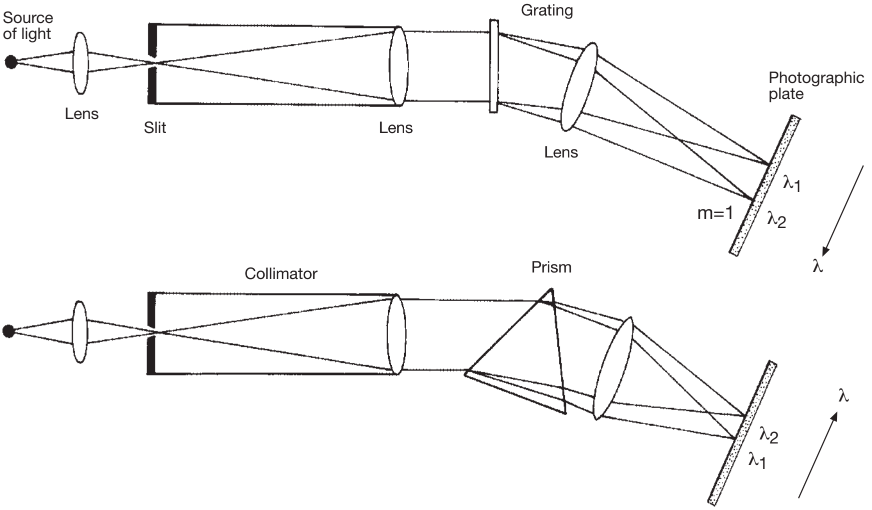

Figure 10.7 The principles of grating and prism emission spectrographs. (Reprinted from ref. [10.2] with permission.)

If a sample is heated to a very high temperature in an electric arc or a spark discharge, elements in the sample will be vaporized and emit a line spectrum, composed of different wavelengths. When this radiation is taken into a spectrograph through the narrow slit (Figure 10.7) and passes a prism or a grating the different wavelengths can be observed as distinct lines. This became the basis for *emission spectral analysis*. The characteristic lines for the actual element were observed in an ocular lens or detected on a photographic plate or film (Figure 10.8).

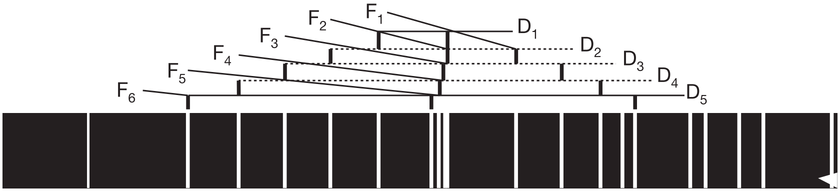

Figure 10.8 The atomic line spectrum of a metal. The lines correspond to transitions between different levels in the electronic shell. The positions of the lines and the combination of lines are a "fingerprint" of the actual element.

The spectroscopic method was used in looking for the RE and other elements. It gave clarity but also confusion. The spectra of heavy metals in the visible and ultraviolet regions are very rich in lines as a consequence of the fact that every wavelength (line) corresponds to a transition between two energy levels in the outer electronic shell of the atom. A heavy metal atom is very complex and has many possible electron transitions. The lines from an unknown element were impossible to predict and could not be known until the element was discovered, which was the reason for confusion. In any case, from the middle of the 19th century spectral analysis developed into a powerful tool for element identification.

How did it start?

10.3
The Color of the Flame Gives Information on the Composition

In the alchemical milieu, where fire was so frequently used, people were fascinated by all the color changes that occurred when different substances were introduced into the flames. Gradually a system of observations was built up. At the end of the 16th century, the alchemist *Leonard Thurneysser*, active in Switzerland and Berlin, discovered that the characteristic color makes it possible to find certain metals in materials.

Andreas Sigismund Marggraf, born in Berlin in 1709, studied at the Bergakademie Freiberg and in other European seats of learning. He is known in chemical history for different reasons. He showed that aluminum oxide, calcium oxide and magnesium oxide are different "earths". He also showed that soda and potash are different substances, sodium carbonate and potassium carbonate respectively. Possibly the color reactions in flames helped him to get these results. In 1758 Marggraf noted the yellow color when soda was heated and the red color from potash.

10.4
The Spectrum – Visible and Invisible

10.4.1
A Prism Splits a Beam of Light According to the Wavelength

In 1666 *Isaac Newton* acquired a glass prism to investigate "the phenomenon with colors". He made these observations:

> Having darkened my chamber, and made a small hole in the window shutters, to let in a convenient quantity of the sun's light, I placed my prism at its entrance, that it might thereby be refracted to the opposite wall.

A spectrum with all the colors of the rainbow was observed on the wall. The phenomenon had been observed earlier but Newton acted more thoroughly than his predecessors. When the light, already split into different colors, was allowed to pass through a second prism, the colored rays were diffracted again but no new colors appeared. Consistently the blue light diffracted most and the red least. Newton also discovered that the second prism could be arranged so that the colors that had been separated by the first prism could be recombined to white light again.

William H. Wollaston (the discoverer of palladium and rhodium) also worked with prisms around the year 1800 and discovered the importance of restricting the width of the incoming light beam. When he let light from the sun pass through a 2-mm slit into a prism of flint glass he saw the beam separated into the components red, yellow, green, blue and violet. He also observed seven dark lines, heralding Fraunhofer's famous discovery of 1814.

10.4.2
Infrared (IR) and Ultraviolet (UV)

Carl Wilhelm Scheele in 1777 made an observation that paved the way for the discovery of ultraviolet light. Since long ago it was known to mineralogists that some silver ores contained a particular white mineral, *hornsilver* or *cerargyrite*. Chemically it was silver chloride and it darkened in sunlight. Scheele carried out some experiments with hornsilver, exposing a number of samples to the influence of different colors of the spectrum. He noted that the blackening was slowest in the red light and most rapid in the violet. Scheele's results were verified by *Johann Wilhelm Ritter* in 1801 [10.3] and by Wollaston in 1802 [10.4] They, however, extended their experiments to the invisible region outside the violet. They were surprised to find that the blackening occurred with the highest speed in that region. An invisible energetic, ultraviolet radiation exists!

The famous astronomer William Herschel discovered infrared light, the invisible heat radiation, in 1800. His method was simple. A blackened thermometer bulb was heated in different regions of light that had been split into colors by a prism. When the bulb was placed in the dark region outside the red radiation it was heated up more than it had been in the red.

10.4.3
Fraunhofer's Lines and Gratings

Joseph Fraunhofer was born in 1787 in Straubing, a village near Munich in Germany. His father was a poor glass worker, unable to provide a formal education for young Joseph. At the age of eleven, however, Joseph had the opportunity to work as an apprentice with a mirror manufacturer in Munich. The experience he then acquired was of great importance for his progress to a prominent position within experimental optics. It became apparent that Fraunhofer was a technical and experimental genius. At the age of 20 he became the foreman for mirror manufacture and at 24 he took over the responsibility for the whole glass manufacture. In 1814 he studied the spectrum that is obtained when the light from a flame containing sodium passed through a prism. He observed a sharp doublet (double line). To find out if the same doublet was present in sunlight he started to study the spectrum of the sun. For this he used a prism of very high quality, a prism that he himself had produced. Furthermore, he made an invention of great importance to the development of spectroscopy. Newton had projected a spectrum on the wall behind the prism. Fraunhofer had the excellent idea of viewing the slit with a telescope, placed behind the prism. This made it possible to measure the angles that the different lines in the diffracted light made relative to a reference line. It can be said that Fraunhofer's work was the beginning of spectroscopy as an exact science.

With his fine instrument Fraunhofer now investigated the spectrum from the sunlight and found that it was crossed by "an almost countless number of strong and weak vertical lines". He determined the positions of about 700 of them and thus created the first precise standards for measuring the dispersion of optical glasses. Eight of the most salient lines were described with the letters A in the dark-red region to H in the violet region. D was the designation for a doublet, the position of which corresponded to the sodium doublet. His experiments convinced him that the dark lines in the doublet were a part of the sunlight and not something that had arisen in the prism. During his whole life he continued to study the dark lines in the sun's spectrum and in spectra from other heavenly bodies. He was never able to explain the phenomenon, and perhaps he was unaware of their great importance and that for all time they would carry his name, the *Fraunhofer lines*. The explanation was obtained though the experiments of Bunsen and Kirchhoff with the spectroscope that they developed. Fraunhofer also saw the possibility of splitting the light beam with a grating and he made his own gratings. The first one, from 1821, was a reflection grating made of thin wires with a diameter as little as 0.04 mm, tightly wrapped round a plate[1]. Later he made transmission gratings of glass by scribing with a diamond. This made accurate measurement of wavelengths possible. Previously, only determination of values for diffraction angles had been feasible. With his "home-made" gratings he now determined the wavelength for the double line of sodium, the D-line, to lie in the range 5882–5897 Å. Modern values are 5896 for the D_1 line and 5889 Å for the D_2 line.

10.5
The Development of Spectroscopy Continues

The German scientists *R. W. Bunsen*, born in 1811 and *G. R. Kirchhoff*, born in 1824, are regarded as the inventors of the spectroscope and the founders of spectral analysis. The year 1859 is generally mentioned as the starting year. The methods were, however, developed gradually and with contributions from many scientists and technicians. This has been mentioned earlier and will be further explained in the following sections.

10.5.1
Separates Red From Red

In 1824, *John Herschel*, son of the astronomer William, found, just as Fraunhofer had done 10 years earlier, that a low content of sodium could be detected by its flame spectrum. He published the result but then became uncertain himself and questioned the correctness of the discovery. He found the yellow line, indicating sodium, in practically all materials he investigated and did not think that the element sodium could be so widespread! The result was, however, correct. Sodium is very much dispersed and its yellow double line in the spectrum detects its presence even in low concentrations.

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[1] A modern grating may have 1000 slits per mm

The Englishman *Fox Talbot* showed in 1834 that, with a prism, it was possible to distinguish between lithium and strontium, although both emit red light when they are heated. The strontium radiation has many red lines and an orange and a blue. The spectrum of lithium contained only one red line.

In the period 1830–1845, *David Brewster*, *John F. Daniell* and *William H. Miller* made important discoveries regarding absorption spectra. When white light passes through sulfur vapor the violet part of the spectrum was extinguished by the sulfur absorption in this part of the spectrum. On the contrary, iodine vapor absorbed in the middle region of the spectrum. When the light passed nitrous fumes, NOX, hundreds of lines or bands were formed in the spectrum. A similar effect was obtained when the absorption spectrum of bromine was studied.

10.5.2
Use of Electricity for Spectral Analysis

It had become clearer that the light from a glowing solid body shows a continuous spectrum while a metal that is vaporized emits a characteristic line spectrum. The yellow doublet in the sodium spectrum was an example. *Charles Wheatstone*, well known from the science of electricity, in 1835 investigated electrical arcs generated between metal electrodes. The metals he used were mercury, zinc, cadmium, tin, bismuth and lead. He used a prism for studying the radiation from the arcs and observed the distinct lines that constituted the spectrum. Further he noted that each metal had its special group of lines, which could possibly be used for element identification.

Two general techniques for material analysis started to develop.

- emission spectral analysis
- absorption spectral analysis

We have reached the middle of the century but spectroscopy has not yet been officially invented.

10.5.3
A Finding in a Fire-ravaged Glass Factory

David Alter was born in 1807 in Allegheny, Pennsylvania, USA. He is of great importance in the development of spectroscopy but is rarely mentioned alongside Bunsen and Kirchhoff. He studied medicine and began to practice his profession in 1831. The number of his patients was obviously limited, as Alter could devote his time to work in other areas quite different from medicine. He worked with telegraphy and designed an electric railway engine. He became one of the first Americans to use Daguerre's photographic process. His picture (daguerreotype) of Fraunhofer's lines in the sun's spectrum attracted attention. Perhaps this work aroused his interest in spectra and spectral analysis. Yet his means for the acquisition of laboratory equipment were restricted, and he had to build for himself. For a person who before the middle of the 19th century had designed and built an electric engine it was perhaps not an invincible obstacle to set up a system to study spectra. Firstly, he needed a good glass material for his prism. Good opportunities may present themselves for anybody who can seize them.

In 1845 the city of Pittsburgh was ravaged by fire. Alter looked for glass in a destroyed glass factory. In a furnace he found glass of very high quality, and from this he made a good prism for spectroscopy. Now he started investigating the radiation that was emitted from electrical arcs and even sparks, formed by electrical discharges between two pins both of the same metal. Alter defined arc spectra for many metals. In 1854 he investigated alloys of two metals and showed that when the radiation from an arc discharge was split in a prism, lines typical for each component appeared [10.5]. He also investigated the absorption spectra of hydrogen and other gases [10.6].

10.5.4
Anders Ångström in Uppsala Makes Spectroscopy Quantitative

Anders Jonas Ångström (1814–1874) became a doctor of physics in Uppsala in 1839 and professor in 1859. He carried out comprehensive pioneering work in spectral analysis. In 1868 he published a work on the sun's spectrum, a work that has been characterized as monumental. He gave there, to six significant figures, wavelengths for more than 1000 Fraunhofer lines. He used the wavelength unit 10^{-8} cm = 10^{-10} m. That unit later got the designation angstrom, Å. This unit is now giving way to the SI unit *nanometer,* nm. 1 Å = 0.1 nm.

Ångström was early very active in using electrically generated arc discharges to excite an unknown sample to emit a characteristic radiation. As early as February 1853, six years before the invention of spectroscopy, Ångström sent a paper for publishing in the German journal *Poggendorff's Annalen* [10.7]. Since the investigation was published in a well-known journal and in German it attracted attention in Europe and had a great influence on the development of spectral analysis. He described investigations of spectra, obtained by splitting radiation from glowing, solid bodies and from vaporized metal atoms in the gas phase and from electrical discharges in gases. Ångström states:

> I have found that the spectrum of the electrical spark in fact can be regarded as two different spectra; one belongs to the gas in which the discharge occurs and the second belongs to the metal or body that is the electric conductor.
>
> …
>
> A question of great interest, the answer to which, however, is still very difficult to give, is this: Why does the spectrum from heated parts in a spark discharge show only certain colors (a line spectrum) while a glowing solid body (without spark discharge) shows all colors in a connected whole. A glowing platinum wire gives a spectrum without distinct lines but platinum in a spark discharge gives a large number of such lines.
>
> …
>
> Already Wheatstone had observed that when the poles consist of different metals the spectrum is composed of lines from both metals. Because of that

> it was of great interest to investigate if two metals in an alloy or in an intermetallic compound also show the lines of both metals or if quite new lines appear. It was shown by my investigations that the first assumption is true. The only difference was that some lines were missing or could be detected only with difficulty. When they were found they were, however, situated in the same positions as the lines obtained from the pure metals. It is very easy to be convinced of that by letting one pole consist of the compound Sn_4Pb. The other pole is from the beginning pure tin or pure lead. From the compound, lines are observed belonging to both metals. The position of these lines can be controlled by successively changing the other pole metal by alloying.

By virtue of the cited investigation the well-known English physical chemist J. Tyndall stated that Ångström ought to be considered as the inventor of spectral analysis [10.8].

10.5.5
The Ångström Laboratory

Since 1997 different scientific institutions at Uppsala University have joined in a center for education and research within fields connected to materials science. The laboratory is named after Anders Johan Ångström (Figures 10.9 and 10.10) whose achievements were described above, and also after his son *Knut Ångström*, also professor in Uppsala. The son Knut devoted a great part of his research to the radiation from the sun [10.10].

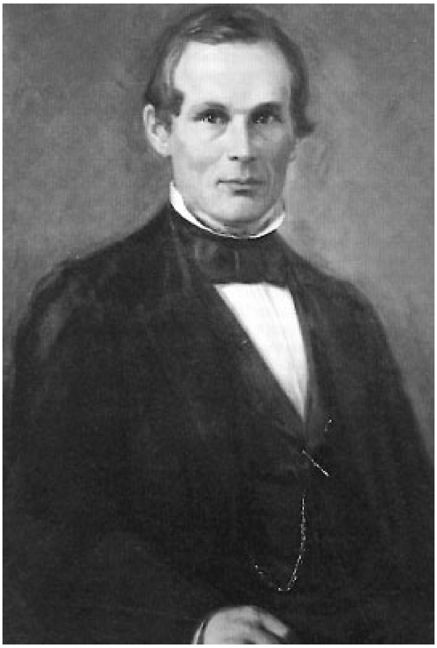

Figure 10.9 Anders Jonas Ångström (1814–1874). Portrait at the Institution for Physics, Uppsala University. (Photo: Teddy Thörnlund. Reprinted with permission.)

Figure 10.10 Ångström's spectrometer from Pistor and Martins, Berlin. (Photo: Teddy Thörnlund. Reprinted with permission.)

10.5.6
A Research Milieu in Heidelberg

10.5.6.1 A Prestigious Position

> When Leopold Gmelin was professor of chemistry at the university in Heidelberg 1817–1851 the chair of chemistry in Heidelberg became a prestigious position. Gmelin was a chemist with a very good reputation. At his institution he had *Friedrich Wöhler* as a co-worker, saw his talents for research and encouraged him to continue his training with Berzelius in Stockholm. Wöhler wrote to Berzelius in July 1823 with an inquiry "if that happiness might be mine to be able to work at Berzelius' laboratory during the coming winter". He got a swift and often cited answer: "He who has studied under the guidance of Leopold Gmelin certainly has very little to learn from me". But Wöhler arrived and became one of Berzelius' friends for life. Gmelin early saw the need for a big chemical encyclopedia and, between 1817 and 1819 edited the *Handbuch der anorganischen Chemie*. Later it was published in several editions. In 1922, Deutsche Chemische Gesellschaft took over the responsibility for the encyclopedia that was edited with the name "*Gmelins Handbuch der anorganischen Chemie*". Since 1981, supplementary volumes have been edited, only in English, by the Gmelin-Institut in Frankfurt am Main.

In 1851 Robert Bunsen became Leopold Gmelin's successor, an appointment that almost created a sensation.

10.5.6.2 Bunsen, Kirchhoff and Spectral Analysis

The invention, in 1859, of optical spectral analysis with studies in the visible wavelength region is linked to *R. W. Bunsen* and *G. R. Kirchhoff*. But as usual many experimentalists in different parts of the world contributed to the final result.

Robert Wilhelm Bunsen (1811–1899) was born in Göttingen, son of a professor of modern languages. He studied chemistry at the university of his home town. The scientific education the young Bunsen had obtained there he broadened during long wanderings to seats of learning in France, Austria and Switzerland. Whenever an opportunity arose he also took the chance to work in mines, at smelting works and in workshops. This experience was of great value later on when he made extensive investigations of blast furnace gases and developed an analysis method that was used all over the world for a whole century. At the age of 25 he succeeded Friedrich Wöhler as a teacher of chemistry at the higher technical school at Cassel. He also had a similar position at the university in Breslau (in present-day Slovakia). There he had as a colleague a physicist from the university in Berlin, Gustav Robert Kirchhoff.

Finally, in 1851 he was appointed professor of chemistry in Heidelberg. There he taught and researched for 38 years until his retirement in 1889 at the age of 78.

Gustav Robert Kirchhoff (1824–1887) was born in Königsberg, son of a chancellor of justice. At the age of 24 he became a teacher at the University of Berlin and later professor of physics in Breslau. There he made Bunsen's acquaintance and a collaboration started that continued for many years. Obviously it was Bunsen, who in Breslau saw the great capacity and potential of his 13-years-younger colleague. It has been said that Bunsen's biggest discovery during the Breslau period was – Kirchhoff. Both were later appointed to be professors in Heidelberg, Bunsen of chemistry and Kirchhoff of physics and physical chemistry. Kirchhoff worked in Heidelberg from 1854 till 1875. Then he returned to Berlin and a professorship of physics there. He co-operated there with Hermann Helmholz, one of the pioneers of physical chemistry. Kirchhoff died in 1887 at the age of 63.

Bunsen had invented the *Bunsen burner* and studied the effect of its flame on different metal salts. When he observed the flame through colored glasses he could identify different metals. Kirchhoff, the physicist, thought that it might be better to let the light pass through a prism and observe the spectrum in a telescope as described by Fraunhofer. The prism was enclosed in a box with blackened walls, see Figure 10.11.

Another important achievement, primarily attributed to Kirchhoff, was the explanation of the relationship between the wavelengths of emitted spectral lines and Fraunhofer lines. Kirchhoff clearly stated that gases absorb light of the same type as they emit, and he drew his own very important conclusions from that. When a flame containing sodium emits its light into the spectroscope the yellow doublet is easily observed. If sunlight is passed into the spectroscope a dark doublet is found in the same position. Thus, Kirchhoff concluded that sodium must be present in the sun's outer atmosphere and it absorbs Na wavelengths from the light the sun emits. Using the spectroscope the emission lines of lithium were established but no corresponding Fraunhofer lines are observed. Thus lithium is not present in the sun's atmosphere (or is present only in very low concentration). Gradually, in the light of these experiments and conclusions, modern spectral analysis, including emission and absorption spectroscopy, was developed.

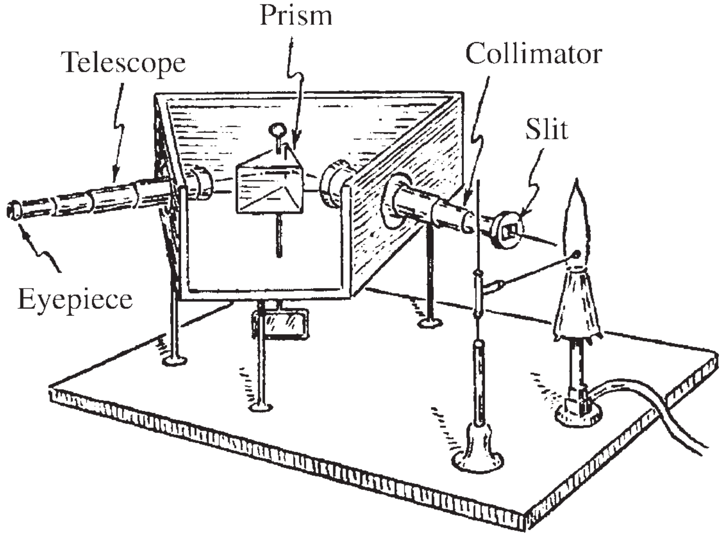

Figure 10.11 Bunsen's and Kirchhoff's spectroscope. Arranged from a figure in the original paper [10.11].

The results of Bunsen's, Kirchhoff's and other scientists' work regarding the eight dark lines that Fraunhofer had designated with letters, are collected in Table 10.1. Their positions in the visible spectrum are also given, as is the cause of their appearances.

Table 10.1 Fraunhofer's dark lines in the visible spectrum of the sun

Designation	Situated in color region	Cause of appearance
A	Dark red	Oxygen in the earth's atmosphere
B	Red	Oxygen in the earth's atmosphere
C	Red	Hydrogen in the sun
D_1, D_2	Yellow (doublet)	Sodium in the sun
E	Green	Iron in the sun
F	Blue	Hydrogen in the sun
G	Violet	Iron in the sun
H	Violet	Calcium in the sun

Most of the explanations date from after Fraunhofer's time

The successful work of Bunsen and Kirchhoff in spectroscopy is characterized by a pronounced ability to summarize their own research and that of other scientists. They could, in their small group, combine practical and theoretical knowledge within chemistry and physics. Spectroscopy as a tool arrived when it was needed. Bunsen and Kirchhoff themselves rapidly discovered the new elements *cesium* and *rubidium*.

Mosander (see Chapter 17 Rare Earth Metals) had discovered four new rare earth metals around 1840. For classical chemical analysis it was almost impossible to detect any further new RE elements. The spectroscope opened up new possibilities and about 1880 a series of new discoveries came. Around 1870 Mendelejev formulated the periodic system of the elements. Some places were empty. There was an expectation that they would be filled in the future as a result of "ordered" discoveries. Even here spectral analysis proved to be of value.

10.6
What Happens in the Atom During Spectral Analysis?

Spectroscopy developed rapidly after the achievements of Bunsen and Kirchhoff, but a knowledge of the real cause and origin of spectral lines was long in coming. It had to wait for the introduction of quantum theory and quantum mechanics. Two Danes took the decisive steps. In 1912 Niels Bjerrum studied the absorption of infrared radiation in gases. He showed that molecules absorb vibration and rotation energy in distinct quanta. Niels Bohr solved the problem of atomic spectra.

> Niels Bohr was born in 1885. His father was professor of medicine at the University of Copenhagen. As a boy Niels spent much time in his father's laboratory and grew up in an intellectually stimulating environment. Together with his brother Harald, a prominent mathematician when adult, he also had time for sport. Both of them became clever soccer players, though Harald was the better.

Niels Bohr was a research student with Rutherford in Manchester. In 1913 he modified his teacher's atomic model. According to Bohr the electrons can only stay in certain *stationary positions*, corresponding to distinct *energy levels*. When electrons move, by excitation, from one level to the next, certain energy quanta $E = h\nu$ (the Planck–Einstein equation) are absorbed. When the electrons move back to their ground-state positions these energy quantities are set free and emitted as radiation, with wavelengths corresponding to each energy quantum. Bohr also shocked his contemporaries by asserting that there it is impossible to make clear and illustrate what really happens to an electron during the transition from one energy level to another. The era had begun in which processes at an atomic level cannot be visualized but have to be described in mathematical terms.

10.7
Atomic Numbers and X-ray Spectra

An important breakthrough occurred in 1913 when the brilliant young scientist Henry G. J. Moseley, at the age of 26, discovered the relationship between the atomic number of an element and its X-ray wavelength: *The square root of the X-ray wavelength is a rectilinear function of the atomic number*. This opened up a completely new way to identify elements. Two years after this discovery, in 1915, Moseley was killed in the Gallipoli battle in the Dardanelles during World War I.

X-ray spectroscopy (Figure 10.12) uses the electron transitions that occur in the inner electron shells of the atom.

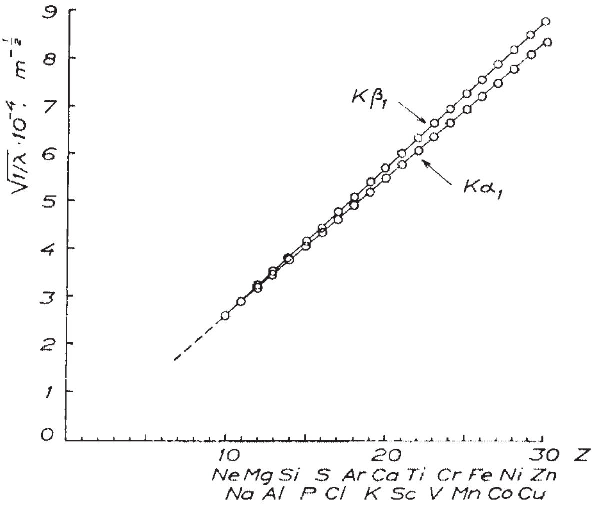

Figure 10.12 Moseley's law for the lines Kα and Kβ in the elements ^{10}Ne–^{30}Zn.

Today, spectroscopy has an extensive use for qualitative and quantitative analysis of complicated materials and this was so in the history of element discoveries since 1850.

> Moseley was one of several eminent scientists launched by Ernest Rutherford. He was able to show, in a paper of 1913, that X-ray frequencies are correlated to the nuclear charges of elements and thus also to the element's position in the periodic table. Moseley used this relationship to anticipate three new elements with atomic numbers 43, 61 and 75. They were discovered in 1937(technetium), 1945 (promethium) and in 1925 (rhenium).

10.8
Modern Spectral and X-ray Analysis

10.8.1
Emission Spectral Analysis

Important work to develop the quantitative technique and make it useful for analysis in many different applications was carried out by H. Lundegårdh [10.12]. He developed the technique for examination of nutrient solutions and plants, difficult to perform by traditional chemical analytical methods. Within biochemistry, the spectrometric technique opened up new possibilities for determination of essential trace elements, present in very low concentrations within the organisms. Many methods for analyzing water were developed, together with powerful spectroscopic methods for analytical investigations in mineralogy and metallurgy.

Spectroscopy today is a diversified science. The radiation that is generated during the excitation is traditionally split according to the wavelength by means of a quartz prism or a grating, nowadays usually the latter. For analysis of metals, wavelengths in the ultraviolet region are mainly used. The positions of the lines give information about the elements present, while their intensities, measured with a photocell for each element, express the concentrations. One single type of detector, the CID (Charge Injection Device) sensor, replaces the conventional set of photo-multipliers (Figure 10.13). The sensor is built up of 260 000 optically active elements.

In *optical emission spectroscopy* the ICP (Inductively Coupled Plasma) technique is a new variant for effective excitation, when very low concentrations need to be ana-

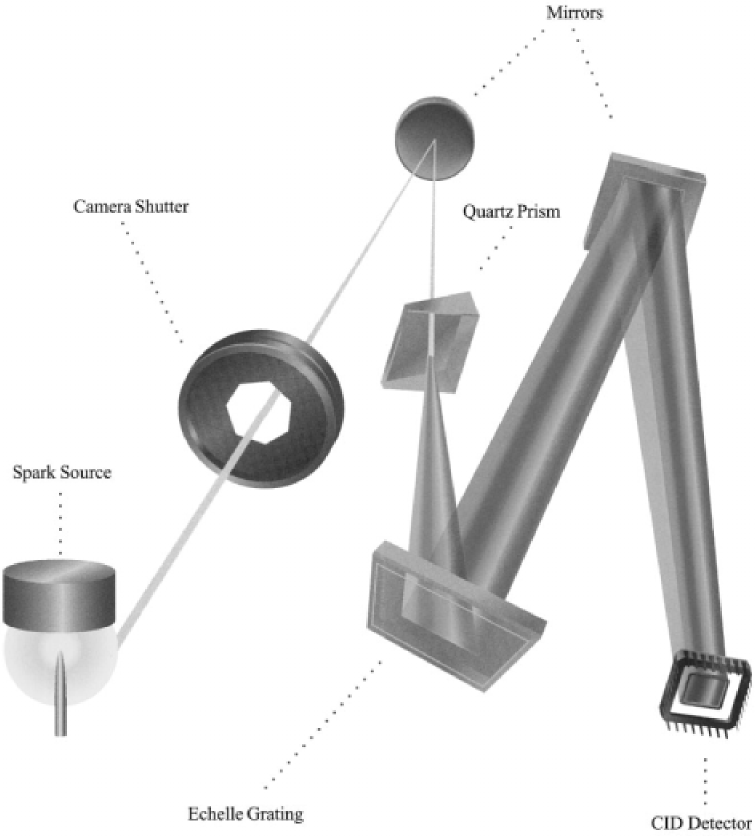

Figure 10.13 A modern Baird spectroscope with a CID detector. (Reprinted with permission of Thermo Optek Nordic AB Stockholm-Bromma.)

lyzed. It is used in the determination of rare earth metals in silicates.

10.8.2
Infrared Spectroscopy

A covalent bond (electron-pair bond) between the atoms in an organic molecule acts as a vibrating elastic spring. The vibration energy is quantized and can thus have certain distinct values but no intermediate ones. If an electromagnetic radiation passes through a solution containing organic molecules, such as fatty acids, and the radiation has a wavelength that corresponds to an increase in the vibration energy, the radiation will be absorbed. If, on the contrary, the wavelength does not match possible increases of the vibration energy the radiation passes without absorption. Radiation corresponding to possible quantum jumps in vibration energy is *infrared radiation* (IR), in the wavelength region 2–50 μm. IR is often used to identify oils by taking the “fingerprint” of an unknown oil.

10.8.3
Atomic Absorption Spectrophotometry

IR is an absorption method. Analysis utilizing absorption measurements can also be done with *spectrophotometry* and *atomic absorption spectrophotometry* (AAS). In the former method a monochromatic light (visible or ultraviolet) is passed through a solution containing a compound of an element with unknown concentration. The light absorption is measured and converted to concentration.

In the AAS method a solution is vaporized in an acetylene–oxygen flame so that the atoms of the unknown element are present in the flame. If, for instance, the intention is to determine the molybdenum concentration, radiation emitted from a cathode ray lamp with a molybdenum electrode is allowed to pass through the flame. If no molybdenum is present the radiation passes through unchanged. With molybdenum present some part of the radiation is absorbed (compare the Fraunhofer lines) and the absorption measures the content. The method (Figure 10.14) is suitable for the determination of very low concentrations in solutions.

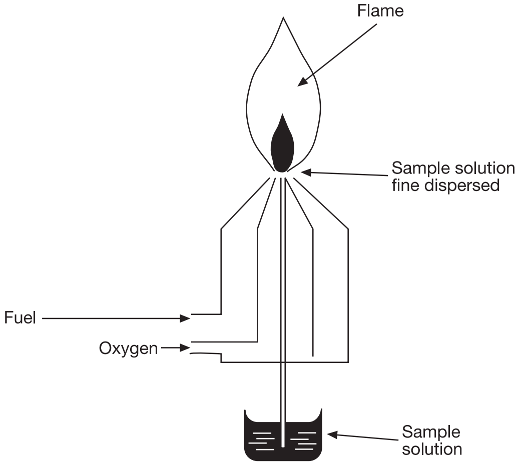

Figure 10.14 The principle of sample solution injection into the flame for AAS.

10.8.4
X-ray Fluorescence Analysis

During X-ray fluorescence analysis the sample is irradiated with X-rays. The sample then "replies" by emitting a secondary X-ray radiation. It is divided into wavelengths using the kind of "grating" provided by a natural crystal. Even in this case, the positions of the lines indicate which elements are present and their intensities the concentrations.

10.8.5
EDS and WDS Analysis

In connection with scanning electron microscopy (SEM), when the sample is irradiated with electrons, X-rays are emitted that may be detected either with a *wavelength dispersive spectrometer* (WDS) or an *energy dispersive spectrometer* (EDS). The latter is illustrated in Figure 10.15, showing the EDS recording of a quantitative analysis. The position along the horizontal axis shows which element has been detected. In Figure 10.15 the elements are W, Mo, Ti, Cr, Fe, Co and Ni. The intensities, on the vertical axis, indicate the contents. In this actual case the analysis revealed that the investigated alloy had the composition (%): Co 45.7, Ni 21.4, Cr 17.4, Fe 5.2, Mo 4.9, W 3.9, Ti 1.0.

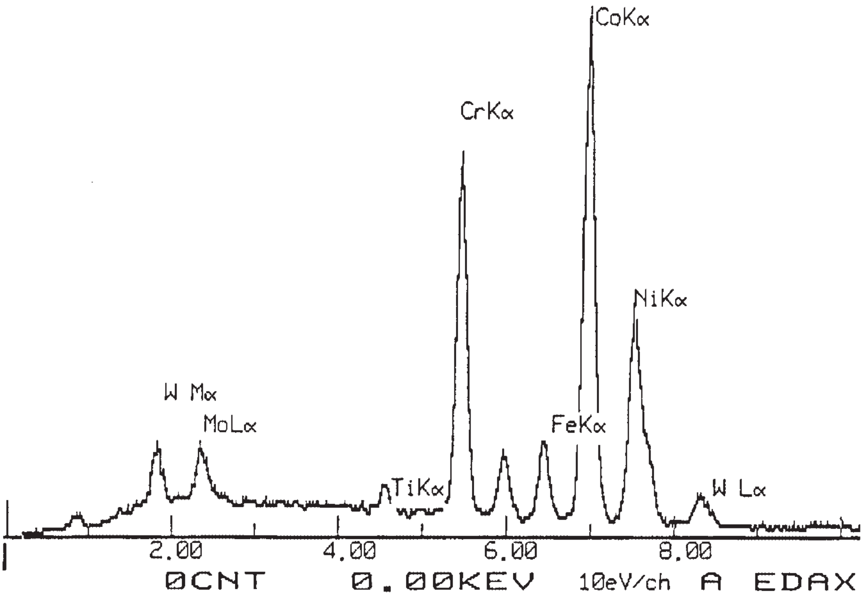

Figure 10.15 EDS analysis of the material in a new type of skate blade. (Reproduced with permission of Bodycote CMK, Karlskoga, Sweden.)

10.8.6
Special Methods for Surface Analysis

For analysis of surfaces special methods have been developed:

- ESCA – Electron Spectroscopy for Chemical Analysis
- AES – Auger Electron Spectroscopy
- SIMS – Secondary Ion Mass Spectroscopy.

10.8.7
Mass Spectrometry

The isotopic composition of an element may be determined in a mass spectrometer. Positive ions of the element are generated by a filament and accelerated by a cathode. Through a fine hole in the cathode the ion ray is projected into a tube in which the ions are influenced by a magnetic field. The ion ray is then deflected. Among isotopes with identical ionic charge the heavier ones take an "outside track", the lighter an "inner track" in the magnetic field. Different isotopes then hit different detectors (Figure 10.16). The intensities of the signals are transformed into electrical signals, which form the mass spectrum (Figure 10.17). The isotope ratios are also computed from these signals.

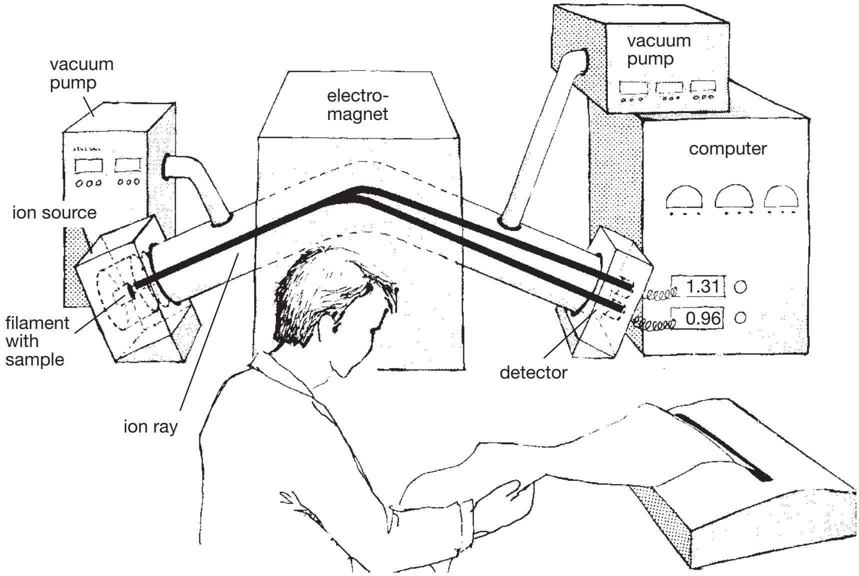

Figure 10.16 The principle of a mass spectrometer. (Reprinted from ref. [10.13] with permission.)

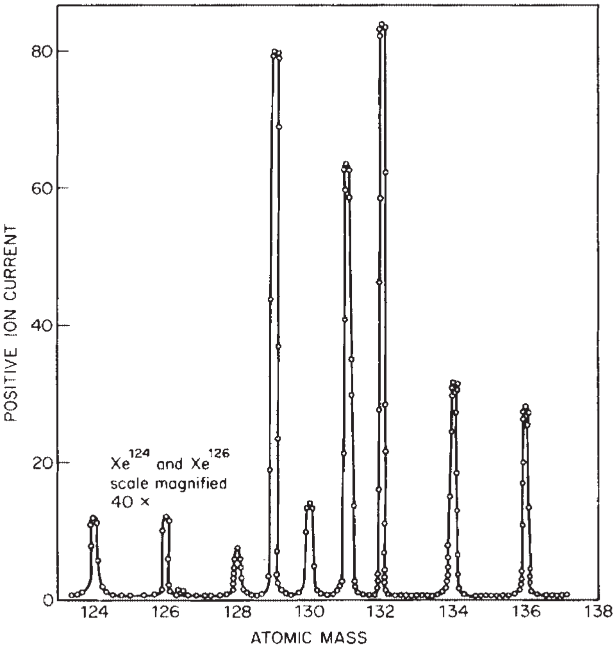

Figure 10.17 Detection of isotopes in the element xenon by a mass spectrometer. (W. J. Moore, *Physical Chemistry*, Longmans, London 1968, p. 447.)

10.8.8
Neutron Activation Analysis (NAA)

Many elements become radioactive when exposed to neutron bombardment inside a nuclear reactor. This is the basis of an extremely sensitive analytical method *neutron activation analysis* (NAA). The induced radioactivity is examined by γ-ray measurement. With computerized data processing it is possible to measure more than thirty elements simultaneously without chemical processing. For many elements and applications, NAA offers sensitivities of the order of parts per billion (pbb). Neutron activation analysis was discovered in 1936 when Hevesy and Levi found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons.

> NAA has been used in many applications. One very special one is the determination of the iridium content in the earth's crust and in a 1-cm thick clay layer round the earth. This clay layer was formed 65 million years ago and defines the boundary between the Cretaceous and the Tertiary periods of geological history. Shells of *foraminifera* are found in all marine environments and in abundance in the limestone above and below the special clay layer. But not in the layer itself. In addition it was shown by NAA that the iridium content of the limestone layers above and below is 0.3 ppb while the concentration in the layer is 10–40 pbb. This is the source of the theory of a giant asteroid collision with the earth at this time, a collision that brought the end of the dinosaur era.

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11
Sodium and Potassium

11.1 Na
Facts about Sodium

11.1.1 Na
The Element

Symbol:	Na
Atomic number:	11
Atomic weight:	22.99
Ground state electron configuration:	$[\mathrm{Ne}]3s^1$
Crystal structure:	Cubic bcc with $a = 4.29$ Å

11.1.2 Na
Discovery and Occurrence

Discovery: Sodium salts have been known from time immemorial. Sodium metal was discovered and isolated in 1807 by Humphry Davy in London.

Most important mineral: Albite, sodium feldspar $NaAlSi_3O_8$
Halite, rock salt NaCl (Figure M12)
Soda, sodium carbonate $Na_2CO_3 \cdot 10H_2O$
Trona $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$

Ranking in order of abundance in earth crust:	6
Mean content in earth crust:	23 600 ppm (g/tonne)
Mean content in oceans:	10 800 ppm (g/tonne)
Residence time in oceans:	$50 \cdot 10^6$ years
Mean content in an adult human body:	0.14%
Content in a man's body (weight 70 kg):	100 g

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11.1.3 Na

Chemical Characterization

Elemental sodium is a soft metal which can be cut with a knife. It reacts violently with water and it oxidizes immediately on exposure to air. Sodium salts impart a characteristic orange/yellow color to flames. The most important compound is sodium chloride, commonly known as “salt”. Other important compounds include sodium carbonate, known as washing soda, and sodium hydrogen carbonate (sodium bicarbonate), known as baking soda. Caustic soda is sodium hydroxide, also called soda lye. Sodium nitrate, known as Chile saltpeter, is used as a fertilizer. The element is also used as a cooling agent in special nuclear reactors (see Chapter 52 The Radioactive Elements). Sodium is a necessary constituent of plant and animal tissue and its ions have an important role in the conduction of messages in nerves.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
Na^{I} as in NaCl, NaOH, Na_2SO_4 and NaH	$Na(g) \rightarrow Na^{+}(g) + e^-$	496	$Na(g) + e^{-} \rightarrow Na^-(g)$
	$Na^+(g) \rightarrow Na^{2+}(g) + e^-$	4562	–52.8

Standard reduction potential: $Na^+(aq) + e^{-} \rightarrow Na(s)$ $E^0 = -2.713$ V

Electronegativity (Pauling): 0.93

Radii of atoms and ions: (WebElements™)		
	Atomic:	180 pm
	Covalent:	154 pm
	Van der Waals:	227 pm
	Na^+ (4-coordinate, tetrahedral):	113 pm
	Na^+ (6-coordinate, octahedral):	116 pm
	Na^+ (8-coordinate):	132 pm

11.1.4 Na

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
971 kg m^{-3} 0.97 g cm^{-3}	23.68 cm^3	371.0 K 97.8 °C	1156 K 883 °C	1226 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
141	142	–	–	–

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
–	$71 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
8	42	97	168	392	890

Mass magnetic susceptibility χ_{mass} at 293 K $+8.8 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
–	–	6.3 GPa	–

11.1.5 Na
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	2.60 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	98.0 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	107.3 $kJmol^{-1}$
Entropy S^0 at 298 K	51.21 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	22.46	28.23	29.92	28.80	20.81	20.92

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$4Na + O_2 \rightarrow 2Na_2O$	–752	–695	–553	–411	–

11.1.6 Na
Nuclear Properties and X-ray

Isotope range, natural and artificial 20–35

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{23}Na	Stable	100	+3/2	2.2175

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{23}Na
Reference compound	$NaBr/D_2O$
Frequency MHz (^1H = 100 MHz)	26.452
Receptivity D^P relative to ^1H = 1.00	0.0927
Receptivity D^C relative to ^{13}C = 1.00	530
Magnetogyric ratio, $radT^{-1}s^{-1}$	$7.0808 \cdot 10^7$
Nuclear quadropole moment, barn	0.1089

Characteristic X-radiation Z	 Element	 Kα_2 keV
10	Ne	0.848
11	Na	1.041
12	Mg	1.253

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	29.9
17.37 keV (MoKα_2)	3.07

Neutron absorption	Thermal neutron capture cross section	0.53 barns

11.1 K
Facts about Potassium

11.1.1 K
The Element

Symbol:	K
Atomic number:	19
Atomic weight:	39.10
Ground state electron configuration:	[Ar]4s^1
Crystal structure:	Cubic bcc with $a = 5.33$ Å

11.1.2 K
Discovery and Occurrence

Discovery: Potassium compounds have been known in terrestrial plants for centuries. Burning of wood and leaching of ashes gave potash, potassium carbonate. Marggraf in Berlin made clear the difference between soda and potash in the 18th century. Potassium metal was discovered and isolated in 1807 by Humphry Davy in London.

Most important mineral: Orthoclase and microcline $KAlSi_3O_8$ (Figure M66–67)
Sylvite (sylvine) KCl
Carnallite $KMgCl_3 \cdot 6H_2O$

Ranking in order of abundance in earth crust:	8
Mean content in earth crust:	$2.09 \cdot 10^4$ ppm (g/tonne)
Mean content in oceans:	399 ppm (g/tonne)
Residence time in oceans:	$6.3 \cdot 10^6$ years
Mean content in an adult human body:	0.2%
Content in a man's body (weight 70 kg):	140 g

11.1.3 K
Chemical Characterization

Elemental potassium is so soft that it can be cut with a knife. It oxidizes immediately on exposure to air and reacts violently with water. As hydrogen gas is evolved in this reaction and burns spontaneously, potassium is always stored under a liquid such as kerosene. Potassium and its salts impart a lilac color to flames. Potassium carbonate, also called potash or pearl ash, is an important raw material for making glass and soft soap. Caustic potash is potassium hydroxide KOH. Potassium nitrate KNO_3 occurs naturally as saltpeter and is used in matches, explosives and fireworks and in pickling meat. Potassium chloride KCl is an important potassium fertilizer. In living beings potassium ions are important for the transmission of nerve impulses.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
K^I as in KNO_3, $KClO_4$, KOH, K_2SO_4, and KH	$K(g) \rightarrow K^+(g) + e$-	418.8	$K(g) + e^- \rightarrow K^-(g)$
	$K^+(g) \rightarrow K^{2+}(g) + e^-$	3052	−48.4

Standard reduction potential: $K^+(aq) + e^- \rightarrow K(s)$ $E^0 = -2.924$ V

Electronegativity (Pauling): 0.82

Radii of atoms and ions: (WebElements™)		
	Atomic:	220 pm
	Covalent:	196 pm
	Van der Waals:	275 pm
	K^+ (4-coordinate, tetrahedral):	151 pm
	K^+ (6-coordinate, octahedral):	152 pm
	K^+ (8-coordinate):	165 pm

11.1.4 K
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
862 kg m^{-3} 0.86 g cm^{-3}	45.36 cm^3	336.7 K 63.5 °C	1032 K 759 °C	757 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
105	104	–	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
13.8	61	175	282	664	1600

Mass magnetic susceptibility χ_{mass} at 293 K	$+6.7 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	3.1 GPa	–

11.1.5 K

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	2.33 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	76.9 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	89.2 $kJmol^{-1}$
Entropy S^0 at 298 K	64.18 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	24.65	29.60	30.16	30.73	20.97	21.59

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4K + O_2 \rightarrow 2K_2O$	−641	−590	−450	–	–

11.1.6 K

Nuclear Properties and X-ray

Isotope range, natural and artificial 35–54

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{39}K	Stable	93.26	+3/2	+0.3915	—	—	—
^{41}K	Stable	6.73	+3/2	+0.2149	—	—	—
^{40}K	Active	0.01	−4	−1.298	$1.28 \cdot 10^9$ y	β^- EC or β^+	1.311 MeV 1.505 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{39}K	^{41}K
Reference compound	KI/D_2O	
Frequency MHz (^1H = 100 MHz)	4.666	2.561
Receptivity D^P relative to ^1H = 1.00	$4.76 \cdot 10^{-4}$	$5.68 \cdot 10^{-6}$
Receptivity D^C relative to ^{13}C = 1.00	2.72	0.0324
Magnetogyric ratio, $radT^{-1}s^{-1}$	$1.2501 \cdot 10^7$	$0.6861 \cdot 10^7$
Nuclear quadropole moment, barn	0.0601	0.0733

Characteristic X-radiation **Z**	 **Element**	 **Kα_2 keV**
18	Ar	2.956
19	K	3.311
20	Ca	3.688

X-ray radiation absorbed by the element **Incoming radiation energy**	 **Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	145
17.37 keV (MoKα_2)	16.4

Neutron absorption	**Thermal neutron capture cross section**	2.2 barns

11.2
The Alkali Metals – A Brief Outline

The elements in group 1 are hydrogen and the alkali metals lithium Li, sodium Na, potassium K, rubidium Rb, cesium Cs and francium Fr. The last one, francium, was discovered in 1939 by *Marguerite Perey* in Paris. It will be described in Chapter 52 The Radioactive Elements. The others will be treated in this and the following two chapters.

The elements Li–Cs are all similar but also show important differences. Their electron shells have a single s-electron in the outermost orbit, and they all form univalent ions in water solution. With water the metals react vigorously – almost explosively – with formation of hydroxides. Being the smallest of the alkali metal atoms, lithium has its 1s-electron near the core and so has the highest ionization energy. In fact it is less reactive than the other alkali metals and more like magnesium. The big cesium atom on the other hand is easiest to ionize (oxidize) and is, as a consequence, the most reactive of all metals.

The different alkali metals are the starting elements in each period and their atoms are the largest within that period. The atomic sizes and the fact that each of the atoms has only one valence electron are reasons for a rather weak metallic bonding and low melting and boiling temperatures. Again lithium, as the smallest, has the biggest interatomic forces and the highest melting and boiling temperatures. The atomic and ionic radii and their influences on some physical properties are shown in Table 11.1.

Table 11.1 Physical properties according to the fact tables for the alkali metals

	Lithium	**Sodium**	**Potassium**	**Rubidium**	**Cesium**
Atomic number	3	11	19	37	55
Atomic radius, Å	1.45	1.80	2.20	2.35	2.60
Ionic radius, Å	0.73	1.13	1.51	1.66	1.81
Melting point, °C	180.5	98	63.5	39	28.5
Boiling point, °C	1342	883	759	688	671
Flame color	Carmine	Yellow	Violet	Bluish red	Blue

See also the overview on page 874 of ref. [11.1]

11.3
Sodium and Potassium in Chemical History

11.3.1
Alkali and Alkali – Saltpeter and Saltpeter

Nowadays it is quite clear that the alkali metals sodium and potassium are the base for two groups of chemicals, alkalis and nitrates:

- Sodium carbonate Na_2CO_3, soda, soda ash
- Sodium hydroxide NaOH, caustic soda
- Sodium nitrate $NaNO_3$, Chile saltpeter or "soda niter"
- Potassium carbonate K_2CO_3, potash
- Potassium hydroxide KOH, caustic potash
- Potassium nitrate KNO_3, saltpeter or "niter"

Potash and soda were used in antiquity for washing. Potash was obtained by burning plants and leaching the ash. Soda came from Egyptian salt lakes. People at that time were, however, unable to distinguish between the two, both of them being called by one general name: *neter* in Hebrew, *nitron* in Greek and *nitrum* in Latin. This was the origin for the designation *natron*, used by the Arabic alchemists. The word *nitrum* later got the meaning potassium nitrate. The name *soda* is thought to have come from an Arabic word *suwwada*, a name for plants, the ash from which was used for soda extraction. At the end of the Middle Ages the designation "alcali"or "alkali"came into use, probably derived from the Arabic word *al-quali* or *al-qili*, ashes of the saltwort plant.

At the end of the 17th century interest arose in the difference between the natural products soda, sodium carbonate on one side and potash, potassium carbonate on the other. The former was called *mineral alkali*, the latter *vegetable alkali*. It was early established that there is a relationship between sea salt and soda and between saltpeter (potassium nitrate) and potash. Johann Bohn in Leipzig made one of the first systematic observations in 1683. He distilled nitric acid with sea salt present, to prepare *aqua regia*. Crystals with an obvious cubic structure were deposited in the retort (he called it "cubic saltpeter"; it was probably cubic sodium chloride). From the reaction between nitric acid and potash, without sea-salt present, he got beautiful crystals of quite a different form (presumably saltpeter, potassium nitrate, which crystallizes in the orthorhombic system in prismatic crystals).

In the 18th century the word *niter* was used and caused confusion. Was it soda or saltpeter? *Etienne-François Geoffroy* in Paris made a distinction, saying that soda is "niter or natron of the ancients"(sodium carbonate) while "modern niter" is saltpeter (potassium nitrate). He and others had observed how saltpeter is formed in the earth below barns by reaction between plants and stale urine. Soda on the other hand could not be manufactured, but was extracted from natural deposits in the earth and from natron lakes, for instance in Egypt.

> *E.-F. Geoffroy* was born in Paris in 1672, the son of a pharmacist. As a boy he learned different work of value for practical physics and chemistry, e.g. turning and grinding of lenses. At 20 he was sent by his father to Montpellier in order to study pharmacy. He did not follow his father's advice but instead studied medicine and became a professor of both medicine and chemistry in Paris. During his time of study he took the opportunity to travel in England, Holland and Italy and made contacts with contemporary authorities within science. In London he became acquainted with Sir Hans Sloane, president of the Royal Society. Etienne-François is known in the scientific literature as Geoffroy the Elder. He had a younger brother, Claude-Joseph, who became a pharmacist and is known as Geoffroy the Younger.

Geoffroy the Elder made many contributions to the development of chemistry in the 18th century. We meet him in connection with arsenic, antimony, zinc, manganese and ammonia. He is also well known for a table of chemical affinities.

Georg Ernst Stahl is well known as one of the founders of the phlogiston theory. He became a professor of chemistry at the University of Halle, Germany in 1693 and Royal physician in Berlin in 1716. As early as 1702 he had distinguished between *natural alkali* (soda) and *artificial alkali* (potash) after observing the differences in crystal form between their reaction products with nitric acid and sulfuric acid.

Andreas Sigismund Marggraf (1709–1782) was one of the great chemists in Germany during the 18th century. He was born in Berlin and studied medicine in Halle and chemistry and metallurgy in Freiberg. During 50 years of active research, Marggraf worked much with "earths" and alkaline earth metals. He discovered that clay contains a special oxide, aluminum oxide, he contributed to knowledge about phosphorus, and he prepared zinc metal by reduction of its oxide and sulfide. And with soda and potash he definitively showed that they are different substances. Yet they are both alkalis with similar reactions in water solutions, and both can be used for soap and glass manufacture, but they have different origins, different compositions and different properties. In 1758 Marggraf discovered that if soda is introduced into a flame it will be yellow while potash colors the flame red. He also observed that if firearms were discharged with gunpowder containing "saltpeter" made of soda, the flame was yellow. With gunpowder with common saltpeter made from urine, the flame was violet. At the end of the century, however, chemists were still confused about alkali. It was firstly a designation for sodium and potassium carbonate but also for the unknown elements with *metallic spirits* expected to be constituents of the substances. Sir Humphry Davy's discovery, in 1807, of the isolation of metallic sodium and potassium by electrolysis of melts, attracted immense attention. It became a sound basis on which the knowledge of both alkali metals and alkaline earth metals could be developed.

In the middle of the 18th century, professor Hermann Boerhave was active as a teacher in the University of Leiden near The Hague in the Netherlands. Today the State University of Leiden is one of the most distinguished universities in Europe. In his textbook *Elementa Chemiae* (1754) he wrote about saltpeter and its use for gunpowder:

> May it please Heaven that men, no longer ingenious in finding means of destroying one another, may cease from cruelly waging war on each other and no longer employ to their own destruction the beautiful inventions of a science in itself so salutary. Therefore I feel compelled to remain silent regarding several other discoveries more dangerous and more detectable.

As we all know his gentle expectation to Heaven was not fulfilled.

11.3.2
Potash

Potash, potassium carbonate, became early known and in great demand as a raw material for manufacturing glass and soap. The valuable product was extracted by burning wood, leaching the ash and filtering and evaporating the solution. Prominent glassmakers in Bohemia, Poland, Germany and Austria got potash from boilers in Hungary. At the end of the 18th century the deliveries almost ceased, as the forests had been devastated.

Potash from North American forests in New England was used for the domestic industry but in the 18th and 19th centuries was also exported to the European glass manufacturers. Browne [11.2] gives a detailed description of these American activities, and says, “the manufacture of potash constituted one of the greatest economic crimes in the history of the United States”. From an agricultural point of view the shipment for two centuries of a most valuable fertilizing ingredient was an enormous wastage, “which is incalculable”.

> Early attempts had been made in all British colonies on the Atlantic seaboard to stimulate the production of potash for export to European countries. Many of the early attempts failed, but in the middle of the 18th century production started. A pamphlet was distributed in 1765, describing the Hungarian process with illustration of the furnaces. The trees that were found to give the best results in burning for potash were hickory, oak, beech, birch, elm, walnut, chestnut and maple. Evergreen woods, such as pine, were avoided. The wood was cut into lengths of 8–9 feet and burned. Water was then filtered through the ash into large iron kettles. After evaporation the black mass – black because of carbonaceous matter – was subjected to red heat in a cast-iron kettle. The white product, still containing a great amount of different impurities, was delivered as “American potash of commerce”.

In old native American cultures, potash from certain plants was used as a protection against putrefaction of foodstuffs.

European chemists became involved in disputes as to whether the alkaline substance in potash was present in the plant or if it was formed in connection with the burning. The latter opinion was generally accepted. *A. S. Marggraf* showed (in 1764) that potash could however be extracted from plants without preceding burning. In France, *Pierre-Joseph Marcquer* (1718–1784) was educated in medicine but devoted interest and work to chemistry and became an important member of the circle round Lavoisier. His textbook *Dictionnaire de Chemie* (1778) was well known and translated into many languages, German among them. In the book he mentioned the problem with vegetable alkali. He pointed out that when plants decompose without burning, potassium tartrate and oxalate are formed. Plant residues from which these substances had been removed also gave also much less potash after burning. Carl Wilhelm Scheele had made similar observations.

11.3.3
Soda

In the 18th century soda was rare and had few applications. Mary Weeks, however, writes about important findings around 1800. Two big deposits at the eastern Mediterranean coast became known. *Luigi Palcani* published the results of two analyses of "natron" samples, one from Constantinople, one from Alexandria [11.3]. Both contained mainly sodium carbonate. C. Bagge was the Swedish consul in Tripoli on the African Mediterranean coast. He described a thin white crust covering the ground at Fezzan in the Sahara [11.4]. The white stuff was delivered to Egypt, Tripoli and to "the land of the Negroes" to be used in bleaching and soap making. Near Cairo and Alexandria lies *Wadi Natrûn* (Natron Valley), below sea level. Lakes in the valley, formed by water from the Nile, dry up in the summers, giving great deposits of natron. In 1784, *Georg Adolph Suckow* described the preparation of soda by burning certain marine plants and leaching their ashes [11.4]. Soda manufacture based on this technique occurred at Alexandria in Egypt, Alicante in Spain, and along the coasts of Italy and France.

11.3.4
He Fell Into an Ecstasy Over an Element ...

Humphry Davy was born in 1778 near Penzance in Cornwall, England. At 17 he was apprenticed to a surgeon, who was also an apothecary. Gradually he began to study natural philosophy and chemistry. The English translation of Lavoisier's Traité *élémentaire de chimie* (1789) now was available and became the textbook for young Humphry. It guided him directly into modern chemical thinking – chemistry without phlogiston.

Around 1790, *Luigi Galvani* and *Allesandro Volta* were working with electricity in Italy. This culminated in 1800 with the construction of the voltaic pile, built up of a large number of copper and zinc plates, separated by felt discs, soaked with salt water. The copper plate at one end of the pile was the positive pole, the zinc plate at the other end the negative. The pile became very important for chemistry and was the basis of electrochemistry.

Davy became interested in the new electrochemistry. In 1801, at 23, he was employed as an assistant lecturer on chemistry at the Royal Institution, founded by the Royal Institute and chartered in 1800 by King George III. The young Humphry astonished both principals and students by teaching Lavoisier's modern chemistry and Galvani's and Volta's quite new electrochemistry.

Davy had absorbed the increasing information about alkalis from the century just passed. But he also saw clearly the lack of understanding. What is present in soda and potash? Which elements colored the flame yellow and violet respectively? Were metals hidden in the substances, and if so which? With his voltaic pile Davy could precipitate copper by electrolysis in his laboratory. Thus, Davy reasoned, let us use the same method to isolate the unknown substances from the water solutions of caustic soda (sodium hydroxide) and from caustic potash (potassium hydroxide). The current passed but it was hydrogen gas and not metal that formed at the cathode. At the anode oxygen was discharged. His efforts resulted in electrolytic decomposition of water, nothing else. He realized that he had to change the method and use molten electrolytes. On 6th October 1807 he electrolyzed molten caustic potash. The cell was the simplest conceivable. Solid potassium hydroxide was placed in a platinum spoon. The spoon was connected to the negative pole of a voltaic pile. The positive pole was connected to a platinum wire, held against the solid hydroxide, avoiding direct contact with the platinum spoon. Potassium hydroxide in contact with the air absorbed a little moisture and became conductive and an electric current began to flow. Heat was developed and some hydroxide melted. At the contact line between melt and platinum spoon Davy saw that small balls with a metallic luster were formed. They were very like droplets of mercury and he realized that he had found what he and many prominent chemists had looked for: the metal in potash and thus also the metal in saltpeter. It is told that Davy became excited to rapture when he saw the new element grow into small spheres and when he saw how it behaved in contact with water. The globules swam around with a hissing sound and burned with a beautiful blue–violet light.

Davy was the first to see this new metal. As he had prepared it from potash he gave it the name *potassium*. Some days later he repeated the experiment, this time with sodium hydroxide. Again a metal was formed at the negative pole, a metal which Davy named s*odium*.

Davy's preparation of potassium and sodium became the starting point for the manufacturing technique *fused salt electrolysis*, which is so important at the present time. He soon used the method to obtain the alkaline earth metals magnesium, calcium and barium.

11.3.5
A French Alternative

Electrolysis was a laboratory method at the time of Davy's discovery, and not suitable for preparing large quantities of sodium and potassium. Considerably greater metal amounts could be produced with an alternative method, developed by *Joseph-Louis Gay-Lussac* (1778–1850) and *Louis Jacques Thenard* (1777–1857) in Paris. They were both professors at the École Polytechnique. In their sodium method, from 1809, sodium hydroxide was mixed with iron filings. When the mixture was heated to a very high temperature, metallic sodium distilled off. A corresponding method was used for potassium.

Gay-Lussac became known for his studies on the properties of gases. In 1802 he formulated a law of gases that is still associated with his name. He found also that volumes of gases involved in a chemical reaction are in the ratio of small whole numbers. In 1804 he made balloon ascensions to study magnetic forces and to observe the composition and temperature of the air at different altitudes.

Thenard was, together with Gay-Lussac, the leading chemist in France in the beginning of the 19th century. He discovered hydrogen peroxide and many organic chemicals. His name is still commemorated in the valuable pigment *Thenard's blue*, cobalt blue. He prepared it by heating clay with cobalt phosphate. Through his textbook *Traité de chimie élémentaire – théorique et pratique* he exerted a great influence on the chemistry of his time.

11.3.6
Why the Names Sodium and Potassium?

In ancient times, substances with cleansing effects were obtainable in two ways: (1) As *soda* from Egyptian salt lakes; (2) by burning plants to yield *potash* and leaching the ash with water. When the differences between sodium and potassium compounds gradually became clear during the 18th century, the base of the former was, as already mentioned, called *alcali minerale* or *natron*, while the base for the latter was called *alcali vegetabile* or *kali*. In the light of this it would be logical, as shown in Table 11.2, to name the metals either *sodium* and *potassium* or *natrium* and *kalium*.

Table 11.2 Reasons for the names of the two most important alkali metals

Compounds of	Ancient designation	Logical element name	18th century designation		Logical element name
			Alkali name	Alternative	
Sodium	Nitron in soda	*Sodium*	Alcali minerale	Natron	*Natrium*
Potassium	Nitron in potash	*Potassium*	Alcali vegetabile	Kali	*Kalium*

When the discoverer Humphry David prepared his first alkali metals from caustic potash and caustic soda he found the names *potassium* and *sodium* natural, and so it remained in all the English-speaking countries. In the German and Swedish languages the element names *natrium* and *kalium* were chosen. Owing to the great influence of Berzelius on the choice of element symbols, Na and K became designations for the two elements. A IUPAC decision means that these symbols are common to all countries irrespective of the element names in their own language.

11.4
Chemical Engineering in a Dramatic Era

11.4.1
Alkalis and Salt – Essential Commodities

Soda and potash and other compounds of the alkali metals have in history been the reason for opening up trade routes and have also given rise to political struggles. In both these respects they have competed with the precious metals gold and silver. In human life they are absolutely necessary, which can scarcely be said about gold and silver. An everyday product like sea salt, sodium chloride, is important in human housekeeping today, and was to a still greater degree earlier, before the time of refrigerators and freezers. During the Napoleonic wars, at the beginning of the 19th century, England maintained a blockade that obstructed the supply of important goods, including salt, to the European continent. Salt was important for flavoring but above all for preservation. The need for salt in the local society had to be met by a great number of "salt boilers" on the coasts of the continent. At the end of the 18th century, salt had also been an important raw material for the growing chemical industry and indirectly for every country's preparedness for war.

11.4.2
Gunpowder and Soap in Competition

Gunpowder contained in former times 10% sulfur, 15% charcoal and 75% saltpeter, potassium nitrate. In China gunpowder was known 2000 years ago; in Europe it had been used since the 14th century. Owing to its high content of saltpeter, every country was dependent on this substance for its warfare and its survival as an independent nation.

In early saltpeter production a "nitrous earth" was essential. This was the result of the decay of organic and animal matter over a long period. Such decomposition, in the presence of potassium and calcium carbonate, formed potassium and calcium nitrate. According to Agricola [11.6] this "slightly fatty earth with an acrid and salty taste", was mixed in a vat with a powder made up of ashes from oak together with unslaked lime. Water was poured in to fill the vat. The calcium nitrate present in the earth reacted with the potassium carbonate in the oak ash to form potassium nitrate:

$$Ca(NO_3)_2 + K_2CO_3 \rightarrow CaCO_3 + 2KNO_3.$$

The calcium carbonate precipitated and could be removed by filtering. The solution contained potassium nitrate formed in this reaction and also present from the original decay process. Water was evaporated leaving white saltpeter to crystallize.

Potash from terrestrial plants was essential to carry this process through and became a strategic product. As it was also used for manufacturing glass and soap, competition arose. At the end of the 18th century the situation became critical, with a lack of potash because of extensive deforestation in central Europe and high import costs from Scandinavia, Russia and North America. The alternative material, soda, was available as a natural product only to a lesser extent and had to be imported from the Mediterranean countries. Laboratory methods to prepare soda were known, but no usable production technique, capable of replacing the imports, was developed. It was quite clear at this time that sea salt and soda had the same main component, the former being available in enormous quantities, the latter a commodity in short supply. In 1783 Louis XVI, king of France, ordered the Academy of Sciences to announce a prize of considerable value. It should be awarded to a person who may "discover the simplest and most economical method of decomposing sea salt on a large scale, in order to secure from it the alkali that serves as its base in a state of purity uncombined with acid or other material; the cost of this mineral alkali not to exceed the price at which it can be extracted from the better foreign sodas". The prize was offered each year until 1788 but was never given to an inventor. The academy had ceased to exist before Leblanc's process was developed.

11.4.3
Leblanc's Soda Process – The Birth of Industrial Chemistry

It is difficult to exaggerate the importance of a large-scale process for making soda from common salt. Leblanc invented his soda process in 1791, which is considered to mark the start of industrial chemical technology. He was just an inventor, not trying to make history – but he did.

11.4.3.1 Opportunity Makes the Man

Nicolas Leblanc was born in 1742 in Ivoy le Pré, a small town in the Departement du Cher in France. As a boy of nine he was fatherless but was brought up by a friend of his father, Dr. Bien in Bourges. He was educated in medicine, qualified as a surgeon and practiced in the medical profession [11.7].

> At the Collège de France in Paris a professor of chemistry *Jean Darcet* (*d'Arcet*) had been active since 1775. He was granted the right to teach in French, in contrast to the general custom of using Latin. This chemist was a man with rooted in the early chemical industry, for instance in porcelain manufacture in Sèvres and in the Royal Mint. He became a successful teacher, and famous scientists including Berthollet, Vauqelin, Forcroy and Haüy listened to and debated with this professor, who had so much knowledge about applied chemistry.
>
> Leblanc began to attend the lectures, his interest for the practical applications of chemistry was strengthened and he also got to know Darcet, Berthollet and other men with influence on science and technology.

Nicolas Leblanc's destiny was formed by a remarkable coincidence. To earn his living he applied for a post as family doctor with the Duc d'Orleans and was employed in 1780. The Duc was interested in his health but also in industrial development and had invested money in a sugar refinery and a cotton mill. Why not also soda manufacture? After a period of introductory cooperation and complementary studies of chemistry in the Collège de France, Leblanc's own mind became more and more taken up with the application of chemistry to industrial problems. He started to work on the soda problem in about 1784. The prize, promised by the Academy of Sciences, certainly contributed to Leblanc's zeal to concentrate his efforts on developing a method for manufacturing soda. He had been informed that sodium sulfate could be reduced by carbon at high temperature and with this reaction in mind he developed a plan for an experimental development. When Leblanc was convinced that his plans were realistic enough, he asked his employer to finance a full-time investigation. The Duc met this proposal favorably, and Leblanc was given his own laboratory space at the Collège. He was also guaranteed a positive interest from professor Darcet.

11.4.3.2 The Leblanc Soda Method

Nicolas, now at the age of about 40, started. As his co-worker he had *J. J. M. Dizé*, a chemist, who, like Leblanc himself, had been educated by professor Darcet. They developed a technique known as the Leblanc process. After much trial and error, omitted in this description, a technique with the following characteristic features was developed (Table 11.3):

Table 11.3 The different steps in Leblanc's soda process

Reaction No.	Process step	Formula
1	Manufacture of sodium sulfate from sea salt, sodium chloride	$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$
2	Reduction of sodium sulfate to sodium sulfide	$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$
3	Transformation of sodium sulfide to soda	$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS$

In practice the sodium sulfate was carefully mixed with limestone and carbon in the ratio 100:100:50 but the proportions could be changed according to the actual equipment. When the mixture was heated at 900°C, reactions 2 and 3 occurred. The process was at first carried out in crucibles, later in a reverberatory furnace and finally in a rotary kiln. After cooling, the mass could not be dissolved in water, as then calcium sulfide would hydrolyze. Instead the material from the kiln was dissolved in an unsaturated soda solution. The result was a saturated soda solution and a precipitated layer of calcium sulfide and carbon.

On 27th January 1791 Leblanc, Dizé and the Duc d'Orleans entered into a definite partnership. The Duc's steward Henri Shee was also a member of the "board". Shee was expected to safeguard the interests of the Duc. A patent was granted on 25th September 1791. It was a secret patent, meaning that no public disclosure was needed. Leblanc was granted the exclusive right to work or license his process for a period of fifteen years.

The soda works were built at St. Denis, a small town near Paris. The Duc d'Orleans was the main owner but Leblanc and Dizé were to oversee the production and they were guaranteed good salaries. Leblanc was satisfied. He could devote himself to practical chemistry, he was recognized as the inventor of an important process and he could provide for himself and his family. The Bastille had been stormed and the social system was in confusion. Yet – whatever regime held the power – soda would be necessary for making glass and for making soap for the laundries. And potash, with its potassium content, could go entirely to the manufacture of gunpowder. So, just to get the work done was Leblanc's job.

11.4.3.3 In the Time of Revolution

Leblanc had underestimated the power of the revolutionary storm. In April 1793 the Duc d'Orleans was arrested and in November he was guillotined and his property confiscated. Thus the soda factory now belonged almost entirely to the state. And for a little while the basis for Leblanc's existence was altered. Would the new state accept the patent? Would Leblanc be allowed to manage the factory? Would he be paid for his work?

The "Commission of Powder and Arms", a subdivision of "The Committee of Public Safety", was given power over all materials related to the production of munitions. Guyton de Morveau, the famous scientist, was the leading member of the Commission. It was decreed:

> All citizens, who have established factories or who obtained patents for invention to make soda from salt, are hereby ordered ...to make known to the Commission within two decades (20 days) the location of these plants, the quantity of soda they put on the market, how much they can furnish, and the date at which they can start their deliveries.

Less than three months after the execution of the Duc, Leblanc got the following letter, in which the new power further announced its attitude:

> Citizen: The Committee of Public Safety is now concerned with securing a large-scale production of soda. It desires to collect all the knowledge possessed by those who have worked on this commodity, particularly on its production from common salt. I know that you have been in a position to contribute to the formation of this new art, whose product will free potash for the manufacture of saltpeter. Accordingly I request that you present yourself to this Commission, to confer on this topic.

What could Leblanc and other soda chemists and manufacturers do? Leblanc appeared before the Commission, described and explained the processes, and handed over drawings of furnaces and other equipment (Figure 11.1).

After that, he had confidently expected to be employed by the Commission to direct the soda works for the benefit of the Nation. Instead he was ordered to move out of the premises and the factory was closed. The Commission took money and accounts. Finished products and raw materials were sold, together with the horses and carts. No payments for salary were made to the three partners in the management. From this time, his life was a continuous struggle against poverty. Leblanc was appointed to different low-paid posts, among them a duty to list and collect into warehouses the scientific materials coming from those who had emigrated or been executed. In the afternoon of 8th May 1794 a procession of prisoners was brought to the guillotine. One of them was Lavoisier. Leblanc had now to make an inventory of

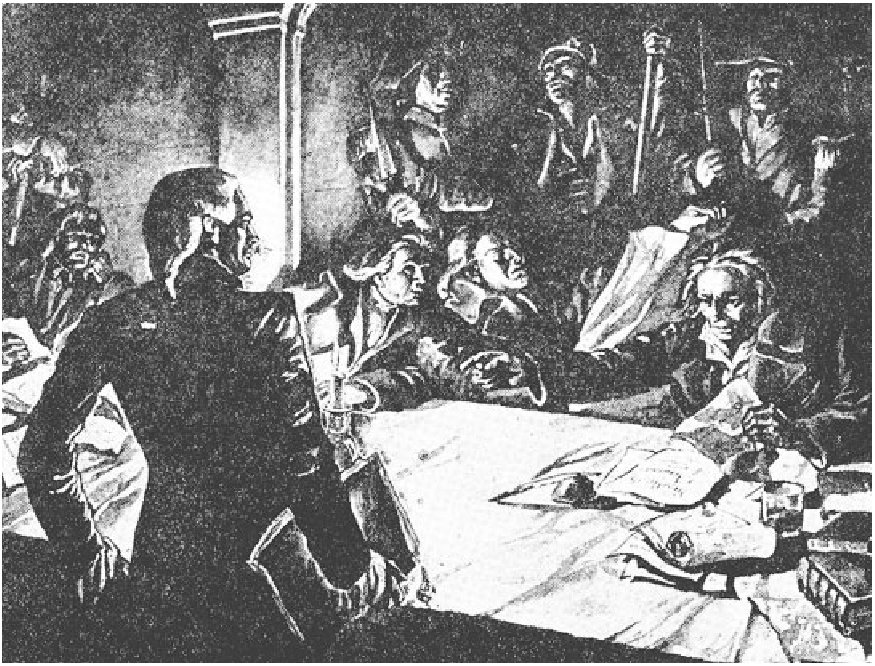

Figure 11.1 Leblanc leaves his patent to the Commission of Powder and Arms [11.7].

Lavoisier's laboratory and mansion on the Boulevard de la Madeleine. In his official report with lists of all items, he made a comment on objects without labels:

> Possibly some of these unlabled objects were used in certain important operations, which may be found in the various works of Lavoisier, who, as is well known, treated chemistry and many other branches of science and art with rare intelligence and success.

Obviously he did not dare to express himself too positively about an "enemy of the state". But in an unpublished essay he wrote:

> ...What will now be the inspiration of our better men, and how can the few of them left to us make themselves heard? I grant you that sparks of the genius of these savants, whose loss France is going to regret for a long time, still glow in the minds of some of their disciples or contemporaries ... This genius for organizing and building is rare, but Lavoisier had it, and so created modern chemistry, to which we owe so much, and which is preparing for us still more discoveries and important reforms.

There are no indications that Lavoisier and Leblanc had met. As a chemist, Lavoisier was well known throughout the world at a time when Leblanc was no more than a modest physician with chemistry as a hobby. They must, however, have known of each other. The age difference was less than one year. They each headed, in fact, one part of the chemical revolution at the end of the 18th century. With Leblanc, industrial chemistry started, large-scale production, and the synthesis of products, the supply of which is insufficient in nature. The political revolution took both their lives, one directly by the guillotine, the other indirectly by imposing successive difficulties on him that in the long run proved unendurable.

11.4.3.4 **…the Life Was at Stake**

In 1795 Berthollet wrote to Leblanc: "The Committee of Public Safety is of the opinion that you are entitled to compensation in proportion to the disinterestedness of which you have given proof in revealing to it your process for making soda." In 1799 it was also decided that Leblanc should receive 3000 francs from public funds. 600 were paid immediately and the rest were to be paid later when the financial position of the state had improved. Leblanc never got his 2400 francs. In his difficult situation he now presented a number of letters to authorities, ministers and research colleagues. Finally, in April 1801, his persistence and reports in his favor bore fruit. The Minister of Finance ordered that the works at St. Denis should be returned to Leblanc on certain tough conditions. The investment of 80 000 francs that the Duc d'Orleans had made should be paid back with interest. In addition, the factory had been closed for several years and needed considerable restoration and modernization. Leblanc with his family moved back to their old house in the factory area and began the nearly hopeless task. But, he did not succeed. He now got stuck in bitterness and again started attempting to influence the authorities. He claimed that at least his demand for 2400 francs from 1799 should be paid. But the bureaucracy was inexorable. Now he had no strength to continue and on 16th January 1806 he shot himself to death.

11.4.3.5 **… But the Process Lived on**

The following year, in 1807, the big glass manufacturer St. Gobain started to use Leblanc soda for mirror glass. The method spread over the European continent and reached a production maximum of 545 000 tonnes in 1880. Then the Solvay method, the ammonia–soda process, gradually took over.

The French debt of 2400 francs was to be paid when the finances of the nation made it possible. The Republic had got better finances. In the Saint Denis suburb of Paris, where Leblanc's soda factory was built, the giant Stade de France was ready for use in 1998 after an investment of 2 600 000 000 francs. When, on 12th July 1998, France exulted there at the victory over Brazil and its world championship in soccer, certainly no thoughts were devoted to the fact that Saint Denis is associated with the republic's outstanding debt owing to citizen Leblanc.

11.5
Sodium in Our Time

11.5.1
Occurrence

11.5.1.1 Feldspar

Sodium is present to a large extent as feldspar in the earth's crust. Plagioclase is a group of the general formula $(Na,Ca)Al(Si,Al)Si_2O_8$ with the extreme minerals being albite $NaAlSi_3O_8$ and anorthite $CaAl_2Si_2O_8$. The plagioclase series is arbitrarily subdivided and named *albite, oligoclase, andesine, labradorite, bytownite,* and *anorthite,* according to the increasing mole fraction of anorthite. Plagioclase minerals are among the most common rock-forming minerals.

11.5.1.2 Sodium Chloride

The abundance of sodium chloride in the oceans is well known but common salt is also found in:

- "Brine lakes", which no outlet to the sea and contain a high concentration of dissolved salts (mainly sodium chloride). Examples are the Great Salt Lake in Utah, and the Dead Sea in the Near East;
- Deposits from dried-up salt lakes;
- Halite (common salt, rock salt). A cubic-crystalline, fibrous or granular aggregate of sodium chloride, NaCl (Figure M12). It is formed by the drying of enclosed bodies of salt water. Subsequently the halite formation has often been buried by other sedimentary deposits and is often associated with clay. Beds of halite range in thickness from a few meters to 30 m. Deeply lying rock salt formations may penetrate sediments above owing to their plasticity and low density, and form salt domes. Halite is widely disseminated over the world; in the United States notable deposits are found in New York, Michigan, Ohio, Kansas, New Mexico and Utah, in Europe at Stassfurt (rich in potassium and magnesium) in Germany and at Wieliczka in Poland.

Australia is without rock salt deposits, but has nevertheless been a big exporter of sodium chloride to Japan, Korea and Southeast Asia. Salt is extracted from the sea. In the very warm region 1300 km north of Perth the water evaporation is high because of the solar radiation, while the rainfall is small. Water from the sea is pumped into big basins for pre-concentration. The water evaporation means that less-soluble calcium sulfate, gypsum, is precipitated. The mother liquor, almost free from gypsum and saturated with sodium chloride, is transferred to production basins, in which pure sodium chloride may crystallize during a whole year. After this crystallization ca. 25% of the total NaCl quantity and the whole content of potassium and magnesium salts in the original seawater are left in solution. It is saved as a future reserve for potassium and magnesium extraction.

11.5.1.3 Sodium Nitrate

Chile saltpeter is composed of sodium nitrate, $NaNO_3$. It is found in South America, particularly in Chile. It occurs in beds that vary in thickness from 15 cm to 3.6 m. These beds, called caliche, are interspersed with deposits of gypsum, sodium chloride and other salts, and sand. The caliche is quarried and purified in Chile before the product is exported. It is used extensively as a fertilizer but not in the manufacture of gunpowder because of its deliquescence.

11.5.1.4 Sodium Carbonate

Very much of the soda used today, especially in the USA, is obtained from natural sources, such as the mineral *trona* $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, found in vast deposits in western Wyoming and in dry lakes in California.

11.6
Manufacture

Sodium and most sodium compounds are manufactured, directly or indirectly, from the earth's giant supply of sodium chloride.

11.6.1
Sodium Chemicals – Two Examples

Sodium compounds are among the most used within the chemical industry. Annually about 30 million tonnes of *sodium hydroxide* (caustic soda) NaOH are manufactured in the world. The bulk is produced by electrolysis of a common salt solution, with chlorine and hydrogen as important by-products. This process is described in Chapter 50 Halogens.

Sodium carbonate (soda) Na_2CO_3 is, next to caustic soda, the most important among the industrial sodium chemicals. As described above, manufacturing started with the Leblanc process. This was, at the beginning of the 20th century, superseded by the less expensive Solvay process, invented by the Belgian chemist Ernest Solvay. About 25 million tonnes of soda are produced annually with the Solvay process. Increasingly, however, sodium carbonate is being obtained from natural sources, such as soda lakes (see above).

The success of the Solvay process lay in the efficient use of the ammonia obtained as a by-product in the coke industry. The key step involves the reaction of ammonia gas and carbon dioxide gas in a saturated sodium chloride solution. That results in the formation of sodium hydrogencarbonate (bicarbonate) $NaHCO_3$ and ammonium chloride. The sodium bicarbonate precipitate is filtered from the solution, dried and heated to form sodium carbonate. Carbon dioxide is obtained by heating limestone $CaCO_3$ in a lime kiln. One noteworthy feature of the Solvay process is the effective use and recycling of materials. The only ultimate by-product is calcium chloride $CaCl_2$, for which the demand is limited. To some extent it is used for deicing roads in winter and for dust control on dirt roads in the summer.

Several hydrated forms of sodium carbonate are manufactured, chief among which is the decahydrate ($Na_2CO_3 \cdot 10H_2O$).

11.6.2
Sodium Metal

A mixture of sodium chloride (28%), calcium chloride (26%) and barium chloride (46%) melts at 600°C. During electrolysis of this melt, sodium metal is formed at the (steel) cathode and chlorine at the (graphite) anode. A special arrangement prevents the sodium from reacting with chlorine and reforming sodium chloride. The produced sodium is liquid. For delivery it is cast into pieces weighing 1–5 kg, and packed in barrels of special steel.

11.7
Uses of Sodium Metal and Its Compounds

45% of manufactured sodium carbonate is used within the glass and ceramics industries, 20% in the manufacture of soap and other washing compounds. Large quantities are also used for making pulp in paper production. As the carbonate ion forms insoluble compounds with the Ca^{2+} and Mg^{2+} cations that make water hard, soda may be used as a water softener.

Metallic sodium is produced in a quantity of more 100 000 tonnes annually. Its most important use is, however, disappearing. The antiknock petrol additive lead tetraethyl $Pb(C_2H_5)_4$ is manufactured by way of a lead–sodium alloy, and the demand is decreasing owing to the changeover to lead-free petrol. However – because of its affinity for chlorine – sodium metal is used to an increasing extent in the production of the metals titanium, niobium and tantalum by reduction of their chlorides. Within organic chemistry, much sodium is used in reduction processes during the manufacture of dyestuffs such as indigo and of pharmaceutical products and vitamins.

New uses for sodium are continually being found. A special type of modern batteries uses sodium as the positive pole and sulfur as the negative. The electrolyte is solid alumina through which sodium ions can migrate. In use (discharging) sodium ions pass through the elctrolyte and combine with sulfur to form a polysulfide. The working temperature is 300°C, which leads to materials and handling problems. Another sophisticated application is as a coolant. Liquid sodium metal has a low viscosity and good conductivity for heat. Because of that, it has turned out to be a good heat transmitter in breeder reactors (see Chapter 52 The Radioactive Elements).

11.8
Potassium in Our Time

11.8.1
Occurrence

11.8.1.1 Feldspar-type Minerals in the Earth's Crust

Potassium is the eighth most common element in the earth's crust. It is present in the feldspar minerals orthoclase and microcline, both with the formula $KAlSi_3O_8$. Orthoclase is a white, cream-yellow, pink or gray mineral. Microcline is white to gray, brick-red or green (Figure M66–67). They are both common rock-forming minerals and are found in granites, acid igneous rocks and in pegmatites. The potassium feldspars are, beside plagoiclase and quartz, the most important minerals in the earth's crust.

11.8.1.2 Chloride Minerals

Feldspar is not important for production of potassium compounds but chloride minerals are: *Carnallite* $KCl \cdot MgCl_2 \cdot 6H_2O$ and *sylvite* (sylvine) KCl. In fact sylvite is the principal ore of potassium compounds. At the beginning of the 20th century the German deposits in Stassfurt, 30 km south of Magdeburg, dominated the extraction of potassium and magnesium salts. Also Wieliczka, 10 km south of Kraków in Poland, has famous salt mines. As the air mixed with salt is considered to be healthy, a sanatorium has been established at the 200-meter level.

During oil prospecting in Canada, large deposits of sylvite (with some halite) were discovered in the province of Saskatchewan. These are gigantic and constitute a reserve of more than 100 billion tonnes, 10 billion of which can be extracted with acceptable economy and have been worked since 1962 using existing mining techniques. That reserve alone is sufficient for a very long time, as the world need at present is 10 million tonnes. The problem with the deposits in Saskatchewan is their great depth. In one mine, worked by the Cominco company, two shafts with depths of 1150 m had to be used, one with elevators for people and for ventilation while the other is used for transporting the mined product out. In horizontal drifts in the deposit level the salt is won using a high-tech method. Navigating by laser beams, tunnel drivers break up the rock salt and the product is transported by an automatic system to the hauling shaft. The product obtained is a mixture of sylvite and halite, which are separated by flotation.

11.8.1.3 Potassium Nitrate

As a mineral, potassium nitrate forms crusts on the surfaces of rocks and stone walls, and occurs as a component of surface soil in Spain, Iran, Egypt and India. In the US it occurs in loose soil in the limestone caves of Kentucky, Tennessee and the Mississippi Valley.

11.9
Uses

Potassium compounds are among the most important base chemicals, especially potassium hydroxide (caustic potash) KOH, potassium nitrate (saltpeter) KNO_3, potassium carbonate (potash) K_2CO_3, potassium chloride KCl, potassium chlorate $KClO_3$, potassium bromide KBr, potassium iodide KI, potassium cyanide KCN, potassium sulfate K_2SO_4 and potassium dichromate $K_2Cr_2O_7$.

As potassium is an essential element for plants its salts are valuable in fertilizers. Potassium chloride obtained from the sylvite deposits and the connected flotation process can be used directly for this purpose. Potatoes, which are sensitive to chlorides, are instead fertilized with potassium sulfate. As a rule, however, fertilizers are mixtures of components containing the elements nitrogen (N), phosphorus (P) and potassium (K). An “NPK” product thus adds all three valuable elements to the soil.

Potassium carbonate, the component in the old potash, is still used for the production of high-quality glass. Potassium chlorate is used in match-heads. Saltpeter was once used in gunpowder and is now found in explosives, fireworks and matches.

11.10
Sodium and Potassium in Biological Systems

Sodium and potassium are both essential for life. They are present as ions. K^+ ions are concentrated inside cells while Na^+ is present in high concentrations in extra-cellular fluids.

This is shown in Table 11.4.

Table 11.4 Sodium and potassium in the human body

	Sodium	**Potassium**
Blood, ppm		
Plasma	3500 (0.35 %)	400
Red cells	250	4000 (0.4 %)
Bone, ppm	10 000 (1 %)	2100 (0.21 %)
Tissue, ppm	2000–8000 (0.2–0.8 %)	16 000 (1.6 %)
Total amount in the body, kg	0.1	0.11–0.14

Details from ref. [11.8].

Control of the sodium concentration may have been very necessary for the early living organisms. It was important to exclude sodium ions present in the surrounding seawater. In non-marine living animals and humans the kidneys still carefully control the sodium concentration in the cells. If the Na^+ concentration within the cells should increase to high values, water would enter and the osmotic pressure would destroy the cell membranes. Should the Na^+ concentration be too high, ions are expelled from the cells by special sodium pumps in the membranes [11.9].

Sodium and potassium cooperate in a remarkable way as carriers of messages in the nerves. To make this possible the permeability of the nerve membranes changes and Na^+ passes in, while K^+ moves in the opposite direction. The sodium pump quickly restores the ion balance and osmotic equilibrium again.

Deficiency of sodium causes muscular spasm, while excess salt in the diet may give high blood pressure. There is a trend to replace common salt in the diet by "low sodium" alternatives, which are salt mixtures containing potassium chloride.

As described above, potassium is an important nutrient and is taken up by plants. In natural ecosystems the potassium from the decomposing plant returns to the soil and remains in clay minerals.

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12
Lithium

12.1 Li
Facts about Lithium

12.1.1 Li
The Element

Symbol:	Li
Atomic number:	3
Atomic weight:	6.94
Ground state electron configuration:	[He]$2s^1$
Crystal structure:	Cubic bcc with $a = 3.51$ Å

12.1.2 Li
Discovery and Occurrence

Discovery: J. A. Arfwedson, working at Berzelius' laboratory, discovered the element lithium in 1817 in the mineral *petalite* found in the iron ore mines on the island of Utö in the Stockholm archipelago.

Most important mineral:	Spodumene	$LiAlSi_2O_6$
	Lepidolite	$KLiAl(F,OH)_2Si_4O_{10}$
	Petalite	$LiAlSi_4O_{10}$ (Figure M13)

Ranking in order of abundance in earth crust:	32–33
Mean content in earth crust:	20 ppm (g/tonne)
Mean content in oceans:	0.18ppm (g/tonne)
Residence time in oceans:	$2 \cdot 10^6$ years
Mean content in an adult human body:	0.03 ppm
Content in a man's body (weight 70 kg):	2 mg

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12.1.3 Li

Chemical Characterization

Lithium has the lowest density of all metals with a density of 0.53 g/cm^3. It resembles sodium in its behavior but reacts more slowly with oxygen and water. Lithium and its compounds are used in batteries, lightweight alloys and in nuclear weapons. Lithium compounds have been found effective in the treatment of manic-depressive illness.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Li^I as in LiH, LiF, Li_2O, and Li_3N	$Li(g) \rightarrow Li^+(g)$	520	$Li(g) + e^- \rightarrow Li\text{-}(g)$
	$Li^+(g) \rightarrow Li^{2+}(g)$	7298	–59.6

Standard reduction potential: $Li^+(aq) + e^- \rightarrow Li(s)$ $E^0 = -3.040$ V

Electronegativity (Pauling): 0.98

Radii of atoms and ions: (WebElements™)		
	Atomic:	145 pm
	Covalent:	134 pm
	Van der Waals:	182 pm
	Li^+ (4-coordinate, tetrahedral):	73 pm
	Li^+ (6-coordinate, octahedral):	90 pm
	Li^+ (8-coordinate):	106 pm

12.1.4 Li
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
536 kg m^{-3} 0.54 g cm^{-3}	12.95 cm^3	453.7K 180.5 °C	1615 K 1342 °C	3573 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
94	86	82	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$46 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
10.4	85.5	124	300	405	530

Mass magnetic susceptibility χ_{mass} at 293 K $+25.6 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
4.9 GPa	–	11 GPa	–

12.1.5 Li
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	3.0 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	147.1 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	159.4 $kJmol^{-1}$
Entropy S^0 at 298 K	29.10 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	12.97	24.77	29.58	28.80	20.85	21.13

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4Li + O_2 \rightarrow 2Li_2O$	–1122	–1070	–932	–795	–

12.1.6
Nuclear Properties and X-ray

Isotope range, natural and artificial	5–11

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^6Li	Stable	7.5	+1	0.8220
^7Li	Stable	92.5	–3/2	3.256

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^6Li	^7Li
Reference compound	$LiCl/D_2O$	
Frequency MHz (^1H = 100 MHz)	14.716	38.864
Receptivity D^P relative to ^1H = 1.00	$6.38 \cdot 10^{-4}$	0.272
Receptivity D^C relative to ^{13}C = 1.00	3.64	1550
Magnetogyric ratio, $radT^{-1}s^{-1}$	$3.937 \cdot 10^7$	$10.398 \cdot 10^7$
Nuclear quadropole moment, barn	$-8.2 \cdot 10^{-4}$	–0.041

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
–	–	–

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	0.502
17.37 keV (MoKα_2)	0.198

Neutron absorption	**Thermal neutron capture cross section**	71 barns

12.2
Discovery

12.2.1
A Versatile Brazilian Prepares the Lithium Discovery

Chemistry and metallurgy were very international at the turn of the century 1800. The discovery of lithium, however, involves international features beyond the ordinary.

> In Rio de Janeiro a boy was born in 1763 and given the imposing name *José Bonifácio de Andrada e Silva* He grew up into a highly talented person and showed a keen interest both in science and in the arts. In the politics of his native country he also became active and worked for improvement of the living conditions both for the native population and for the Negro slaves. At 55 he became Prime Minister of his country and signatory of the new constitution of the Brazilian State. Of course he has a prominent position in the history of his country and is described as *The Greatest Man in Brazilian History* [12.1].

Strangely enough, he also has a place in the history of lithium. It was José Bonifácio de Andrada e Silva, who found and described the mineral petalite in a Swedish iron ore mine on the island Utö in the Stockholm archipelago, a mineral in which the element lithium was discovered. How was that possible?

After his first education in Rio, José was sent to the University of Coimbra in Portugal to complete his studies in scientific subjects, especially chemistry, mineralogy and geology. Later, in connection with his election as a member of the Brazilian academy of sciences he was given the opportunity to make a very long study tour in Europe. He visited France, Germany, Italy, Holland, Hungary and the Scandinavian countries. Before he returned to South America, José stayed for some time as a teacher in the University of Coímbra. From his visit in Sweden he described, in a German journal, a mineral that he had found on the island of Utö. The year was 1800. As far as he knew it had not been described earlier. He called it petalite.

Andrada's description did not seem to create much interest in the new mineral. In 1817, the enthusiastic Swedish mineralogist *E. Th. Svedenstierna* visited Utö, recognized the petalite and collected a big sample. He sent mineral pieces to experienced scientists including Berzelius, Wollaston, Haüy, K. C. v. Leonhard and others. On 9th

September 1817, he received an encouraging letter from Abbé Haüy, in which this leading mineralogist wrote that his (Haüy's) geometric investigation had shown that the petalite, without any doubt, was a specific mineral.

Andrada was later honored by the mineralogical science community, which gave the name *andradite* to a calcium–iron garnet mineral.

12.2.2
A New Employee Makes an Analysis and Ends Up in the History of Science

Thus petalite arrived at Berzelius' laboratory for investigation in 1817. *Johan August Arfwedson* (Figure 12.1), a young inexperienced chemist, was given the task of making the analysis. Johan August was born in 1792. He became a trainee at the Bergskollegium (Board of Mining and Metallurgy) in Stockholm with the possibility of attending Berzelius' lectures and also working in his laboratory on mineral analyses. At first he had to carefully study manganese and its different oxides. Then one day he found the white petalite mineral on his table. Its composition was unknown but should now be revealed by his analysis. He started as he had been taught.

Figure 12.1 Johan August Arfwedson (1792–1841)

> He ground the sample in a mortar, weighed 1 g of it into a crucible, mixed it with potassium carbonate and fused it. After leaching in water and acidification with diluted hydrochloric acid the solution was evaporated to dryness. The silicic acid was thus dehydrated and stayed undissolved under new treatment with diluted hydrochloric acid. It was filtered off, ignited and weighed as SiO_2.

> In the filtrate, aluminum and iron were precipitated as hydroxides with ammonia and their contents were determined. The result confused Arfwedson. The sum of the oxides he had determined was 96 but not 100%. It was a divergence too great, even for a chemist without much experience. What was the reason? Did the mineral contain sodium? He dissolved the mineral sample without using sodium or potassium carbonate, precipitated the silica and all metals except the alkali metals. He added sulfuric acid and evaporated to dryness. Now he could weigh the presumed sodium sulfate and recalculate its weight to sodium hydroxide. The confusion increased. The sum of the components clearly exceeded 100%! And the result was the same after several repeated tests.

Young Arfwedson was surely discouraged by his own results. They had to be wrong! What would Berzelius' reaction be? Request his new assistant to try to get a job somewhere other than in analysis? The opinion was the reverse. Arfwedson's work with petalite was very much appreciated by Berzelius. The account of the results was quite in line with his own attitude to science: Always claim experimental honesty, never fake a result.

Berzelius reported Arfwedson's confusing facts to Wilhelm Hisinger in a letter in January 1818 [12.3]:

> ... All these facts have led us to expect that petalite perhaps contains a new alkali ... of such a great saturating capacity that, when the salt is computed as a sodium salt, the excess in weight arises through the fact that the salt contains much less base than a sodium salt[1]. If this is true, Arfwedson has had the good fortune to make in his second mineralogical analysis one of the most remarkable discoveries which can be made in this manner ...

It was clear that a new alkali metal had been discovered. Arfwedson investigated and described several of its compounds but failed in his attempts to isolate the element in metallic form. As this new alkali was first found in the mineral kingdom – unlike the common water-soluble sodium and potassium compounds – Berzelius and Arfwedson gave the new element the name lithion, "from stone". The mineral petalite is nowadays known as lithium aluminum silicate, $LiAl(Si_2O_5)_2$.

At the time of the petalite analysis, Arfwedson was 25 years old. Berzelius was 38, and ought not yet to have got tired of fame and honor. In 1803 he had discovered cerium and in 1817, the year of the lithium discovery, he had found and named the element selenium. It would have been tempting to add the element lithium as further "scalp" to the collection, at least in the form of shared priority with Arfwedson. It is also quite clear that Berzelius' contribution to the element discovery was considerable. In science history Arfwedson alone is stated as discoverer of lithium. This was

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[1] A content of 4% Li_2O in the petalite should give a weight of 0.1470 g of Li_2SO_4 in Arfwedson's crucible. He calculated as if it was Na_2SO_4. The calculated amount of Na_2O then is 0.0642 g, corresponding to 6.4% Na_2O in a sample size of 1 g. The sum then would be 96 + 6.4 = 102.4%. If – on the other hand – he had thought that the alkali metal had been potassium, the calculated amount of K_2O should be 0.0795 g, the K_2O content 7.95% and the total sum 104%. Arfwedson's result and confusion in 1817 may in fact be used in teaching stoichiometry in modern chemistry education.

Berzelius' wish, and an expression of his generosity, often reported, towards colleagues and students. In March 1818 he wrote to his friend Alexandre Marcet, Swiss doctor and chemist, working in London, and told him about Arfwedson's element discovery in petalite. He also mentioned that the element had been found in the Utö minerals spodumene and lepidolite.

12.2.3
The Mines on the Island of Utö

Utö is an island in the Stockholm archipelago. A silver mine was opened there in 1607 but was soon closed as the silver amount was small. Mining of iron ore – a hematite with an iron content of 40% – had occurred in several mines since the Middle Ages and was speeded up at the beginning of the 17th century. The ore was shipped to blast furnaces on the Swedish mainland and was, to a small extent, also used in local blast furnaces, situated on neighboring islands. In the biggest and deepest mine two pegmatite veins were found. They were rich in many non-ferrous minerals, especially petalite.

Mining on Utö ended in 1878.

12.2.4
Journeys and Informal Conversations in the Wake of Lithium

12.2.4.1 To France

The work on lithium had built up confidence between Berzelius and Arfwedson and the co-operation continued. In the summer of 1818, Arfwedson was sent to England, taking with him samples of Berzelius' recently discovered element selenium which he gave to Alexandre Marcet, Sir Humphry Davy and W. H. Wollaston. Later Berzelius himself arrived and together they visited several British scientists. Thereafter they continued to France and met the former abbot René Just Haüy, now 75 years old. Berzelius informed Arfwedson that they were going to meet *a noble scientific patriarch*. He was the leading mineralogist of this time. Two other gentlemen also took part in the French journey:

> These were *Count Gustav Löwenhielm*, newly appointed Swedish minister in Paris, and the 23-year-old *Nils Wilhelm Almroth*, mineralogist and coin-assayer. During the stay in Paris, Berzelius had the opportunity to meet several colleagues and scientists within chemistry and physics: C. L. Berthollet, P. L. Dulong, J.- L. Guy-Lussac and L. J. Thenard. The Swedish group stayed eleven months in Paris. In the summer of 1819, Berzelius, Arfwedson and Almroth made a study tour through Auvergne and the *Massif Central*. They particularly wished to study volcanic rocks and minerals in this region with its beautiful scenery. It was tough traveling, for three weeks, on foot, on horseback and with rickety horse-drawn vehicles. C. G. Bernhard [12.4] has described this venture. Not only Berzelius' great scientific interest but also, in an amusing way, his robust attitude to all the daily cares of the primitive journey.

12.2.4.2 To Utö

Berzelius also collaborated with the German chemist F. Wöhler, who also had been Berzelius' student. In the summer of 1824 he was in Stockholm, worked in Berzelius' laboratory and assisted with the translation of scientific articles into German. Berzelius liked to give his co-workers rest and recreation, and arranged a trip to Utö. In *Early Recollections of a Chemist*, Wöhler himself described the journey:

> One of my best memories is a very cheerful excursion to Utö in company with Berzelius, Hisinger, Arfwedson and Carl Retzius. This island is situated in the Baltic Sea about twenty km from the coast and is known for its rich iron ore mines and as the first finding-place for petalite and spodumene, in which minerals Arfwedson discovered lithion. We stayed overnight in Dalarö and sailed the following morning at 5 o'clock in a small boat out to the island, favored by wind and weather. After having paid a visit to the foreman for the mines we went to see these hideous holes and started hunting spodumene, petalite, red and blue tourmaline, apophyllite, datolite and so on. Both the first-mentioned minerals we found abundantly and in big boulders. In some few hours we collected three full boxes; most rare was the red tourmaline and the beautiful crystals of datolite. After a refreshing dinner with the foreman we departed for Dalarö in a rather heavy sea. After accommodation there – disturbed by the bedbugs and Berzelius' snoring – we started our journey back to Stockholm. In wonderful morning sunshine we passed sweet-scented forests, which I, eight months ago, had passed in pouring rain.

12.2.5
Lithium Metal

Around 1800 there was a very active group of chemists in England, a group that exerted a great influence on the development of two fields in particular: the chemistry of gases and electrochemistry. We have met Henry Cavendish, Joseph Priestley, and Sir Humphry Davy. The discoverer of the element niobium, *Charles Hatchett* (see Chapter 22 Niobium), argued with great vigour for an increased interest and knowledge of mineralogy among the chemists in his country. He encouraged a young apothecary's apprentice to collect and classify minerals and rocks. The young man's name was *William Thomas Brande* (1788–1866). William improved his general knowledge of chemistry and wrote a much appreciated textbook *Manuals of Chemistry*, becoming a teacher of chemistry and mineralogy. He could also devote himself to his interest for mineralogy in the family circle as he married Charles Hatchett's daughter. Influenced by Humphry Davy, however, he became fascinated by electrochemistry and in 1812 he succeeded Davy at the Royal Institution. When a new alkali metal had been discovered in Sweden it aroused an enormous interest in England. For Brande it was natural to repeat Davy's pioneering work with potassium and sodium. As early as 1818 he prepared a small amount of lithium metal. In the second (1821) edition of his book *Manuals of Chemistry* Brande himself describes the experiment:

> When lithia is submitted to the action of the Voltaic pile, it is decomposed with the same phenomena as potassa and soda; a brilliant white and highly combustible metallic substance is separated, which may be called lithium, the term lithia being applied to its oxide. The properties of this metal have not hitherto been investigated, in consequence of the difficulty of procuring any quantity of its oxide.

Bunsen and Mathiesen in 1854 prepared lithium in a sufficiently large quantity for determination of the properties of the element. They fused lithium chloride in a porcelain crucible and conducted current from six carbon–zinc cells, connected in series, through the melt.

12.3
Occurrence

12.3.1
Minerals

In the earth crust lithium is enriched in granitic pegmatites and occurs as an essential component in some twenty minerals. The following four minerals are common:

- Amblygonite, a phosphate: $(Li,Na)AlPO_4(F,OH)$, lithium sodium aluminum phosphate, containing fluorine
- Spodumene, a silicate, $LiAlSi_2O_6$, lithium aluminum silicate. It is a rock forming mineral in granites and pegmatites
- Petalite, a silicate, $LiAlSi_4O_{10}$ (Figure M13)
- Lepidolite, $KLi_2Al(Al,Si)_3O_{10}(F,OH)_2$, a mica, potassium lithium aluminum silicate, containing fluorine (Figure M13)

Large deposits of spodumene have been found in Manono in the Democratic Republic of Congo and of petalite and lepidolite in Bikita in Zimbabwe. Investigations of pegmatite deposits in Greenbushes, Western Australia, have also revealed large reserves of spodumene.

A pegmatite at Bernic Lake, Manitoba in Canada is mined for tantalum, niobium and lithium. A lepidolite in the pegmatite is, in addition, the only known commercial source of the element rubidium. In North Carolina, a rich lithium source is known as the “tin-spodumene belt”. The ore was used for production of lithium carbonate until 1998, when the last mine there was closed.

In northwest China, in the Altai mountains, considerable deposits of spodumene have been reported.

12.3.2
Natural Brines

Large lithium reserves are available in South America. A resource of special interest is the dried up salt lake Atacama, 2500 m above sea level in northern Chile. The main component is halite, rock salt, NaCl. In cavities a concentrated salt solution is present, in which the lithium content is as high as 0.15%. This solution is transported to nearby Antofagasta. In a chemical factory there the lithium carbonate is prepared from the chloride. This carbonate is an important export product. Lithium-containing brines are also available in Nevada in the USA. The brines are pumped from the ground through a series of open dams. Through solar evaporation over 12 to 18 months the brine increases its lithium concentration to about 0.6%. Soda is added and lithium carbonate precipitates.

The production of lithium as ores and brines is not published because of the importance of the element in nuclear weapons. The USGS world production value [12.5] for the year 2000 is 14 000 tonnes but does not include US production. Chile produced 5300 tonnes, Australia, China and Russia at least 2000 tonnes each.

12.4
Manufacture

Spodumene and petalite as concentrates are used directly, especially in the glass industry.

For chemicals, lithium carbonate is the best raw material. Preparing the carbonate from spodumene is an energy-intensive and costly process. Because of that most lithium carbonate production has shifted to chemical treatment of brines. Lithium metal is obtained by electrolysis of a salt melt containing 55% lithium chloride and 45% potassium chloride, a mixture that melts at 352°C. The metal is rolled into thin foils that can used as anodes in lithium batteries, but it can also be plated onto foils of copper or nickel.

12.5
Uses

12.5.1
Glass and Ceramics

The use of lithium in glass and ceramics applications is continuing to expand throughout the world because of the increased durability it imparts to the glass or ceramic product. Some glass and ceramics manufacturers use lithium carbonate, but lithium minerals are preferred because of the additional alumina and silica contained in the mineral product. Petalite is particularly desirable because of its very low iron content. Addition of lithium lowers melting points and reduces the coefficient of thermal expansion. Lithium-containing “pyroceramics” expand and contract very little at extreme temperatures and are thermal shock-resistant. An exciting use is for the nose-cones of spacecraft but, in fact, the use in cookware consumes the greatest part of pyroceramics produced [12.5].

12.5.2
Catalysis and Components in Organic Chemistry

In the production of plastics, synthetic rubbers and pharmaceuticals, lithium compounds are used as catalysts to an increasing extent. As a single example the important copolymer styrene–butadiene may be mentioned. Its formation is catalyzed by *n*-butyllithium.

In preparative organic chemistry, lithium aluminum hydride Li_3AlH_6, is used as a reducing agent.

The grease industry has been another important market for lithium. Lithium hydroxide is used for production of lithium lubricants. These greases retain their lubrication properties over a wide temperature range.

12.5.3
In Aircraft

Aluminum alloys with lithium may be used for wings and structural components in airplane manufacturing. Reduction of weight leads to a considerable fuel saving during the lifetime of the aircraft. These alloys will probably be used in the future for military and large passenger aircraft, in spite of the competition from carbon-reinforced plastics. An actual Al–Li alloy has 2.5% Li, 1.3% Cu, 0.8% Mg, 0.12% Zr and the remainder Al. The density is 10% lower than for aluminum while the modulus of elasticity is 10% higher [12.6].

12.5.4
New Batteries

New batteries use lithium anodes and different types of cathode. Primary cells, non-rechargeable, have been commercially available since 1990. They are used in watches, cameras, microcomputers, implanted pacemakers and similar applications. They are also used in different missile programs. Lithium primary cells are characterized by:

- usefulness over a wider temperature range than aqueous cells
- greater energy density than conventional batteries
- very good storage properties with low rate of self-discharge

Batteries of the lithium type cannot have water-based electrolytes as lithium reacts violently with water. Instead the electrolyte consists of lithium salts dissolved in organic solvents such as propylene carbonate or dimethyloxyethane. A solid cathode can be built up of manganese dioxide, copper oxide and silver chromate, or of graphite loaded with sulfur dioxide or thionyl chloride $SOCl_2$. In lithium-iodine batteries the anode material is covered with a conducting plastic such as polyvinylpyridine, acting as the electrolyte. The positive electrode consists of iodine in polyvinylpyridine.

The belief that lithium batteries may be the best way to power electric vehicles (EVs) has strongly stimulated interest in lithium. New battery configurations continue to be developed. Pyrrole is a suitable electrode material for rechargeable lithium batteries. In a flat cell, polypyrrole and lithium films are sandwiched together. In a cylindrical cell the two films are wound concentrically.

12.5.5
A Special Use

One use of lithium carbonate – in fact a very significant one – is as an additive to fused cryolite Na_3AlF_6 in primary aluminum production. The melting point is decreased, the electrical conductivity improved and the energy consumption is lowered. Most importantly, the environment benefits as the fluorine emission decreases by 20–30%.

12.5.6
Advanced Nuclear Applications

Lithium is, and is expected to be, important in advanced nuclear applications. Among the fusion reactions that have been proposed for power generation, the one between deuterium and tritium has the best prospect for success because it requires the lowest plasma temperature. Tritium is prepared from lithium. As coolants in a possible fusion reactor, fused lithium metal or molten fluorides of lithium and beryllium have been proposed. For breeder reactors a molten salt fuel is used, composed of beryllium fluoride, thorium fluoride and uranium fluoride together with the fluoride of the isotope ^7Li.

12.5.7
Lithium and Hydrogen

Lithium reacts with hydrogen at 750°C forming lithium hydride LiH. When this white powder reacts with water, hydrogen gas is liberated – 2800 liters for every kilogram of hydride. That makes it possible to use lithium to store hydrogen.

12.6
Lithium Saves Life

Lithium is not essential for vital functions but has an effect on the nervous system. It has an important use as a medicine for treatment of manic-depressive illness. Two Danish doctors and brothers, Carl and Fritz Lange, reported at the end of the 19th century that lithium might prevent and cure depressions. The observation was forgotten. An Australian scientist, John Cade, found and followed the trail and in 1949 published results showing that lithium salts can, in a miraculous way, help manic people to a normal life. Why? Owing to the chemical similarities between lithium and sodium ions, the former may interfere with and influence the messages of the nerves, conveyed by the latter. For many people lithium prophylaxis has produced a wonderful freedom from fluctuations in the frame of mind with all the disturbances of life they can lead to.

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13
Rubidium and Cesium

13.1 Rb
Facts about Rubidium

13.1.1 Rb
The Element

Symbol:	Rb
Atomic number:	37
Atomic weight:	85.47
Ground state electron configuration:	[Kr]5s^1
Crystal structure:	Cubic bcc with $a = 5.585$ Å

13.1.2 Rb
Discovery and Occurrence

Discovery: R. W. Bunsen and G. Kirchhoff in Germany discovered the new element in 1861 during spectroscopic studies of lepidolite.

Most important mineral: Follows lithium in lepidolite (Figure M13)

Ranking in order of abundance in earth crust:	22
Mean content in earth crust:	90 ppm (g/tonne)
Mean content in oceans:	0.12 ppm (g/tonne)
Residence time in oceans:	$2.5 \cdot 10^6$ years
Mean content in an adult human body:	4.6 ppm
Content in a man's body (weight 70 kg):	320 mg

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13.1.3 Rb
Chemical Characterization

Rubidium is a silvery white and very soft metal that colors a flame yellowish-violet. In chemical behavior rubidium resembles sodium and potassium and reacts violently with water. It is a widely distributed element, usually associated with other alkali metals in minerals. The rate of radioactive decay of the isotope ^{87}Rb can be used in geological age determination (see Chapter 4 Geochemistry). Rubidium is found in small quantities in tea, coffee, tobacco and other plants.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Rb^I as in Rb_2O and RbCl	$Rb(g) \rightarrow Rb^+(g)$	403	$Rb(g) + e^- \rightarrow Rb^-(g)$
	$Rb^+(g) \rightarrow Rb^{2+}(g)$	2633	−46.9

Standard reduction potential: $Rb^+(aq) + e^- \rightarrow Rb(s)$ $E^0 = -2.924$ V

Electronegativity (Pauling): 0.82

Radii of atoms and ions: (WebElements™)		
	Atomic:	235 pm
	Covalent:	211 pm
	Rb^+ (6-coordinate, octahedral):	166 pm
	Rb^+ (8-coordinate):	175 pm

13.1.4 Rb

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
1532 kg m^{-3} 1.53 g cm^{-3}	55.76 cm^3	312.5 K 39.3 °C	961 K 688 °C	364 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
59	58	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$90 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
22	110	275	480	990	2600

Mass magnetic susceptibility χ_{mass} at 293 K	$+2.49 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	2.5 GPa	–

13.1.5 Rb
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	–2.20 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	72.5 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	80.9 kJmol^{-1}
Entropy S^0 at 298 K	76.77 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	25.51	31.06	30.44	20.79	21.01	21.74

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
–	–	–	–	–	–

13.1.6 Rb
Nuclear Properties and X-ray

Isotope range, natural and artificial	74–102

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{85}Rb	Stable	72.17	–5/2	1.353	–	–	–
^{87}Rb	Active	27.83	–3/2	2.751	4.8 · 10^{10} y	β$^-$	0.283 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{85}Rb	^{87}Rb
Reference compound	RbCl/D_2O	
Frequency MHz (^{1}H = 100 MHz)	9.655	32.721
Receptivity D^P relative to ^{1}H = 1.00	7.66 · 10^{-3}	4.93 · 10^{-2}
Receptivity D^C relative to ^{13}C = 1.00	43.8	282
Magnetogyric ratio, radT^{-1}s^{-1}	2.593 · 10^7	8.786 · 10^7
Nuclear quadropole moment, barn	0.274	0.132

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
36	Kr	12.598
37	Rb	13.336
38	Sr	14.098

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	105
17.37 keV ($MoK\alpha_2$)	86.0

Neutron absorption	**Thermal neutron capture cross section**	0.39 barns

13.1 Cs
Facts about Cesium

13.1.1 Cs
The Element

Symbol:	Cs
Atomic number:	55
Atomic weight:	132.91
Ground state electron configuration:	$[Xe]6s^1$
Crystal structure:	Cubic bcc with $a = 6.14$ Å

13.1.2 Cs
Discovery and occurrence

Discovery: R. W. Bunsen and G. Kirchhoff in Germany discovered the new element in 1860 during spectroscopic studies of mineral water.

Most important mineral: Pollucite $(Cs,Na)_2Al_2Si_4O_{12}\cdot H_2O$ (Figure M13)

Ranking in order of abundance in earth crust:	46–47
Mean content in earth crust:	3 ppm (g/tonne)
Mean content in oceans:	$3 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	$600 \cdot 10^3$ years
Mean content in an adult human body:	1 ppm
Content in a man's body (weight 70 kg):	70 g

13.1.3 Cs

Chemical Characterization

Cesium is silvery with a tinge of gold. Its spectrum contains two bright lines in the blue region (accounting for its name). Cesium melts at 28 °C and is one of the three metals that are liquid at or around room temperature. The other two are gallium (m.p. 30 °C) and mercury (m.p. –39 °C). It is the most electropositive element and reacts explosively with water, even with ice. The natural source yielding the greatest quantity of cesium is the rare mineral pollucite. Ores of this mineral are found on the island of Elba and in Maine and South Dakota. The radioactive isotope cesium-137 which is produced by nuclear fission became world famous after the Chernobyl disaster because of its injurious effects. The isotope can, however, also be used in medical and industrial research.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Cs^I as in Cs_2O, Cs_2S, CsF and CsCl	$Cs(g) \rightarrow Cs^+(g)$	376	$Cs(g) + e^- \rightarrow Cs^-(g)$
	$Cs^+(g) \rightarrow Cs^{2+}(g)$	2234	−45.5

Standard reduction potential: $Cs^+(aq) + e^- \rightarrow Cs(s)$ $E^0 = -2.923$ V

Electronegativity (Pauling): 0.79

Radii of atoms and ions: (WebElements™)		
	Atomic:	260 pm
	Covalent:	225 pm
	Cs^+ (6-coordinate, octahedral):	181 pm
	Cs^+ (8-coordinate):	188 pm

13.1.4 Cs
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
1880 kg m^{-3} 1.88 g cm^{-3}	70.69 cm^3	301.7 K 28.5 °C	944 K 671 °C	242 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
37	36	–	–	–

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
–	–	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
45	188	435	670	1340	2950

Mass magnetic susceptibility χ_{mass} at 293 K $+2.8 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
–	–	1.6 GPa	–

13.1.5 Cs
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	2.09 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	67.8 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	76.1 $kJmol^{-1}$
Entropy S^0 at 298 K	85.23 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	25.82	31.17	31.00	20.79	21.34	22.90

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4Cs + O_2 \rightarrow 2Cs_2O$	–616	–560	–	–	–

13.1.6 Cs
Nuclear Properties and X-ray

Isotope range, natural and artificial	112–148

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{133}Cs	Stable	100	+7/2	2.582

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{133}Cs
Reference compound	$CsNO_3/D_2O$
Frequency MHz (^1H = 100 MHz)	13.116
Receptivity D^P relative to ^1H = 1.00	0.0484
Receptivity D^C relative to ^{13}C = 1.00	276
Magnetogyric ratio, $radT^{-1}s^{-1}$	$3.533 \cdot 10^7$
Nuclear quadropole moment, barn	–0.0037

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
54	Xe	29.459
55	Cs	30.625
56	Ba	31.817

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	319
17.37 keV (MoKα_2)	41.2

Neutron absorption	**Thermal neutron capture cross section**	30 barns

13.2
Discovery

13.2.1
Cesium – Named From the Blue Sky

Once Bunsen and Kirchhoff had developed their spectroscope in the middle of the 19th century they were keen to use it to examine different natural products. Mineral waters were attracting great interest at this time. What did waters from different springs contain? Why did they have effects on people's health? In 1860 the two scientists wrote to the academy of sciences in Berlin:

> We brought a droplet of mineral water from Dürkheim into the flame in front of the spectroscope. Then we could recognize the characteristic lines of sodium, potassium, lithium, calcium, and strontium. From a larger water volume we precipitated calcium, magnesium and strontium with well-known chemical methods. The remaining solution was evaporated to dryness and the residues were moistened with nitric acid and dissolved in alcohol. From this solution lithium was precipitated with ammonium carbonate. The spectroscope revealed the presence of sodium, potassium and some lithium in the filtrate. In addition we observed two remarkable blue lines, very close together. One of them was in the part of the spectrum where a well-known strontium line is situated. No element, earlier identified, has a pair of lines in this part of the spectrum. Our conclusion is that we have discovered a new alkali metal and we propose the name cesium for this new element. The background of the name is the designation *caesium*, used by the ancients for the blue of the upper part of the firmament.

In 1846, before the development of spectroscopy, C. F. Plattner, the metallurgy professor in Freiberg, had analyzed the mineral pollucite from Elba. He was recognized as a very clever mineral analyst but failed in this investigation. When he summed all the components he had determined, the total was 92.75%. After the discovery of cesium it was shown that pollucite has a considerable content of this element. Plattner died in 1858 and never heard of the alkali metal that had created such great difficulties for him.

13.2.2
Rubidium – More Red Than Red

In 1861, Kirchhoff's team investigated a lepidolite (Figure M13) from Saxony. This mineral is a mica, a lithium potassium aluminum fluorosilicate. They dissolved a sample and precipitated potassium with platinum chloride. When the precipitate was treated with boiling water, part of it dissolved. This procedure was repeated several times and after each time they investigated the remaining precipitate in the spectroscope. At the beginning only potassium lines were visible. Gradually these weakened as lines from a new element, more difficult to dissolve in boiling water, appeared. In particular, a pair of two brilliant red lines attracted their attention. The year after the cesium discovery the two scientists had thus found yet another new element. From the impressive dark-red color of the lines the discoverers named the new metal rubidium after rubidus, the Latin designation for the deepest red.

13.3
Rubidium in Our Time

13.3.1
Occurrence and Manufacture

Rubidium is not too rare in the earth crust, being more abundant than lead. As stone melts crystallized when the earth's crust was formed, rubidium followed potassium in all minerals, as the ionic radii of these two elements are very similar. Consequently there are no typical rubidium minerals. This has been discussed in Chapter 4, Geochemistry. Lepidolite, a lithium-rich mica, is an exception. In that mineral, rubidium can substitute for lithium to such a great extent that as much as 2.5% may be present. One such source is the pegmatite at Bernic Lake, Manitoba in Canada. From mines there, a rubidium-containing lepidolite fraction is obtained and separated as a by-product. However, this is not a very profitable business. The demand for rubidium in the whole world is only about 2 tonnes per year and this quantity is obtained in a few hours at Bernic Lake [13.1]. This lepidolite is worked in chemical plants in the US. From the mixed alkali carbonates, rubidium is isolated as sulfate or chloride by advanced separation processes.

13.3.2
Uses

Rubidium, like sodium, ignites spontaneously in air and reacts violently with water. There is no great incentive to find technical applications for rubidium. Why use rubidium when sodium may perform – as it often does – the same function at a much lower cost?

The small quantities of rubidium produced are mainly used for research purposes. With rubidium atoms a very special research success has been achieved in physics.

If rubidium atoms are cooled almost to 0 K, thus just above absolute zero, a so-called Bose–Einstein condensate (BEC) may be formed for a moment. In a BEC the atoms have lost their individuality, all having the same quantum state, the same energy and speed. It creates new possibilities for controlling the atoms, yet within the rules expressed by the uncertainty principle. There is some similarity between a BEC and laser light. In the latter all the photons are exactly the same, in the former all the atoms. Some day BECs will perhaps be tools for nanotechnology, and allow the construction of super-tiny structures, for example chips for future computers. Eric Cornell of the National Institute of Standards and Technology, Carl Wieman of the University of Colorado and Wolfgang Ketterle of the Massachusetts Institute of Technology were awarded the 2001 Nobel Prize in physics for the achievement of Bose-Einstein condensation in dilute gases of alkali metal atoms, and for fundamental studies of the properties of the condensates.

The rubidium isotope ^{87}Rb is radioactive and makes up 27.8% of all natural rubidium. Because of that it is used in the rubidium/strontium technique for dating rocks. This is described in Chapter 4 Geochemistry.

Some rubidium compounds are used in more ordinary applications. Rubidium carbonate is added to the melt during the manufacture of certain special glasses. Rubidium bromide is used as a luminescent material in viewing screens. Rubidium is also used in the manufacture of photocells and as a scavenger in vacuum tubes to remove traces of gases.

13.4
Cesium in Our Time

13.4.1
Occurrence and Manufacture

The main source is a feldspar-type mineral, pollucite, cesium sodium aluminum silicate, which is mined at Bernic Lake in Canada and also, to some extent, in Bikita in Zimbabwe.

During the processing of pollucite the ground mineral is dissolved and silica and alumina are removed from the solution. Salts of alkali metals are present in the filtrate. The separation of these was once very time consuming, as it had to be done with fractional crystallization. Nowadays an ion-exchange technique is used, which makes the separation fast and simple. Cesium hydroxide is prepared from the pure cesium solution, and is the base for cesium chloride, iodide, carbonate and other compounds. Cesium metal is prepared by reduction of cesium chloride with calcium metal.

13.4.2
Uses

Various figures are reported for the world demand for cesium, but it is certainly small although much greater than for rubidium.

13.4.2.1 The Time Standard of Our Time

A transition between two levels in the hyperfine structure of the cesium isotope ^{133}Cs corresponds to a frequency of 9 192 631 770 Hz (Hz = Hertz = cycles/second). A cesium atomic clock is a device that measures this frequency with an accuracy of 0.0002 Hz, corresponding to a time measurement accuracy of two nanoseconds per day or one second in 1 400 000 years. It is the most accurate realization of a unit that mankind has yet achieved.

In 1967 the 13th General Conference on Weights and Measures defined the second on the basis of vibrations of the cesium atom. From that moment the world's timekeeping system no longer had an astronomical basis. A second is instead defined as the duration of 9 192 631 770 cycles of microwave light absorbed or emitted by the hyperfine transition of ^{133}cesium atoms. The cesium clock is the time standard of our time.

13.4.2.2 Other Uses of Cesium

Cesium metal and salts have a diversified application in modern engineering. Some examples:

- With other alkali metals cesium forms alloys with very low melting points, which can be used in certain applications. Cesium with 9% sodium melts at –30°C.
- Cesium metal has a great affinity for oxygen and is because of that used as a scavenger in vacuum tubes.
- Cesium iodide is used for prisms and windows letting infrared radiation, up to 50 µm, pass. It is also used as a scintillation detector for direct conversion of X-rays and γ-radiation into electrical signals.

Cesium is used as a catalyst in the hydrogenation of organic compounds. Some other catalysts are doped with cesium, giving an improved catalytic effect. An important example is the vanadium pentoxide that catalyzes the oxidation of sulfur dioxide to sulfuric acid. The addition of cesium is expensive but profitable as it reduces the bed inlet temperature, saving energy and start-up time. It also maximizes the SO_2 conversion and reduces emissions.

The metal can be used in ion propulsion systems to steer satellites. The metal is ionized and the ions are accelerated through an electric field. As they pass out through a nozzle they apply a force to the satellite. The heavier the ions, the larger the impulse delivered and cesium with its high atomic mass is suitable [13.2]. 1 kg of cesium in outer space could propel a vehicle 140 times as far as the burning of the same amount of any known liquid or solid.

13.4.3
Cesium and Radioactive Pollution

Radioactive cesium isotopes are formed during the fission of uranium in nuclear power stations and in atomic bombs. After the disaster at Chernobyl, Ukraine in 1986 the most intensive radiation during the first three weeks came from iodine isotopes. Then ^{134}cesium (half-life 2 years) and ^{137}cesium (half-life 30 years) dominated. It is the latter that is responsible for the prolonged radioactive pollution. The cesium pollution in Sweden gave local activities 50–75 times larger than those caused by the atmospheric nuclear weapon tests in the 1960s. As cesium has great similarities with potassium it is absorbed by plants and transferred to meat and milk in grazing animals (see section 52.3.1 in Chapter 52 The Radioactive Elements).

13.5
Biological Roles

Rubidium salts are not considered to have any vital properties, either toxic or essential. The element is, however, similar to potassium and – like potassium – has a slight stimulatory effect on metabolism. Plants will absorb rubidium readily, but as the element concentration is so low in soils there is almost nothing to absorb. Onions contain less than 1 ppm but soya beans 220 ppm [13.2].

Cesium has no known biological role. The concentration of cesium has been determined as 0.2 ppm in tea-leaves and as low as 3 ppb in vegetables and fruits. The very dangerous uptake of radioactive cesium is treated above.

References

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13.2 J. Emsley, *Nature's Building Blocks. An A–Z Guide to the Elements*, Oxford University Press, Oxford, 2001

14
Magnesium and Calcium

14.1 Mg
Facts about Magnesium

14.1.1 Mg
The Element

Symbol: Mg
Atomic number: 12
Atomic weight: 24.31

Ground state electron configuration: [Ne]$3s^2$

Crystal structure: Hexagonal hcp with $a = 3.21$ Å and $c = 5.21$ Å

14.1.2 Mg
Discovery and Occurrence

Discovery: Identified as an element in 1755 by J. Black in Edinburgh. The metal was prepared in 1808 by H. Davy in London.

Most important mineral:		
	Magnesite	$MgCO_3$
	Dolomite	$CaMg(CO_3)_2$
	Carnallite	$KMgCl_3 \cdot 6H_2O$
	Kieserite	$MgSO_4 \cdot 4H_2O$
	Olivine	$(Mg,Fe)_2SiO_4$

Large quantities of magnesium are also obtained from seawater.
Next to sodium, magnesium is the most abundant cation in seawater.

Ranking in order of abundance in earth crust: 7
Mean content in earth crust: 23 300 ppm (g/tonne) (2.33%)
Mean content in oceans: 1290 ppm (g/tonne) (0.13%)
Residence time in oceans: $10 \cdot 10^6$ years
Mean content in an adult human body: 270 ppm
Content in a man's body (weight 70 kg): 20 g

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14.1.3 Mg
Chemical Characterization

Magnesium is a malleable and ductile, a silvery white metal that is relatively unreactive. However, it tarnishes slightly in air. The metal is not attacked by oxygen, water, or alkalis at room temperature but reacts with acids. When heated it combines with oxygen and emits a brilliant white light. With the exception of beryllium, it is the lightest metal that remains inert under ordinary conditions. Alloyed with aluminum or copper the metal is used when lightness is an essential factor, for example in castings for aircraft parts. Magnesium is the central atom in chlorophyll, essential for the photosynthesis by green plants.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Mg^{II} as in MgO, MgCO$_3$, and MgSO$_4$·4H$_2$O	$Mg(g) \rightarrow Mg^+(g) + e^-$	738	No negative ion of magnesium exists
	$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	1451	
	$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^-$	7733	
	$Mg^{3+}(g) \rightarrow Mg^{4+}(g) + e^-$	10 543	

Standard reduction potential: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E^0 = -2.356$ V

Electronegativity (Pauling): 1.31

Radii of atoms and ions: (WebElements™)		
	Atomic:	150 pm
	Covalent:	130 pm
	Van der Waals:	173 pm
	Mg^{2+} (4-coordinate, tetrahedral):	71 pm
	Mg^{2+} (6-coordinate, octahedral):	86 pm
	Mg^{2+} (8-coordinate):	103 pm

14.1.4 Mg
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
1738 kg m^{-3} 1.74 g cm^{-3}	13.98 cm^3	923 K 650 °C	1363 K 1090 °C	1024 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
160	157	154	150	–

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$14.6 \cdot 10^{-6}$	$24.8 \cdot 10^{-6}$	$29.1 \cdot 10^{-6}$	$35.4 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1173 K**
6.2	39.4	56	100	277	287

Mass magnetic susceptibility χ_{mass} at 293 K	$+6.8 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
45 GPa	17 GPa	43 GPa	0.32

14.1.5 Mg
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	8.95 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	127.6 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	147.7 kJmol^{-1}
Entropy S^0 at 298 K	32.68 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	15.76	24.87	28.18	34.31	20.79	20.83

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Mg + O_2 \rightarrow 2MgO$	–1139	–1097	–990	–880	–650

14.1.6 Mg
Nuclear Properties and X-ray

Isotope range, natural and artificial	20–34

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{24}Mg	Stable	78.99	+0	–
^{25}Mg	Stable	10.00	+5/2	–0.8555
^{26}Mg	Stable	11.01	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{25}Mg
Reference compound	$MgCl_2/D_2O$
Frequency MHz (^{1}H = 100 MHz)	6.122
Receptivity D^P relative to ^{1}H = 1.00	$2.68 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	1.53
Magnetogyric ratio, radT^{-1}s^{-1}	$-1.639 \cdot 10^7$
Nuclear quadropole moment, barn	0.199

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
11	Na	1.041
12	Mg	1.253
13	Al	1.486

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	40.2
17.37 keV (Mo$K\alpha_2$)	4.14

Neutron absorption	**Thermal neutron capture cross section**	0.064 barns

14.1 Ca
Facts about Calcium

14.1.1 Ca
The Element

Symbol:	Ca
Atomic number:	20
Atomic weight:	40.08
Ground state electron configuration:	$[Ar]4s^2$
Crystal structure:	Cubic fcc with $a = 5.59$ Å

14.1.2 Ca
Discovery and Occurrence

Discovery: Limestone and calcite were known in antiquity. The element calcium was prepared in 1808 by H. Davy in London.

Most important mineral:	Calcite	$CaCO_3$ (Figure M14)
	Dolomite	$CaMg(CO_3)_2$
	Gypsum	$CaSO_4 \cdot 2H_2O$ (Figure M15) Alabaster is a variety of gypsum, known as a decorative stone
	Apatite	$Ca_5[(F,Cl,OH)(PO_4)_3$

Ranking in order of abundance in earth crust:	5
Mean content in earth crust:	$4.15 \cdot 10^4$ ppm (g/tonne)
Mean content in oceans:	412 ppm (g/tonne)
Residence time in oceans:	$0.8 \cdot 10^6$ years
Mean content in an adult human body:	1.4 %
Content in a man's body (weight 70 kg):	980 g

14.1.3 Ca
Chemical Characterization

Calcium is a silvery white, malleable and ductile metal that burns with a yellow-red flame. In air it forms a white coating of oxide and nitride and it reacts violently with water. The element is an essential element for life as a transmitter of nerve impulses and for clotting of blood. Its ions may bind to negatively charged groups in proteins and can in this way switch the activity of enzymes “on” and “off”. Apatite, a calcium phosphate, builds skeletons and teeth.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ca^{II} as in $Ca(OH)_2$, $CaCl_2 \cdot 6H_2O$, and Ca_3N_2	$Ca(g) \rightarrow Ca^+(g) + e^-$	590	A negative ion of calcium does not exist
	$Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$	1145	
	$Ca^{2+}(g) \rightarrow Ca^{3+}(g) + e^-$	4912	
	$Ca^{3+}(g) \rightarrow Ca^{4+}(g) + e^-$	6491	

Standard reduction potential: $Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \quad E^0 = -2.84$ V

Electronegativity (Pauling): 1.00

Radii of atoms and ions: (WebElements™)		
	Atomic:	180 pm
	Covalent:	174 pm
	Ca^{2+} (6-coordinate, octahedral):	114 pm
	Ca^{2+} (8-coordinate):	126 pm

14.1.4 Ca

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
1550 kg m^{-3} 1.55 g cm^{-3}	25.86 cm^3	1115 K 842 °C	1757 K 1484 °C	647 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
–	206	192	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$22 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
7	32	47.5	78	200	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+14 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
20 GPa	7.5 GPa	20 GPa	0.33

14.1.5 Ca
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	8.53 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	154.7 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	178.2 $kJmol^{-1}$
Entropy S^0 at 298 K	41.42 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	19.50	25.31	30.38	39.71	20.95	21.84

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$2Ca + O_2 \rightarrow 2CaO$	–1208	–1167	–1065	–960	–810

14.1.6 Ca
Nuclear Properties and X-ray

Isotope range, natural and artificial 35–53

Naturally occuring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half life**	**Decay mode**	**Decay energy Q**
^{40}Ca	Stable	96.94	+0	–	–	–	–
^{42}Ca	Stable	0.65	+0	–	–	–	–
^{43}Ca	Stable	0.13	–7/2	1.3173	–	–	–
^{44}Ca	Stable	2.09	+0	–	–	–	–
^{46}Ca	Stable	0.004	+0	–	–	–	–
^{48}Ca	Active	0.19	+0	–	6 · 1018 y	β^-	0.278 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{43}Ca
Reference compound	$CaCl_2/D_2O$
Frequency MHz (^1H = 100 MHz)	6.730
Receptivity D^P relative to ^1H = 1.00	$8.68 \cdot 10^{-6}$
Receptivity D^C relative to ^{13}C = 1.00	0.0496
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-1.803 \cdot 10^7$
Nuclear quadropole moment, barn	–0.0408

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
19	K	3.311
20	Ca	3.688
21	Sc	4.086

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	171
17.37 keV ($MoK\alpha_2$)	19.6

Neutron absorption **Thermal neutron capture cross section** 0.44 barns

14.2
Alkaline Earth Metals – A Brief Outline

The elements in group 2 are the alkaline earth metals beryllium Be, magnesium Mg, calcium Ca, strontium Sr, barium Ba and radium Ra. The last one, radium, is more interesting for its radioactive properties than for its similarity with the other alkaline earth elements. It will be described in Chapter 52 The Radioactive Elements. The others will be treated here and in Chapters 15 and 16.

Table 14.1 shows that the first element, beryllium, is very different from the other members of the group. Atomic and ionic radii are small, melting and boiling points high. Owing to the small size of its atom, beryllium has a large ionization energy and a comparatively small tendency to form ions. Unlike the other members of the group, beryllium metal is unreactive towards air and water. In fact beryllium is very like aluminum, something that we also noted in connection with the problem of finding a place for the element in the periodic table (see Chapter 3). The heavier group 2 metals, Ca, Sr, Ba and even Ra are almost as active as the group 1 metals. As a whole the alkaline earth elements are more typically metallic than the alkali metals.

Table 14.1 Physical properties according to the fact tables for the alkaline earth metals

	Beryllium	**Magnesium**	**Calcium**	**Strontium**	**Barium**
Atomic number	4	12	20	38	56
Atomic radius Å	1.05	1.50	1.80	2.00	2.15
Ionic radius Å	0.41	0.71	1.14	1.32	1.49
Melting point °C	1287	650	842	777	727
Boiling point °C	2970[a]	1090	1484	1382	1640
Flame color	None	None	Orange-red	Scarlet	Green

See also the overview on page 882 of ref. [14.1].

[a] Under pressure.

14.3
Magnesium and Calcium in Chemical History

14.3.1
Known Since Antiquity

Before the element calcium was discovered its carbonate had been known as limestone for centuries. In the same way the carbonate of magnesium was known as magnesia or magnesia alba. People in antiquity were familiar with the decomposition of carbonates by thermal treatment, calcination, at a high temperature of about 1000°C. The corresponding oxides formed, quicklime CaO and magnesia usta MgO, were called earths. When these oxides were slaked by adding water the solution became basic, alkaline, owing to the formation of hydroxides. That is the reason for the name *alkaline earth metals* for the group 2 elements[1].

14.3.2
Lime

Calcium hydroxide $Ca(OH)_2$, called slaked lime, is formed by the action of water on calcined limestone. A mixture of slaked lime, sand and water has been used since ancient times as a mortar to bind stone to stone in bricklaying and as an internal and external plaster for walls. Carbon dioxide from the air reacts with the calcium hydroxide, forming calcium carbonate. Finally the mortar becomes a hard mixture of this carbonate and silicate from the sand. Although the composition of lime and the mechanism of its hardening were unknown in ancient times, considerable practical knowledge was developed and documented.

Vitruvius, living in the first decades AD, described in *De Architectura* methods for the preparation of lime, its properties and uses. He says that when the limestone is heated to a high temperature it keeps its volume but loses about one-third of its weight. He believes that water has "boiled off". The real weight decrease is in fact 44% if calcination is complete, but the observation is interesting as a testimony of quantitative thinking. The Scottish chemist Joseph Black showed that the ancient lime burners had been right regarding the weight decrease but wrong concerning the reason for it. In 1755 he published a famous treatise *Experiments upon magnesia alba, Quicklime, and some other Alkaline Substances*. Here he proved that the reason for weight loss on calcination of carbonates is the escape of carbon dioxide, which he called "fixed air".

Joseph Black (1728–1799) was a professor of chemistry in Edinburgh and Glasgow. He laid an important basis for physics and chemistry and introduced the concepts of heat of fusion and heat of vaporization. He was also one of the very first to distinguish *temperature* from *quantity of heat*. His experiments with limestone and the discovery of "fixed air" involved a new interest in gases in chemistry. He passed carbon dioxide

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[1] About earths and earth metals see also Chapter 17 Rare Earth Metals.

into caustic soda and found that the gas is fixed there, a process in which a milder alkali, soda, is formed.

14.3.3
Gypsum

When the hemihydrate of gypsum (see section 14.5.1.6) is ground and mixed with water to a paste this may be kneaded to form different objects: figurines, bowls, stucco work and so on. The mass reverts spontaneously to gypsum, preserving the shape of the component and giving it a certain hardness. People in antiquity were familiar with this process and in several Egyptian tombs gypsum objects have been found. The Greeks used gypsum for utility goods while the Romans preferred limestone. These latter objects had a better resistance against water and humidity in air. Around 975 AD, the Persian pharmacologist *Abu Mansur Muwaffaq* wrote *Book of Pharmacological principle*. There he described, for the first time, the use of gypsum as a bandage for bone fractures.

14.3.4
Magnesia Alba and Usta

Two quite different minerals were for centuries known as *magnesia*. One was the brownish-black *magnesia nigra*. The other was white and because of that was called *magnesia alba*. The black mineral appears to have been the manganese mineral pyrolusite, which is described in Chapter 27 Manganese. Magnesia alba had similarities with limestone, but, in reality, what was the difference? Joseph Black made it clear. In his booklet of 1755, *Magnesia Alba, Quicklime and other Alkaline Substances*, cited above, he showed that magnesia alba has its own earth, its own oxide, *magnesia usta*, completely different from lime. When magnesia alba is calcined, magnesia usta is formed in the same way as limestone is transformed into lime. Black's achievement in this respect has made him discoverer of the element magnesium, even if he shares the priority with Humphry Davy, who in 1808 prepared the metal by fused-salt electrolysis.

14.3.5
The Bitter Salt From Epsom

In the summer of 1618, Henry Vicker herded his cattle at Epsom in Surrey, England. A hollow in the ground, filled with water, put him in a quandary. Not a single one of his thirsty animals liked to drink the water. He himself found that the water was bitter and undrinkable. However, it gradually proved to have some advantages over common fresh water. It had a healing effect on small wounds and it got the reputation of being good for the health of those who forced themselves to drink it. By the middle of the century Epsom had become a spa town that attracted wealthy visitors from England and the Continent.

The demand for the salt from Epsom became so large that it had to be extracted from other wells and was sold with the false trade description “Salt from the healthy spring of Epsom”. Many chemists in the 18th century became interested in the mysterious Epsom salt. *Caspar Neuman* (1683–1737), a pharmacist and professor of chemistry in Berlin, added sulfuric acid to the mother liquor left after the crystallization of sodium chloride from sea water. He obtained crystals of a salt with the same characteristics as Epsom salt. He thought that the bitterness was connected to magnesia alba. Obviously Neuman had a feeling that the Epsom salt contained a chloride or a sulfate of the metal in the white magnesia. A. S. Marggraf synthesized magnesium chloride and observed that the same substance was obtained from seawater after crystallization of sodium chloride. In modern chemical language: Seawater contains magnesium chloride, which is more soluble than sodium chloride, information that Torbern Berman in Uppsala had also discovered and published. Finally in 1806 the Epsom salt was described as the mineral *epsomite* $MgSO_4 \cdot 7H_2O$.

A curious note about the bitterness of magnesium salts is given in ref. [14.2]. Webster’s Yorkshire Beer may owe some of its unique taste to the high levels of magnesium sulfate in the water used to brew it.

14.3.6
Carving in Stone

In 1760, A. S. Marggraf, working in Berlin, investigated different soft, hydrous minerals from the mountains in Saxony. They were serpentines, talc, asbestos and steatite (soapstone). Some of them were so soft that different objects could be cut of the stone: mortars, boxes, bowls, teapots. Marggraf reported that the mineral type is well known but that *nobody knew the composition*! He himself made up his mind to find the answer. He dissolved samples in sulfuric acid and found that the solution contained a component that was neither lime nor alumina. When the solution was evaporated to a small volume no alum was formed but crystals identical with Epsom salt. Marggraf was thus the first to demonstrate that minerals of that type contain magnesium.

> The minerals Marggraf examined are today described in the following way:
> - *Serpentine,* a series of minerals with the approximate composition $Mg_3Si_2O_5(OH)_4$
> - *Talc,* a very soft, light-green or gray mineral $Mg_3Si_4O_{10}(OH)_2$ with a soapy feel
> - *Steatite*, an impure talc-rich rock
> - *Soapstone*, a mineral name applied to *steatite* or massive talc
> - *Asbestos,* a term applied to a group of magnesium-containing silicate minerals that readily separate into thin, strong fibers (see further Chapter 40 Silicon)

In New England, both native Americans and colonizers had earlier found useful applications for the soft stones. Per Kalm, a Finlander and disciple of Linné (Linnaeus), became professor of economy at Åbo University in 1747. During the period 1747–1751 he undertook a journey in North America, a study tour that attracted much attention. In his report from the tour he wrote [14.2]:

> Mr. Benjamin Franklin gave me a piece of stone which, on account of its indestructibility in the fire, is made use of in New England for making melting furnaces and forges. It consists of lapis ollaris or serpentine stone and of asbestos...Another stone is called soapstone by many of the Swedes being as smooth as soap on the outside. They make use of it for rubbing spots out of their cloths.... The old boilers or kettles of the Indians were either made of clay or of different kinds of potstone (lapis ollaris). The Indians notwithstanding their being unacquainted with iron, steel, and other metals, have learnt to hollow out very ingeniously these pots or kettles of potstone. The old tobacco pipes of the Indians are likewise made of clay or potstone or serpentine stone.

14.3.7
Magnesium and Calcium Metals

At the Royal Institution in London, Davy was anxious to go further with the alkaline earths after his successful experiments with potassium and sodium in 1808. The fascinating story about this and his cooperation with Berzelius is related in Chapter 16 Strontium and Barium.

Antoine-Alexandre-Brutus Bussy was a professor of chemistry at the École de pharmacie in Paris. He was attached to the school for more than 50 years, 30 of which were as its principal. In 1831, Bussy prepared magnesium by a method quite different from Davy's and in greater quantity. He let magnesium chloride react with metallic potassium. Water dissolved potassium chloride from the content of the reaction crucible and shining balls of magnesium became visible. In 1833, Michael Faraday developed a method for preparing magnesium by electrolysis of the fused chloride, a method verified by Bunsen in 1852. The technique later became used for the industrial production of magnesium. In the first decades of the 20th century, magnesium was obtained from carnallite from deposits in Germany. The quantities were small, but sufficient for the limited need in the world at that time. In the 1930s production increased owing to the introduction of the light, corrosion-resistant magnesium alloy *electron*, containing aluminum, manganese and zinc. Also an aluminum alloy with 4% magnesium was used and increased the demand for magnesium. The use of magnesium in the aircraft industry in World War II resulted in demand of quite a different order, and large-scale production methods had to be developed.

After Davy's first calcium preparation the development of alternative methods was limited. At the end of the 19th century, Henri Moissan in France, the discoverer of fluorine, prepared the element by reduction of calcium iodide with potassium. From the beginning of the 20th century, production was based on the electrolysis of fused calcium chloride.

14.3.8
Etymology

On the *Magnesia* peninsula in Thessaly on the Aegean Sea, beautiful white stones were known from an early date. They were given the name *magnesite*. It was natural to name the corresponding metal *magnesium*. In old Rome the designation *calx* was used for limestone, chalk and lime. Its genitive, *calcis,* became a natural base for the element name *calcium*.

14.4
Magnesium in Our Time

14.4.1
Occurrence

In the earth's mantle there is a preponderance of magnesium silicates such as olivines $(Mg,Fe)_2SiO_4$ and pyroxenes $(Mg,Fe)SiO_3$. This controls the distribution of the element between mantle and crust. In the crust, magnesium is globally widespread and ranked seventh in order of abundance among the elements. It occurs particularly in deposits of the sedimentary or metamorphic carbonate minerals magnesite and dolomite but also as evaporite minerals epsomite and carnallite. Weathering of igneous rocks containing olivine has resulting in soft minerals such as talc and fibrous minerals such as serpentine and asbestos. Some magnesium minerals and their formulas are presented in Table 14.2.

Table 14.2 Some important magnesium minerals

Mineral	Formula
Forsterite, an olivine	Mg_2SiO_4
Enstatite, a pyroxene	$MgSiO_3$
Chrysotile, a serpentine	$Mg_3Si_2O_5(OH)_4$
Talc	$Mg_3Si_4O_{10}(OH)_2$
Magnesite	$MgCO_3$
Dolomite	$CaMg(CO_3)_2$
Epsomite	$MgSO_4 \cdot 7H_2O$
Carnallite	$KMgCl_3 \cdot 6H_2O$

Resources from which magnesium and magnesium compounds can be recovered are virtually unlimited and the reserves of magnesite alone are estimated at 1.8 billion tonnes. The content of magnesium in seawater is high, 1200 g/m^3, thus being more than one-tenth of the sodium content. Seawater is therefore the main modern source of magnesium metal and many magnesium compounds.

14.4.2
Manufacture of Magnesium Metal

There are two major techniques practiced for the production of primary magnesium metal. The first of these is the electrolysis of magnesium chloride, prepared from seawater; the second is the thermal reduction of magnesium oxide. Demand for magnesium is also being met by expanding magnesium recycling. Alloys used for structural applications can be recycled into products displaying the same chemical, physical and mechanical characteristics as primary material. This attribute is being actively encouraged within the industry, given its positive impact upon the environment. Recycling uses only 5% of the energy required to produce the primary product.

14.4.2.1 **Primary Magnesium Metal From the Sea**

The dominating production method is the electrolysis of magnesium chloride. In 1940, Dow Chemical built a magnesium factory at Freeport in Texas, USA with an extraction based on seawater. Slaked lime was added to the water to precipitate magnesium hydroxide. Originally the lime was obtained by burning mussel shells, also obtained from the sea. This was forbidden for environmental reasons and lime was replaced by calcined dolomite. As often occurs when changes are imposed on an industry to improve the environment, both a technical and an economic gain resulted. The burned dolomite not only changed the pH to precipitate magnesium hydroxide, it also added extra magnesium. These processes are still the main elements of the methods for magnesium recovery from seawater, the *DOW process* and the Norwegian *Hydro process*. In the former, the magnesium hydroxide is dissolved in hydrochloric acid and magnesium chloride may crystallize. The chloride is added to a molten electrolyte, slowly and continuously, so that water of crystallization is removed. Electrolysis is performed at 800°C with a steel cathode and a graphite node. Molten magnesium metal collects on the surface of the fused electrolyte. In the Norwegian process, the magnesium hydroxide is transformed to magnesium oxide, which is mixed with coke. When chlorine gas is passed through the mixture at a high temperature magnesium chloride is formed and is decomposed by electrolysis of the fused salt. Chlorine gas, evolved at the anode, is returned to the process.

14.4.2.2 **Thermal Reduction – The Pidgeon Process**

L. M. Pidgeon (1903–1999) was a professor of chemistry and metallurgy in Canada. He developed a process for the production of magnesium metal, using the reaction at high temperature, about 800°C, between calcined dolomite and ferrosilicon. Owing to the demand for magnesium during World War II, six magnesium plants were built throughout North America and Canada.

14.4.3
Uses of Magnesium Metal and Compounds

14.4.3.1 Magnesium Metal – Advantages and Disadvantages

Magnesium is being increasingly used as a construction material. Its big advantage is the low density (1.74 g/cm^3, compared to 2.7 for aluminum, 4.5 for titanium and 7.87 for iron). Another benefit is the good castability. The low tensile strength has been improved by adding different alloying components, for instance 9% Al. A drawback is the poor corrosion resistance. On the surface no thin, dense, and protecting oxide is spontaneously formed – unlike on aluminum. When magnesium and its alloys are used, therefore, they have to be protected by chromating and lacquering, as described in Chapter 24 Chromium.

In all work with magnesium the risk of fire deserves attention. If magnesium starts to burn, water must not be used in an attempt to extinguish it, as this makes the situation worse. At the high temperature, magnesium is oxidized by the water, hydrogen is evolved and the fire becomes explosive. An incipient fire must instead be put out with sand, which keeps the air out.

In new research projects, non-combustible magnesium alloys are being developed. Investigations of the effect and mechanism of elements that may suppress the combustibility of magnesium are continuing. Calcium has been mentioned as an alloying element.

14.4.3.2 The Main Applications

Magnesium is an important alloying metal for aluminum, as, for instance, in the alloy AA 5052 with 2.5% Mg. In fact 43% of the total magnesium metal produced in 2000 was used for such alloying purposes. Different magnesium cast alloys accounted for 34%, while 13% was used for desulfurization in the iron and steel industry. World production was 430 000 tonnes and the figure is increasing annually.

14.4.3.3 In the Automotive Industry

Magnesium has a long tradition of use as a lightweight material in automotive construction. Racing cars used magnesium parts in the 1920s, but magnesium castings were not extensively used in commercial vehicles until 1936 when the Volkswagen Beetle was introduced. Presently, around 15–25 kg of magnesium is used in many cars. Applications include transmission casings, intake manifolds, cylinder head covers and inner boot-lid sections. One of the most common alloys used in the automotive industry is AZ91D, a magnesium alloy with 9% Al and 0.3–1% Zn. A new magnesium alloy, developed by GM, containing 4–6% Al and 1.5–3.5% Ca has such a high tensile strength and such good creep properties that it may have the potential to replace aluminum and iron in power train components.

14.4.3.4 **In Aviation and Space Technology**

In aircraft engines, magnesium alloys are being used in both civil and military aircraft, mostly as castings in component cases and gearboxes. Civil applications include intermediate casings and gearboxes. Magnesium alloys are also used for helicopter transmission casings.

As magnesium alloys are the lightest structural metals available they have been specified, as sand cast or forged alloys, for the production of critical components in the construction of satellite components since the earliest space programs. Magnesium alloys with 3 or 6% Al and 1% Zn are used. A magnesium–lithium alloy has the advantage of being the lightest alloy available and is used.

14.4.3.5 **Some Special Magnesium Metal Applications**

The first use of metallic magnesium was in pyrotechnics and as a flashlight in photography. The combustion temperature is above 2000°C and the light is intensely white. The metal's great affinity for oxygen has made it an important reducing agent, as, for instance, in the Kroll process for manufacturing titanium (see Chapter 18 Titanium).

Owing to its strong reducing capability, the metal magnesium may be used for *cathodic protection* of iron and steel components, water heaters, storage tanks, pipelines, and so on (Figure 14.1). Together with the steel object, magnesium forms a galvanic cell in which it acts as a *sacrificial anode*. The anode reaction is $Mg \rightarrow Mg^{2+} + 2\ e^-$. At the cathode no metal attack occurs. Hundreds of tonnes of magnesium are used annually for this purpose.

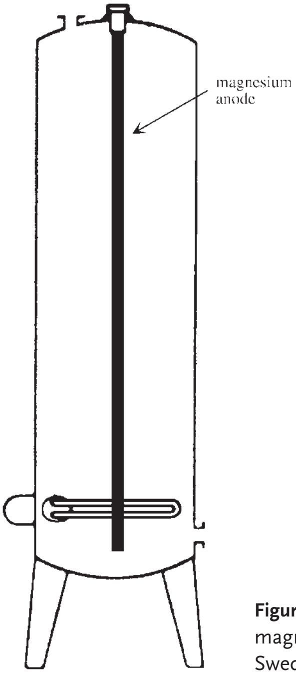

Figure 14.1 Cathodic protection of a water heater with a central magnesium anode. (Reprinted from Bulletin No. 100, 1987, Swedish Corrosion Institute. With permission.)

14.4.3.6 Magnesium Oxides and Compounds

Magnesium oxide MgO, obtained by calcination of magnesite, is mainly used as a refractory material for lining furnaces for iron and steel production as well as for the manufacture of glass and cement.

A special but very important use of magnesium is for alkylation reaction in organic synthesis (alkyl groups R are methyl CH_3, ethyl C_2H_5, propyl C_3H_7, etc.). Organometallic compounds are used as tools for these syntheses. They are readily formed when alkyl halides (RCl, RBr, RI) react with metals of low electronegativity, in particular magnesium:

$$C_2H_5Cl + Mg \rightarrow C_2H_5MgCl$$

The magnesium derivatives are known as *Grignard reagents*, named after *V. Grignard* in France, who developed them and for that shared the Nobel Prize in 1912. An example of their use is the synthesis of an alcohol from formaldehyde:

$$C_2H_5MgCl + H \cdot CHO + (H^+) \rightarrow C_2H_5CH_2OH$$

The reaction occurs in ether, as water must be excluded. An intermediate alkoxy magnesium chloride must, however, be decomposed by aqueous acid in a separate step at the end of the reaction.

14.5
Calcium in Our Time

14.5.1
Occurrence

14.5.1.1 Minerals

In the earth's crust calcium is ranked fifth in order of abundance among the elements. It is common in all natural waters and essential for all life. Most calcium is present in combination with sodium, magnesium and aluminum in silicate minerals. During weathering of silicates, calcium and sodium ions are most easily released. Unlike sodium, calcium forms compounds with low solubility with different anions, including carbonate CO_3^{2-}, sulfate SO_4^{2-}, fluoride F^-, and phosphate PO_4^{3-}. The corresponding minerals are common in sedimentary rocks. Different minerals and their formulas are shown in Table 14.3.

Table 14.3 Some calcium minerals

Mineral	Formula
Anorthite, a feldspar	$CaAl_2Si_2O_8$
Augite, a pyroxene	$(Mg, Fe,Ca)SiO_3$
Calcite (Figure M14)	$CaCO_3$
Dolomite	$CaMg(CO_3)_2$
Gypsum (Figure M15)	$CaSO_4 \cdot 2H_2O$
Fluorite, fluorspar	CaF_2
Apatite	$Ca_5(PO_4, CO_3)_3(F, OH, Cl)$

14.5.1.2 **Limestone**

Calcite, a white mineral, sometimes with pale shades of yellow or blue, is the principal constituent of *limestone*. Note that limestone is a rock, not a mineral. As limestone in the general meaning has been formed as a sediment in a marine environment it often contains the fossilized remnants of dead animals and plants. It is mainly the hard parts, such as shells and skeletons, that are preserved. Coral limestone from the sea is quite white. Red and brown limestone, such as the common orthoceratites, are colored by finely dispersed iron oxide and other iron compounds. The mineral glauconite, a mica, is a group of green minerals consisting of hydrated silicates of potassium and iron. If present it gives a green tone to the limestone.

Marl is the designation for loose limestone, earthy or powdery, usually impure calcium carbonate precipitated on the bottoms of ponds largely through the chemical action of aquatic plants. The calcium carbonate in marl may range from 90% to less than 30%.

All the limestones mentioned have been formed during the last 600 million years of the geological history of our earth. Their richness in fossils gives important information about the development of the forms of life. All this has happened within the *Phanerozoic era*, the youngest eon in the geological history of earth, the one we ourselves belong to. It is named after the Greek word *phaneros*, visible, and *zoion*, animal.

14.5.1.3 **Marble**

Marble is a type of recrystallized limestone. The recrystallization process probably occurred about 2000 million years ago in connection with volcanic activity. The carbonates were heated to a high temperature and simultaneously at such a high pressure that decomposition was avoided. Under these circumstances calcite and dolomite were recrystallized to marble. Marble is a fine-grained rock, although the grains may be very small, almost invisible, as in *statuario*, the completely white *Carrara marble*. The white semi-transparent Greek marble from the island of Paros was the material for many famous statues.

14.5.1.4 **Fluorite or Fluorspar**

Fluorite CaF_2 is found in many different colors. It occurs in veins, usually as a gangue mineral associated with lead, tin and zinc ores. It is the principal ore of fluorine, and is used as a flux in metallurgy and in the preparation of glass and enamel, and for the manufacture of hydrofluoric acid.

14.5.1.5 **Apatite**

Apatite is a group of variously colored minerals consisting of calcium phosphate together with fluorine, chlorine, hydroxyl or carbonate in varying amounts. When not specified, the term usually refers to *fluorapatite*. Large and beautiful apatite crystals, variously colored, are present in some magnetite iron ores rich in phosphorus. The beautiful forms and colors have given the mineral its name: Greek *apa'te* means seduction, deceit. The mineral is easily confused with other minerals.

14.5.1.6 **Gypsum – Plaster of Paris**

Gypsum is a widely distributed mineral and the commonest sulfate mineral, frequently associated with halite and anhydrite in beds, inter-stratified with limestone, shale and clay.

From a pure, saturated solution of calcium sulfate the dihydrate $CaSO_4 \cdot 2H_20$ crystallizes if the temperature is below 60°C. If the crystallization occurs at a higher temperature the anhydrous salt $CaSO_4$ is formed. From common seawater, with its high content of sodium chloride, anhydrous calcium sulfate may also be formed at temperatures down to 30°C [14.3]. During geological periods these processes have occurred in nature and formed the minerals *gypsum*, the dihydrate, and *anhydrite*, anhydrous calcium sulfate.

Gypsum has the characteristic of giving off part of its water when it is heated to between 100 and 200°C. Then the *hemihydrate* is formed:

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2\ H_2O + 1\ 1/2 H_2O$$

When this is ground and mixed with water, a paste called *Plaster of Paris* is obtained. Components formed from the plaster revert spontaneously to gypsum, preserving the shape.

Alabaster is a variety of gypsum, and is known as a decorative stone. It is white but sometimes beautifully shaded with light-colored tones of yellow or red. Its usefulness is limited by its softness (hardness 2 on Mohs scale). A gypsum curiosity is the yellow *Desert rose*, found in the Sahara.

14.5.2
Water Hardness

Industrial water and tap water is never completely clean. Rainwater dissolves atmospheric gases, carbon dioxide and the more aggressive sulfur dioxide, if present. Once it reaches the ground, the water reacts with the rocks. Because of its easy release in weathering, calcium ion is present in most fresh waters. Its concentration varies considerably, of course, according to the type of surrounding rocks. The concentration of calcium is used as a measure of the *water hardness*. Other ions present may be magnesium Mg^{2+}, iron Fe^{2+}, hydrogencarbonate (bicarbonate) HCO_3^-, sulfate SO_4^{2-} and so on.

14.5.2.1 Temporary Hardness

The so-called temporary hardness is caused by metal ions dissolved as hydrogencarbonates. This type of hardness disappears when the water is heated.

$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H_2O$
$Mg^{2+} + HCO_3^- \rightarrow MgCO_3 + H_2O$
$Fe^{2+} + 1/4\ O_2 + 2OH^- \rightarrow FeOOH + 1/2\ H_2O$ rust

The soluble hydrogen carbonates are transformed to a mixed precipitate of $CaCO_3$, $MgCO_3$ and rust, a *boiler scale*. This can be a serious problem in boilers producing steam for manufacturing processes and also in water heaters at home. Boiler scale can be removed by adding vinegar (acetic acid) and heating.

14.5.2.2 Permanent Hardness

Permanent hardness is caused by calcium sulfate with ions of Ca^{2+} and SO_4^{2-} dissolved in the water. This hardness cannot be removed by heating. Addition of soda Na_2CO_3, however, softens the water by precipitating $CaCO_3$, leaving a water containing sodium sulfate. This water makes it easier for soaps and shampoos to foam. The problem of precipitation of insoluble calcium stearate or palmitate is also avoided.

14.5.2.3 Water Types

The water hardness is expressed as the number of milligrams Ca per liter or in °dH ("German degrees"). 1 °dH corresponds to 10 mg CaO per liter. 1 mg Ca/liter = 0.14 °dH. Water types are presented in Table 14.4.

Table 14.4 Different water types

Water type	mg Ca per liter	°dH
Very soft	0–15	0–2
Soft	15–35	2–5
Medium hard	35–70	5–10
Hard	70–150	10–20
Very hard	>150	>20

14.5.2.4 Softening and Deionization

Deionized water has a hardness of zero. This type of water was earlier produced by distillation. Today an ion-exchange technique is used. *Water softeners* generally have a single resin, a cationic resin, to remove calcium and magnesium ions. Deionization equipment, which removes all ions (metallic and non-metallic) from the water, uses two columns, operating in series. One contains cationic resin and removes metallic ions, the other has an anionic resin to remove the acid radicals.

14.5.3
Manufacture of Calcium Metal

Before World War II calcium metal was made by electrolysis of fused calcium chloride at 800°C. A metal with 98% calcium was obtained. In a modern method, a variant of the *Pidgeon magnesium process,* briquettes of lime and aluminum powder are heated in evacuated retorts at 1150°C. Calcium metal with a purity of 99% is formed and evaporated. The calcium vapor is condensed in the water-cooled ends of the retorts. By repeated vacuum distillation the purity can be improved to 99.9%. The metal is stored and transported in steel barrels filled with argon.

14.5.4
Use of Calcium Metal and Compounds

14.5.4.1 Calcium Metal

Metallic calcium is characterized by its great affinity for oxygen and nitrogen. Because of that it is used as a scavenger metal to remove residual amounts of air from vacuum tubes. It is used also as a reducing agent in the production of some metals. Magnesium is preferred but calcium must be used in the reduction of some of the rare earth metal oxides. Attempts are being made to develop the use of calcium as an alloying element in magnesium and aluminum alloys.

The modern steel industry is a big user of calcium metal. As described in Chapter 8 Iron, the oxygen content in molten raw steel is high. Oxygen is removed by *deoxidizing* with aluminum or silicon. Small slag particles, oxides of aluminum and silicon, remain as inclusions in the solid steel and wear the tools during subsequent machining of the steel (turning, drilling, milling). An important alternative, especially for stainless steels, is deoxidation with calcium (or a silicon-calcium alloy). The addition of calcium creates difficulties. The metal will be oxidized at the very hot surface of the steel before it has finished its job as deoxidizer. Introducing calcium wire or powder in a thin-walled iron tube, which is fed into the molten steel, has solved this problem. When the iron tube melts, the calcium metal is already deeply within the steel and reacts, as intended, with the dissolved oxygen. The calcium oxide formed floats up to the slag. Oxide particles remaining in the steel are harmless from the machining point of view. The same process is also used to remove sulfur from cast iron and steel.

14.5.4.2 Limestone and Lime

Calcium carbonate is used on a large scale for many purposes. Pure limestone, with a content of 98–99% $CaCO_3$, 0.5% $MgCO_3$ and less than 0.3% other oxides, ground to very fine particles is used as a filler for paper and makes it dazzling white. Ground limestone is also used as a filler in plastics, especially PVC. It improves stiffness, impact strength and dimensional stability.

Large quantities of lime are used in the steel industry to line furnaces and as a component of molten slags, which take an active part in the refining of steel. For production of this type of lime, rocks can be used that contain at least 80% of the carbonates of calcium or magnesium and which, after calcination, give a product that slakes on the addition of water.

Lime is also important in some modern "green" technology. It is used to absorb the sulfur dioxide in many industrial gases and also to neutralize solutions containing sulfuric or hydrochloric acids before they are discharged into the environment.

"Liming" for prevention of the acidification of the landscape does not use lime itself but limestone powder. Sulfuric acid arriving in lakes from acid rain is eliminated by the reaction:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

14.5.4.3 **Cement**

Cement is a lime-consuming product. *Portland cement* was developed and patented in 1824 by its British inventor *Joseph Aspdin* (1799–1855). Aspdin heated a mixture of finely ground limestone and clay in his kitchen stove and ground the mixture into a powder that hardened after the addition of water [14.4]. The term portland cement was used because concrete made from cement resembled the stone on the Isle of Portland on the British coast.

Portland cement is manufactured from limestone together with additives containing alumina and silica (shale, clay and sand). A mixture of raw materials is fed into the upper end of a tilted rotating, cylindrical kiln. Burning fuel is forced into the lower end of the kiln. At 1480°C the material partially fuses, and pellets of *cement clinker* are formed. Cooled clinker is combined with gypsum and ground so fine that nearly all of it passes through a No. 200 mesh sieve (75 microns). This fine gray powder is portland cement. Cements for use under salt water may contain as much as 5% iron oxide. Some rocks, called cement rocks, are naturally composed in suitable proportions, but in general the cement plants make synthetic mixtures.

A properly designed concrete mixture contains about 10 to 15% cement, 60 to 75% aggregate and 15 to 20% water. Aggregates are inert granular materials such as sand, gravel or crushed stone, which, along with water and portland cement, are essential ingredients in concrete.

All portland cements are hydraulic cements, which means that they harden through a chemical reaction with water. The initial hardening is caused by the hydration of tricalcium silicate Ca_3SiO_5, which forms jelly-like hydrated silica and calcium hydroxide. These substances crystallize and bind together the particles of sand or stone that are always included. The calcium hydroxide formed increases the pH, which protects the steel reinforcing bars against corrosion.

14.5.4.4 **Gypsum**

The use of gypsum, or *plaster of Paris* as it is called, for different objects – figurines, bowls, stucco work and so on – has been described in the historical section. In our time the most important – and very large – application is for producing gypsum wallboard (drywall), which has almost replaced other wall coverings in buildings.

14.6
Biological Roles

14.6.1
Magnesium

By the end of the 18th century it was known that plants contain magnesium. However, it was not until the beginning of the 20th century that the German chemist Richard Willstätter discovered magnesium's great role in green plants. *Chlorophyll,* Figure 14.2, has magnesium as the central atom. As this molecule is essential for photosynthesis by green plants, the metal is vital for plants.

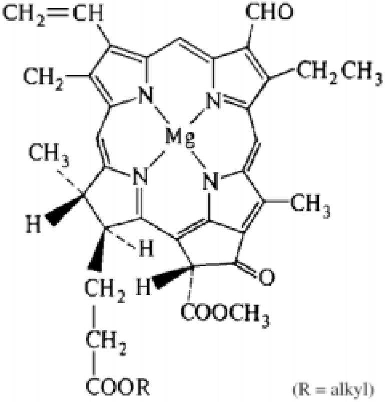

Figure 14.2 Chlorophyll.

14.6.2
Calcium

Calcium is an essential element for all living things. In fact the role of calcium cannot be over-emphasized. The metal is important for hormonal activities and essential for fertilization and cell division. The element also controls the mechanical stability of the walls and membranes in cells and stimulates muscle contractions.

Another important function is the use of calcium carbonate for the external shells of marine organisms. In mammals including humans, skeletons and teeth are made of apatite. Bones in the human body may contain up to 17% calcium. Bones in the body must not be looked on as "dead" material, some sort of non-living mineral. On the contrary, bone is made up of millions of cells and a matrix that is calcified. Two types of cell are involved in bones, namely the osteoclasts that reabsorb the calcified matrix and the osteoblasts that rebuild it. These two cell types must be well coordinated; otherwise pathological situations may arise. They also keep the calcium level in the blood steady, making all calcium functions in the body possible. We need a daily dose of calcium and also of vitamin D, which regulates bone growth.

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15
Beryllium

15.1 Be
Facts about Beryllium

15.1.1 Be
The Element

Symbol:	Be
Atomic number:	4
Atomic weight:	9.01
Ground state electron configuration:	$[He]2s^2$
Crystal structure:	Hexagonal hcp with $a = 2.29$ Å, $c = 3.58$ Å

15.1.2 Be
Discovery and Occurrence

Discovery: N. L. Vauquelin discovered the element in 1798 in the precious stones beryl and emerald. The metal was isolated in 1828 by A. A. B. Bussy in Paris and by F. Wöhler in Göttingen, Germany.

Most important mineral:	Beryl and emerald	$Be_3Al_2(SiO_3)_6$ (Figure M16)
	Bertrandite	$Be_4Si_2O_7(OH)_2$

Ranking in order of abundance in earth crust:	48
Mean content in earth crust:	2.8 ppm (g/tonne)
Mean content in oceans:	$5.6 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	100 years
Mean content in an adult human body:	0.004 ppm
Content in a man's body (weight 70 kg):	0.3 mg

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15.1.3 Be

Chemical Characterization

Beryllium is a lead-gray metal. It tarnishes slowly in air owing to oxide formation. This thin oxide layer gives beryllium its ability to scratch glass. Aquamarine and emerald are precious forms of the mineral beryl. Alloys containing beryllium are being used more and more in industry owing to their lightness, stiffness and dimensional stability. Because X-rays easily pass through pure beryllium, the element is used as the window material for X-ray tubes. As beryllium and its compounds are very toxic, stringent precautions with specially designed exhaust hoods are needed to avoid exposure in industrial workplaces.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Be^{II} as in BeO, BeF$_2$, and Be$_3$N$_2$	Be(g) → Be$^+$(g) + e$^-$	899.5	No negative ion of beryllium exists
	Be$^+$(g) → Be^{2+}(g) + e$^-$	1757	
	Be^{2+}(g) → Be^{3+}(g) + e$^-$	14 849	
	Be^{3+}(g) → Be^{4+}(g) + e$^-$	21 007	

Standard reduction potential: Be^{2+}(aq) + 2e$^-$ → Be(s) $E^0 = -1.97$ V

Electronegativity (Pauling): 1.57

Radii of atoms and ions: (WebElements™)		
	Atomic:	105 pm
	Covalent:	90 pm
	Be^{2+} (4-coordinate, tetrahedral):	41 pm
	Be^{2+} (6-coordinate, octahedral):	59 pm

15.1.4 Be

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
1848 kg m^{-3} 1.85 g cm^{-3}	4.88 cm^3	1560 K 1287 °C	3243 K 2970 °C	1820 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
367	218	168	129	93

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$1.3 \cdot 10^{-6}$	$11.3 \cdot 10^{-6}$	$15.1 \cdot 10^{-6}$	$19.1 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
–	28	53	111	260	–

Mass magnetic susceptibility χ_{mass} at 293 K $-13 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
300 GPa	132 GPa	138 GPa	0.14

15.1.5 Be
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	10.0 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	297 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	324 $kJmol^{-1}$
Entropy S^0 at 298 K	9.50 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
1.83	16.44	23.06	27.58	30.00	30.00

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Be + O_2 \rightarrow 2BeO$	–1159	–1120	–1023	–927	–

15.1.6 Be
Nuclear Properties and X-ray

Isotope range, natural and artificial	6–14

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^9Be	Stable	100	–3/2	–1.178

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^9Be
Reference compound	$Be(NO_3)_2/D_2O$
Frequency MHz (^1H = 100 MHz)	14.052
Receptivity D^P relative to ^1H = 1.00	0.0139
Receptivity D^C relative to ^{13}C = 1.00	79.3
Magnetogyric ratio, $radT^{-1}s^{-1}$	$3.760 \cdot 10^7$
Nuclear quadropole moment, barn	–0.0529

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
3	Li	–
4	Be	0.109
5	B	0.183

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	1.11
17.37 keV ($MoK\alpha_2$)	0.257

Neutron absorption	Thermal neutron capture cross section	0.009 barns

15.2
Discovery

15.2.1
Precious Stones Known Since Antiquity

Two gemstones, beryl and emerald, have been known since ancient times, the former yellow like gold the latter a lovely green. In the Old Testament, precious stones are mentioned in different contexts, as for example in the instructions for the High Priest's breastplate:

> And thou shalt make the breastplate of judgment with cunning work ... And thou shalt set in settings of stones, even four rows of stones; the first row shall be a sardius, a topaz, and a carbuncle; this shall be the first row. And the second shall be an emerald, a sapphire, and a diamond. And the third row a jacinth, an agate and an amethyst. And the fourth row a beryl, and an onyx, and a jasper; they shall be set in gold in their inclosings. And the stones shall be with the names of the children of Israel, twelve according to their names, like the engraving of a signet; every one with his name shall they be according to the twelve tribes .... (Exodus, chapter 28:17–21)

It is notable that the beryllium-containing stones emerald and beryl were mentioned by name in these early times. Pliny the Elder writes in the first century AD that beryl and emerald are closely related and of the same nature.

In the eastern desert region of Egypt, near the Red Sea, emerald mines were located at Mt. Zabara. The ruins of the old mine sites can still be found. The green emeralds from these mines were Queen Cleopatra's favorite gems, and the mines were named in her honor. She was the ruler of Egypt in the period 51 to 30 BC but the mines had been worked long before then, as can be seen from adornments in the tombs of the Pharaohs, Tutankhamen among others. The emeralds from Egypt were highly praised by Greeks and Romans, who made use of emerald for their most fashionable jewelry. Gemstones from these mines have been found in the buried Roman cities of Pompeii and Herculaneum.

In 1817, M. Fredric Cailliaud rediscovered the mines and found that they were almost in the same condition as when they were once closed down, with underground rooms, stopes, so big that hundreds of miners might have worked simultaneously. In the dark they could follow the veins and pick up the precious stones by hand. The ancient Egyptians' understanding of mining techniques was impressive.

Skilled alchemists early tried to make synthetic beryls and emeralds. In the so-called Stockholm Papyrus [15.1], descriptions are given for these syntheses. The Papyrus was found in Alexandria in the early years of the 19th century and is dated to the 3rd or 4th centuries AD. Together with the so-called Leyden Papyrus, it is the only original document from this early period and of great value for the history of chemistry, especially from the beginning of alchemy.

15.2.2
Emerald – A Royal Nose Adornment

In the 16th century, the huge Spanish area in South and Central America was divided into two kingdoms – New Spain north of Panama with Mexico as the capital and Peru to the south with Lima as the capital. The former was rich in silver and gold, the latter in emeralds. In 1590, the priest *Father José de Acosta* described emeralds from Peru:

> The Kings of Mexico did esteem them very much; some pierced their nostrils and hang therein an excellent emerald ... The greatest store is found in the New Kingdome of Grenada and in Peru, near into Manta and Puerto Viejo. Towards that place which they call the land of emeraldas ... In the year one thousand five hundred eighty and seven, in which I came from the Indies, they brought two chests of emeralds, every one weighing at least four arrobas [1 arroba = 25 lbs. = 11 kg], whereby we may see their abundance. The Holy Scripture numbers these emeralds among the precious stones which the hie Priest carried on his Ephod or briestplate ... .
>
> (Cited from Mary Weeks, who makes an addition: "The term smaragdus as used in the Bible may have included other green gems as well as the emerald.")

15.2.3
... Destroys Precious Stones but Discovers a New Element

The chemists at the end of the 18th century were interested in beryl and emerald as more than just material for jewelry. What elements were present in the gems? Great experts made several analytical mistakes. Klaproth analyzed an emerald from Peru and found that it contained 66% silica, 31% alumina and a little iron oxide. Beryl had been analyzed by Bergman, who gave the composition calcium aluminum silicate. The same result was reported by Vauquelin. The great French chemist, however, did a U-turn, for which there was a special reason. A close friend of his, *Abbé René-Just Haüy* (1743–1822), had began his career in the service of the Catholic Church and thus bore the clerical title "Abbé". Now he was committed to mineralogy, a science in which he had become a pioneer. He had derived the fundamental laws of crystallography and, in the last decade of the 18th century, was making the final preparations for the publication of his great work *Traité de minéralogie*, containing descriptions of crystal theory and the classification of minerals. Vauquelin told him about the chemical problems with beryl and emerald. Haüy became interested and set about a crystallographic investigation of the two precious stones. He established that they are geometrically identical. Could it then be correct that they differ regarding composition? Vauqelin himself was very active at this time and had recently, in 1797, discovered the element chromium in the red lead of Siberia (see Chapter 24 Chromium). After an urgent request from Haüy, however, he started to analyze the minerals again.

> He obtained an emerald from Peru, brought it into solution and precipitated aluminum hydroxide by careful addition of potassium hydroxide. When this reagent was added in excess in order to dissolve the aluminum hydroxide he found something very important. A large part of the white hydroxide remained undissolved, an observation he had not made in his first investigation. Could it be the hydroxide of a new, undiscovered element? He separated this hydroxide by filtration, dissolved it in acid and prepared the salts, which he also examined. They had a sweet taste and he gave the new oxide the name *glucina*, meaning "sweet".

The new discovery was announced to the French Academy of Sciences on the 26th of the month *Pluviose* in year 6 of the revolutionary calendar (February 15 in 1798). The composition he presented for emerald was 65% silica, 14% alumina, 13% glucina, 2.6% lime, 3.5% chromium oxide and 2% of moisture and other volatile components. He finished by presenting the Academy with a sample of the new earth glucina.

Vauquelin now examined a beryl from Siberia, showing that this gemstone mineral also contained silica, alumina and glucina as main components. It had no lime and chromium oxide but instead some iron oxide. J. F. Gmelin in Germany confirmed this result. Vauquelin had in fact discovered a new element and his priority was not questioned. He, but not Haüy, is mentioned in tables of element discoverers – again something of an accident.

The choice of name for the new element did not please Vauquelin's colleagues in Europe. Sweet taste is a bad basis for a name choice and, in addition, not at all unique to this new element. Try the salts of yttrium, Klaproth wrote, there is a sweet taste even there! As the element is present in the mineral beryl, why not call it beryllium? And so it was, although it took a very long time for the new name to become customary. Even in the 1950s, the name *glucinium* could be used in France for Vauquelin's element.

Gradually it became clear that the mineralogist Haüy's view had been correct. The green emerald, the yellow beryl and also the blue aquamarine are all beryllium aluminum silicates. The formula may be written $Be_3(Al,X)_2(SiO_3)_6$. The variable atom X is the element giving the specific color. In the case of emerald, chromium replaces aluminum to some, very limited, extent. Parts of the incoming white light are absorbed to produce electron transitions between d-orbitals within the Cr^{3+} ions. As a result, most of the red and violet colors are absorbed while the blue and green are transmitted. The emerald takes on a green color. For both the yellow beryl and the blue aquamarine, iron is responsible for the color. It is not uncommon for one specific metal to give different colors to a colorless mineral. The reason may be that it is included in ion complexes with different oxidation numbers. It can also be that the metal is not all bound in the complex but occurs as pigmentation.

Beryllium aluminum silicate, just discussed, is not the only beryllium mineral to occur as precious stones. Chrysoberyl $BeAl_2O_4$ with a small amount of iron is also used as a gem. It is usually yellow, pale green or brown. A transparent variety of chrysoberyl is alexandrite, named after Alexander II, tsar of Russia. It has a green color in daylight but is red in artificial light.

In gemstone terminology, cutting *en cabochon* is a preparation method that brings out a special optical phenomenon, a *star*. Chrysoberyl cut in that way exhibits a band that moves across the summit of the gemstone and resembles the slit pupil of the eye of a cat. Such a gemstone is called a *cat's-eye*. Internal reflection of light from parallel, tiny inclusions causes the "cat's eye" effect.

15.2.4
The Next Step – Beryllium Metal

Antoine-Alexandre-Brutus Bussy (1794–1882) was a pharmacist and doctor. He became professor of chemistry at the École de Pharmacie in Paris. An inorganic chemistry experiment he performed in 1828 entitles him to a position in the story of element discoveries. Beryllium chloride and potassium metal were mixed in a platinum crucible, which was closed by a platinum lid. The crucible was heated by a spirit lamp. The reaction was so violent that the crucible became white hot. After washing the residue with water, elemental beryllium remained as a grayish-black powder. Independently, and about the same time, F. Wöhler in Germany carried out the same reaction.

In the decades after Davy the technique of electrolysis of fused salts was developed rapidly, at the same time as electrotechnology was being transformed. The first to prepare beryllium in this way was the French chemist *Paul Lebeau*. Around 1900, he electrolyzed a fluoride melt of potassium and beryllium in a nickel crucible. He used a graphite anode, with the nickel crucible as the cathode. The voltage and current were 80 V and 20 A respectively. On the inside of the crucible, beryllium crystals were deposited with a purity better then 99.5%.

15.2.5
The Chemistry of Beryllium Confuses and Becomes Clearer

Beryllium was a problematic element. The metal was so much like aluminum that it was obviously trivalent, with the oxide formula Be_2O_3. Berzelius had favored that formula in 1815. Gradually indications of divalent beryllium appeared. The problem became acute as knowledge of the periodic system of the elements grew. Group III A (group 13 in the modern periodic table) ought to be the place for trivalent beryllium. But the element boron already occupied the first position there. In group IIA (group 2) there was a free position before magnesium. Such a place, however, presupposes the oxidation number 2 for beryllium. In 1873, Jean-Charles Gallissard de Marignac studied the double fluorides of beryllium and alkali metals and found evidence for divalent beryllium. (For more about Marignac see page 447 in Chapter 17 The Rare Earth Metals.)

Lars Fredrik Nilson and Otto Pettersson [15.2] investigated beryllium between 1878 and 1880. In their experimental work they melted emeralds together with potassium carbonate, and prepared beryllium oxide. They mixed the oxide with carbon and passed chlorine gas through the mixture at high temperature. Beryllium chloride was formed, which sublimed and was deposited. The gas density of vaporized beryllium chloride was determined to be 2.83 ± 0.10 (relative to air) in the temperature range 686–812°C. Using Avogadro's law they calculated the density of gaseous beryllium chloride making different assumptions regarding its formula. The results of these calculations are shown in Table 15.1.

Table 15.1 Calculated gas density values for beryllium chloride

Assumed formula	Calculated gas density	In agreement with experiment
Be_2Cl_6	8.31	No
$BeCl_3$	4.155	No
$BeCl_2$	2.770	Yes
BeCl	1.385	No

From these results the two scientists concluded that beryllium is divalent and they abandoned their earlier opinion about a trivalent element. Beryllium belongs to group 2 in the periodic table.

15.2.6
Beryllium in an Atomic Theory Breakthrough

In 1930 two scientists, *W. Bothe* and *H. Becker*, observed that when α-particles in the radiation from the radioactive elements polonium or radium penetrated beryllium a previously unknown radiation was produced. The charge of the particles in this new radiation was examined in a cloud chamber, but no tracks were formed. Thus, the new particles had no charge. *James Chadwick* in 1932 solved the problem by proposing a particle having a mass about the same as the proton but without a charge. This particle he called the *neutron*. The reaction that produced the neutron was:

$${}^{4}_{2}He + {}^{9}_{4}Be \rightarrow {}^{12}_{6}C + {}^{1}_{0}n$$

15.3
Occurrence

15.3.1
Bertrandite and Beryl – Industrial Beryllium Minerals

Only two beryllium minerals are of commercial importance for the preparation of beryllium metal and its compounds. Bertrandite $Be_4Si_2O_7(OH)_2$, containing less than 1% Be, is the principal beryllium mineral mined in the USA, while beryl $Be_3Al_2(SiO_3)_6$ (Figure M16) with 4% Be is the mineral produced in other countries. In the year 2000 the world total mined production was 280 tonnes (counted as beryllium), 185 tonnes in the USA, 55 tonnes in China and 40 tonnes in Russia. About 65% of the world's beryllium resources are concentrated in the United States. The deposits are mainly situated at Gold Hill and Spor Mountain, both in Utah, and on the Seward Peninsula in Alaska [15.3].

15.3.2
Emerald for Gemstones

Emerald is less common than diamond and much more expensive than gold. The total production per year in the world is estimated at around 15 million carat (1 carat = 0.2 g). Colombia produces 60% of the emeralds in the world, Zambia 15%, Brazil 10% and Russia 5%. Madagascar, Zimbabwe, Pakistan and Afghanistan together account for the remaining 10%.

In Columbia the Muzo mine, 100 km north-west of the capital Bogotá was mined by the Incas, was forgotten, but was rediscovered in the 17th century, and mining is still going on. In Colombia there is also an eastern emerald belt. Colombian emeralds occur in calcite veins.

15.4
Manufacture

Commercial production of beryllium metal began in 1957 but the market for it has not grown to the size once imagined. Today the US mainly supplies processed beryllium products. Treatment of bertrandite with hot sulfuric acid gives a solution containing beryllium sulfate and other metals. Separation occurs by liquid–liquid extraction and ion exchange. After separation, beryllium carbonate is precipitated and can be transformed into different salts and to the oxide. The metal is prepared by reduction of beryllium fluoride with magnesium or by electrolysis of fused beryllium chloride.

Beryl is only slightly soluble in sulfuric acid. After melting the mineral (melting point 1650°C) and quenching in water the solubility in sulfuric acid is increased. An alternative is to start with an alkali treatment, melting or sintering in sodium hydroxide or carbonate.

15.5
Uses

15.5.1
Special Applications

Beryllium metal has some drawbacks. It is brittle, expensive and toxic. On the other hand it has some unique positive properties. It is light, non-magnetic and reluctant to spark, thus being suitable for non-sparking tools. It has a surprisingly high modulus of elasticity *E* and is thus very stiff. Its *E*-value is 300 GPa compared to 210 for steel, 105 for titanium and 70 for aluminum. Because of this high modulus and its low density, beryllium appeals to designers, especially for applications within aircraft and space. Its very high heat capacity (specific heat) is also important in this connection. On absorbing a certain quantity of heat, the temperature of a given mass of beryllium increases considerably less than would the same mass of aluminum, magnesium or titanium, as shown in Table 15.2. This gives the metal good dimensional stability over a wide temperature range. However, the density of the material ought also to be considered as the low density counteracts the positive beryllium effect. Even so, if a constant metal volume is considered a beryllium component is still favored (see Table 15.3).

Table 15.2 Calculated temperature increases for the addition of 10 kJ (2.39 kcal) to 1 kg of different metals

Metal	Heat capacity $J\,K^{-1}\,kg^{-1}$	Temperature Increase °C
Beryllium	1820	5.5
Aluminum	901	11.1
Magnesium	1024	9.8
Titanium	522	19.1

Table 15.3 Calculated temperature increases on addition of 10 kJ (2.39 kcal) to a component with a volume of 200 cm^3 of different metals

Metal	Heat capacity $J\,K^{-1}\,kg^{-1}$	Component weight g	Temperature Increase °C
Beryllium	1820	370	14.8
Aluminum	901	540	20.6
Magnesium	1024	348	28.1
Titanium	522	902	21.2

In the US space shuttles, some brake components and structural parts use beryllium. Both the low density and the high heat capacity are significant here.

The nuclei of beryllium atoms are simple: 4 protons and 5 neutrons. Because of that their scattering of X-rays is negligible and the radiation is transmitted. Thin foils of the metal are therefore used as window material for X-ray tubes. On the other hand, beryllium atoms reflect neutrons and that is the reason for the metal's use in reflectors, moderators and control rods in research reactors. The fusion reactor *Tokamak*, described in Chapter 9 Hydrogen, is lined with beryllium to protect the steel from neutron attack and to prevent the plasma from being poisoned. Other applications for metallic beryllium include high-speed computer components.

Beryllium oxide, beryllia, is an electrical insulator but a good heat conductor. It is transparent to microwaves and may be used in microwave communication systems. Beryllia serves mainly as a substrate for high-density electronic circuits for high-speed computers, lasers and automotive ignition systems.

15.5.2
Volume Products

The main uses of beryllium are far more humdrum than those described in the previous section.

Beryllium-copper alloys with 2% beryllium are used in a wide spectrum of applications. They have good electrical and thermal conductivity, they are strong, hard, corrosion and fatigue resistant, and nonmagnetic. Beryllium–copper may be looked at as the spring alloy within the copper family. An alternative for springs – without beryllium – is nickel brass, described in Chapter 7 Copper. Components of beryllium–copper are used as springs, connectors and switches in instrumentation and control systems, in radar and telecommunications systems, in automobiles and also in home appliances. Large quantities are used as beryllium–copper tubes in oil and gas drilling.

15.6
Beryllium – A Toxic Element

Beryllium is toxic. When present it binds to the important phosphate-containing systems in the body and may create serious problems. Owing to the very low levels in the environment it causes no general concern. As a consequence of its negligible presence in nature, biological systems have had no opportunity to develop protection against the element. As beryllium and its oxide are being used more and more in industry, strong precautions are necessary to avoid exposure to fumes and dust released during fabrication.

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16
Strontium and Barium

16.1 Sr
Facts about Strontium

16.1.1 Sr
The Element

Symbol:	Sr
Atomic number:	38
Atomic weight:	87.62
Ground state electron configuration:	[Kr]$5s^2$
Crystal structure:	Cubic fcc with $a = 6.08$ Å

16.1.2 Sr
Discovery and Occurrence

Discovery: Identified as an element in 1790 by A. Crawford in London and Glasgow. The metal was prepared in 1808 by H. Davy in London.

Most important mineral:	Celestine	$SrSO_4$ (Figure M17)
	Strontianite	$SrCO_3$

Ranking in order of abundance in earth crust:	15
Mean content in earth crust:	370 ppm (g/tonne)
Mean content in oceans:	7.9 ppm (g/tonne)
Residence time in oceans:	$4 \cdot 10^6$ years
Mean content in an adult human body:	4.6 ppm
Content in a man's body (weight 70 kg):	320 mg

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16.1.3 Sr
Chemical Characterization

Strontium is a chemically reactive, ductile metal. It is silvery white when freshly cut but oxidizes readily upon exposure to air. When burned it emits a brilliant red color. This is the reason for using strontium in fireworks and flares.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Sr^{II} as in $SrSO_4$ and $SrCO_3$	$Sr(g) \rightarrow Sr^+(g) + e^-$	550	No negative ion of strontium exists
	$Sr^+(g) \rightarrow Sr^{2+}(g) + e^-$	1064	
	$Sr^{2+}(g) \rightarrow Sr^{3+}(g) + e^-$	4138	
	$Sr^{3+}(g) \rightarrow Sr^{4+}(g) + e^-$	5500	

Standard reduction potential: $Sr^{2+}(aq) + 2e^- \rightarrow Sr(s) \quad E^0 = -2.89$ V

Electronegativity (Pauling): 0.95

Radii of atoms and ions: (WebElements™)		
	Atomic:	200 pm
	Covalent:	192 pm
	Sr^{2+} (6-coordinate, octahedral):	132 pm
	Sr^{2+} (8-coordinate):	140 pm

16.1.4 Sr
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
2540 kg m^{-3} 2.54 g cm^{-3}	34.50 cm^3	1050 K 777 °C	1655 K 1382 °C	301 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
–	36.4	32.5	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$22 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
50	200	300	525	945	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+13.2 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	6.1 GPa	–	0.28

16.1.5 Sr
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	8.2 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	136.9 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	164.4 $kJmol^{-1}$
Entropy S^0 at 298 K	52.3 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	22.2	26.4	32.0	37.7	21.0	22.4

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Sr + O_2 \rightarrow 2SrO$	–1124	–1082	–983	–880	–

16.1.6 Sr
Nuclear Properties and X-ray

Isotope range, natural and artificial 75–102

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{84}Sr	Stable	0.56	+0	–
^{86}Sr	Stable	9.86	+0	–
^{87}Sr	Stable	7.00	+9/2	–1.093
^{88}Sr	Stable	82.58	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{87}Sr
Reference compound	$SrCl_2/D_2O$
Frequency MHz (^1H = 100 MHz)	4.334
Receptivity D^P relative to ^1H = 1.00	$1.90 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	1.09
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-1.164 \cdot 10^7$
Nuclear quadropole moment, barn	0.335

Characteristic X-radiation **Z**	 **Element**	 **Kα_2 keV**
37	Rb	13.336
38	Sr	14.098
39	Y	14.882

X-ray radiation absorbed by the element **Incoming radiation energy**	 **Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	114
17.37 keV (MoKα_2)	91.6

Neutron absorption	**Thermal neutron capture cross section**	1.2 barns

16.1 Ba
Facts about Barium

16.1.1 Ba
The Element

Symbol:	Ba
Atomic number:	56
Atomic weight:	137.33
Ground state electron configuration:	[Xe]6s^2
Crystal structure:	Cubic bcc with a = 5.03 Å

16.1.2 Ba
Discovery and Occurrence

Discovery: Identified as an element in 1774 by C. W. Scheele in Sweden. The metal was prepared in 1808 by H. Davy in London.

Most important mineral:	Barite (baryte)	$BaSO_4$
	Witherite	$BaCO_3$

Ranking in order of abundance in earth crust:	14
Mean content in earth crust:	425 ppm (g/tonne)
Mean content in oceans:	0.013 ppm (g/tonne)
Residence time in oceans:	$30 \cdot 10^3$ years
Mean content in an adult human body:	0.3 ppm
Content in a man's body (weight 70 kg):	20 mg

16.1.3 Ba
Chemical Characterization

Barium is a silvery metal, highly reactive. Salts of the element impart a green color to flames. Barium metal has few practical applications but barium sulfate is widely used. It is opaque to X-rays and is used as an X-ray contrast medium. Finely ground barite, suspended in water, is pumped down into the bore holes during drilling for oil. It prevents *blowouts*.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ba^{II} as in $BaCO_3$, $BaCl_2$ and $BaSO_4$	$Ba(g) \rightarrow Ba^+(g) + e^-$	503	No negative ion of barium exists.
	$Ba^+(g) \rightarrow Ba^{2+}(g) + e^-$	965	
	$Ba^{2+}(g) \rightarrow Ba^{3+}(g) + e^-$	3600	

Standard reduction potential: $Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$ $E^0 = -2.92$ V

Electronegativity (Pauling): 0.89

Radii of atoms and ions: (WebElements™)		
	Atomic:	215 pm
	Covalent:	198 pm
	Ba^{2+} (6-coordinate, octahedral):	149 pm
	Ba^{2+} (8-coordinate):	156 pm

16.1.4 Ba
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
3510 kg m^{-3} 3.51 g cm^{-3}	39.12 cm^3	1000 K 727 °C	1913 K 1640 °C	204 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
–	20	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$20.6 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
70	360	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K $+1.9 \cdot 10^{-9}$ m^3kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
13 GPa	5 GPa	11 GPa	0.30

16.1.5 Ba
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	8.01 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	150 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	180 kJmol^{-1}
Entropy S^0 at 298 K	62.8 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	24.3	26.36	33.9	39.1	39.7	39.9

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Ba + O_2 \rightarrow 2BaO$	–1057	–1014	–915	–815	–

16.1.6 Ba
Nuclear Properties and X-ray

Isotope range, natural and artificial 114–150

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{130}Ba	Stable	0.11	+0	–
^{132}Ba	Stable	0.10	+0	–
^{134}Ba	Stable	2.42	+0	–
^{135}Ba	Stable	6.59	+3/2	0.8379
^{136}Ba	Stable	7.85	+0	–
^{137}Ba	Stable	11.23	+3/2	0.9365
^{138}Ba	Stable	71.70	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{135}Ba	^{137}Ba
Reference compound	$BaCl_2/D_2O$	
Frequency MHz (^{1}H = 100 MHz)	9.934	11.113
Receptivity D^P relative to ^{1}H = 1.00	$3.30 \cdot 10^{-3}$	$7.86 \cdot 10^{-3}$
Receptivity D^C relative to ^{13}C = 1.00	1.88	4.49
Magnetogyric ratio, radT^{-1}s^{-1}	$2.658 \cdot 10^7$	$2.993 \cdot 10^7$
Nuclear quadropole moment, barn	0.16	0.245

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
55	Cs	30.625
56	Ba	31.817
57	La	33.034

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	330
17.37 keV ($MoK\alpha_2$)	42.8

Neutron absorption	**Thermal neutron capture cross section**	1.3 barns

16.2
Strontium and Barium in Chemical History

16.2.1
Heavy Spar – Barite

Professor Torbern Bergman in Uppsala had asked Carl Wilhelm Scheele to try to solve the problem of the chemistry of pyrolusite or "Braunstein" that had existed for hundreds of years. The cooperation within the Scheele–Gahn–Bergman trio led to clarity and to the discovery of the element manganese, described in Chapter 27. Incidentally, Scheele discovered a new alkaline earth, barium oxide, and its sulfate, *heavy spar* $BaSO_4$. In February 1774, Scheele wrote to Gahn asking if he had not observed some white crystals that in some cases occurred with pyrolusite. It is easy to believe, he wrote, that the white substance is gypsum or limestone but that is not the case! It is in fact a new earth, bound to sulfuric acid. "I am anxious to learn what name Herr Professor Bergman will give to this new earth. He thinks that there is much of it in the mountains". Scheele himself chose the designation *heavy spar* for the sulfate and *baryte (barite)* for the earth, the barium oxide. The reason was the Greek word *barys,* heavy. One example of Scheele's experimental competence and imagination, much talked of, is the method he used to prepare water-soluble barium. Every chemist knows how difficult is to dissolve barium sulfate. He mixed the heavy spar with powdered charcoal and honey. On heating, the sulfate was reduced to sulfide, easily soluble in hydrochloric acid. Addition of potassium carbonate precipitated barium carbonate.

Barium carbonate, present in nature as *terra ponderosa* or *witherite*, was discovered in England and was described by *William Withering*, a colleague of Joseph Priestley. Scheele was the first to make clear the difference between barium and calcium (1774) and his achievement is quite on a par with Black's regarding magnesium oxide in 1755. In the latter case both Black and Davy are mentioned as the discoverers of the element, in the barium case Davy alone. Another inconsequence in the history of the elements.

Heavy spar had, in fact, been known for a long time and had been the subject of several experiments and speculations. *J. G. Wallerius*, who preceded Torbern Bergman as professor of chemistry in Uppsala, had thought that the substance was gypsum. Markgraf showed that it was a sulfate but also supposed the metal to be calcium.

16.2.2
Bolognian Stone – Shining in Darkness

In 1603 *Vincenzo Cascariolo*, an Italian cobbler and amateur alchemist in the countryside near Bologna, made a notable observation. He had found a heavy stone and ground it to a grain size of meal. He mixed the powder with the white of eggs and made cakes of it. These he laid in layers with coal and calcined for 4–5 hours. To his tremendous amazement he found that the calcined stone shone in darkness if it had first been exposed to the sun. It phosphoresced[1]. This mysterious and magical ability to accumulate light and emit it in the dark created a sensation. The substance he had prepared became known as *Bolognian Stone*.

> In 1640 a Professor F. Licetus at the University of Bologna published a text *Litheophosphorus Sive De Lapide Bononiensi* in which he presented Cascariolo as an honest man of humble circumstances who was given to assiduous pursuit of activity in the science of chemistry.

Bolognian Stones fascinated J. W. von Goethe, who collected many and examined them in Weimar in 1784.

The magic stones also found their way to Gahn and his laboratory in Falun. After Scheele's fundamental work with barium, Gahn could rapidly establish that barium was also the main component in Bolognian Stone. Cascariolo had carried out his experiments with barite $BaSO_4$.

16.2.3
Terra ponderosa *From Strontian*

In 1787, a mineral was found in a lead mine in Strontian, Scotland, that proved difficult to identify. It was considered to be a kind of witherite, barium carbonate. *Dr Adair Crawford* (1748–1795) took an interest in the substance because at his hospital, Saint Thomas' in London, he prepared barium chloride from carbonate and examined the medical properties of the chloride.

He was an Irishman educated in Glasgow, and he later became professor of chemistry in Woolwich. At his hospital in London Dr Crawford heard about the new bari-

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[1] Phosphorescence is one type of luminescence (Latin, *lumen* – light). When certain materials absorb energy (from sunshine or from a UV-lamp), the electrons become excited and jump from the inner orbits of the atoms to the outer. When the electrons fall back to their original state, a photon of light is emitted. The interval between the two steps may be short or long. If the interval is short, the process is called *fluorescence*. If the interval is long, the process is called *phosphorescence*. When yellow phosphorus oxidizes in air, emitting a green radiation it is not phosphorescence but *chemiluminescence*.

In the actual case of Bolognian Stone, perhaps BaS is formed together with a certain excess of Ba, dissolved interstitially. The stone then behaves like an impure semiconductor, displaying phosphorescence.

um carbonate from Strontian. Was it perhaps easier to dissolve in hydrochloric acid than the witherite he used now? If so it should make the preparation of barium chloride easier. He found something quite different. The new mineral did not contain barium. He made a note that "This mineral possesses different properties from the terra ponderosa (baryta) of Scheele and Bergman."

In 1790 he prepared the chloride of the new metal and compared it with barium chloride. To choose a name for the element was simple. Without discussion it was *strontium*. Dr Crawford sent a sample of the new mineral, strontium carbonate, to his fellow-countryman, the Irish chemist *Richard Kirwan* (1733–1812). He was a pioneer in the field of quantitative analysis and he published his results about the newly discovered alkaline earth metal [16.1]. Fourcroy and Vauquelin also investigated the new mineral [16.2]. The discovery in their native country of a bright new element encouraged Scottish chemists to investigate the mineral at home. *Thomas Charles Hope* (1766–1844) had succeeded Joseph Black as professor of chemistry in Edinburgh in 1795. He investigated strontium carbonate, *strontianite,* and determined the properties of this carbonate and several other strontium salts. He also described the flame colors for barium (green), calcium (red) and strontium (brilliant red). Hope has gone down in history for one further achievement. He was the first to discover that water has its maximum density at + 4°C.

16.2.4

The Actual Metals in the Alkaline Earths

In Lavoisier's element list of 1789, lime (*chaux*) was mentioned as an element, but before he died in 1794 he expressed the view that in all probability not all of the metallic substances present in nature were known. All those that have a stronger affinity for oxygen than does carbon cannot be reduced and obtained in the metallic state. Because of that they cannot present themselves in any other guise than their oxides. "It is possible that all substances we call earths in reality are metal oxides, although they are not reducible with methods we do have at our disposal."

What Lavoisier was seeking around 1790, methods for isolating metals with very strong affinities for oxygen, became available as a consequence of Sir Humphry Davy's achievements. His discovery of potassium and sodium was published in the English newspapers in January 1808 and created a sensation. For a little while Davy became a well-known person in Europe among more than chemists. In Sweden the news was known in March, surprisingly early considering the blockade during the Napoleon war. It was natural for Berzelius to take a great interest in Davy's investigations with electrolysis, as he himself had experimented with the Voltaic pile. Now he engaged his friend *Magnus Martin Pontin*, physician at court, and together they repeated Davy's experiments with potassium and sodium. After that they had one goal in view: Isolation of the alkaline earth metals. At the end of March Berzelius wrote to assessor Gahn in Falun about the fascinating possibilities that seemed to open up. "What prospects of confirming the great Lavoisier's feeling about the nature of the alkaline earths!"

In the first experiments with lime, Berzelius and Pontin met with difficulties. Calcium forming at the cathode was immediately re-oxidized. A masterstroke saved the situation. Mercury was selected as the cathode material. As calcium was formed it became alloyed with mercury. Berzelius expressed his satisfaction:

> Lime constitutes a considerable part of our planet's crust. We have succeeded in decomposing this earth (lime) by reduction and prepared a small quantity of its metal as an amalgam. This element has probably never before existed as a metal and free from oxygen.

At the Royal Institution in London Davy was equipped with powerful Voltaic piles. One had 24 square plates of copper and zinc, the edge length 12 in (300 mm) each. A second battery had 100 plates, 6 in (150 mm), a third 150 plates, 4 in (100 mm). He worked with the hypothesis that the earths, analogous to the alkalis, are composed of oxygen and a very reactive metal. When he started experiments with the oxides of barium and strontium he also met with difficulties due to the high melting points and the low electrical conductivity. However, in one experiment with strontia he used both the 100 and the 150 plate piles in series and improved the conductivity by adding moisture and boric acid. At both electrodes a vigorous reaction occurred. Round the negative pole a substance burned with a red flame. Davy was convinced that he had seen traces of the metal in strontia but that the element, owing to the high temperature and the contact with air, was oxidized at the same rate at it was reduced.

Davy was disappointed. On June 30th 1808 he reported to the Royal Institution mainly negative results, but continued [16.4]:

> ...Whilst I was engaged in these experiments, in the beginning of June, I received a letter from Professor Berzelius of Stockholm, in which he informed me that in conjunction with Dr. Pontin he had succeeded in decomposition of barytes and lime, by negatively electrifying mercury in contact with them, and that in this way he had obtained amalgams of the metals of these earths [see Figure 16.1]. I immediately repeated these operations with perfect success; a globule of mercury, electrified by the power of the battery of 500, weakly charged, was made to act upon a surface of slightly moistened barytes, fixed upon a plate of platina. The mercury gradually became less fluid, and after a few minutes was found covered with a white film of barytes; and when the amalgam was thrown into water, hydrogen was disengaged, the mercury remained free, and a solution of barytes was formed.

Davy used this new technique successfully. He prepared amalgams of the earth metals magnesium, calcium, strontium and barium, distilled the mercury off, and thus isolated the elements, although only in small quantities and not pure. In a letter of July 10th 1808 he acknowledges Berzelius and Pontin, stating that it was the letter from Stockholm that put him on the right track. With the letter he sent special compliments to Dr. Pontin. It seems to have made a deep impression on Davy that the personal physician of the King assisted Berzelius in his electrolytic examinations.

In tables of about element discoverers Davy is given the full priority for the alkaline earth metals. Berzelius role in the discoveries is not mentioned, in spite of Davy's own tribute.

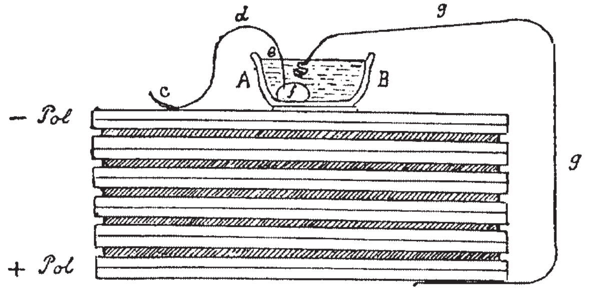

Figure 16.1 The Voltaic pile used by Berzelius and Pontin for electrolysis with mercury (f) as a cathode [16.3].

16.3
Strontium in Our Time

16.3.1
Occurrence

In nature the most important strontium mineral is *celestite* $SrSO_4$ (Figure M17). As a rule the mineral is colorless but it also occurs with a sky-blue color, which is the reason for its name. The mineral occurs in a zone round the tropical and subtropical parts of the earth. The main deposits are found in Mexico, Spain and Turkey and in these countries 312 000 tonnes of strontium was extracted as celestite in 2000. The total production of celestite in the world that year corresponded to 319 000 tonnes of strontium [16.5].

Another mineral is strontianite $SrCO_3$, in which the element was discovered. Of the two, celestite and strontianite, the former occurs much more frequently in deposits of sufficient size to make mining attractive. Strontianite would be the more useful as the element is very often used in the form of carbonate. However, few deposits have however been discovered that are suitable for mining. A deposit in China, a very large one, seems to be the only one in the world developed for strontianite mining.

As strontium's ionic radius is only a little larger than calcium's (Sr 1.31 Å, Ca 1.14 Å) the element also appears with calcium in gypsum and anhydrite.

16.3.2
Manufacture

The carbonate is prepared from celestite by mixing the mineral with powdered coal and heating the mixture to 1100°C. Strontium sulfide is formed and is dissolved in water. Strontium carbonate is precipitated by adding carbon dioxide or soda. Elemental sulfur is an important byproduct. Germany and Mexico are the largest producers of strontium carbonate. The chloride and other chemicals may be produced from the carbonate.

The metal is prepared by electrolysis of a fused salt mixture containing strontium chloride and potassium chloride (to decrease the melting point). An alternative method is reduction of strontium oxide by aluminum at so high a temperature that the strontium metal is distilled off and can be condensed (the boiling point for strontium is 1382°C).

16.3.3
Uses of Strontium

The electron radiation in a cathode-ray tube that activates the color phosphors in a TV screen also creates an X-rays. Strontium has the ability to block this X-ray emission. Because of that so much strontium carbonate is added to the melt during the manufacture of glass for the screens that the resulting content corresponds to 8–12% strontium oxide. The law requires that viewers are shielded from the X-rays in this way and this has created the major use of strontium and demand continues to increase with the increased popularity of larger screen sizes. Flat-screen technology may reduce the demand for strontium in TV applications.

Another major end use for strontium is as strontium ferrite $SrO(Fe_2O_3)_6$ in permanent ceramic magnets. Because of their high coercive force, insensitivity to high temperatures and corrosion resistance they are used extensively in small motors for automobile windshield wipers and magnetically attached decorative items.

As the compound strontium titanate $SrTiO_3$, the element has a rather original use: in imitation diamonds. It has, in fact, a higher dispersion than diamond and is thus more colorful. Its hardness is, however, much lower, 5.5 compared to 10 on Mohs scale. It is known as *fabulite* in the jewelry industry. It has to a large extent been replaced by cubic zirconia CZ, which has higher hardness and better matches the dispersion of diamond.

As strontium burns with a brilliant red flame it has been used for pyrotechnics. It is treated below (in this chapter) in section 16.5.

16.4
Barium in Our Time

16.4.1
Occurrence

Barium sulfate, *barite, heavy spar*, is a very important industrial mineral. More than 5 millions tonnes are mined each year, mostly in China. Other important sources are the Massif Central in France together with Turkey, North Africa, India, Mexico and the USA. Barium carbonate, *witherite*, is nowadays economically unimportant

16.4.2
Manufacture

The mined ore is enriched by flotation and the barite mineral obtained is mixed with coal and heated to 1000°C. The barium sulfate is then reduced to barium sulfide. Carbon dioxide is passed into its water solution and barium carbonate is precipitated. An equivalent amount of hydrogen sulfide is formed and is transformed to elemental sulfur. To obtain barium metal, a mixture of barium oxide and aluminum powder is pressed into briquettes. On heating to 1100°C an aluminothermic reduction to barium metal occurs.

16.4.3
Uses

16.4.3.1 Barite and Blanc Fix

Large quantities of finely ground barite is stirred into water to a highly concentrated, heavy suspension, which is pumped down into the bore holes during drilling for oil. The suspension cools and lubricates the bore bars, tightens the walls of the boreholes and prevents *blowouts*. This use accounts for more than 80% of all the barite used.

Barium carbonate can be manufactured from mined heavy spar. From this carbonate a very pure barium sulfate can be prepared. It is called *blanc fix* and is used as a white pigment in photographic paper and in high-quality paper for maps and playing-cards. Art paper is also made in this way. Barium sulfate is used as an effective contrast medium for X-ray examinations in medicine. The compound has a very low solubility in water and is therefore not poisonous (although barium ions are rather toxic).

16.4.3.2 Barium and Cultural Heritage

Frescos are old paintings embedded in plaster. In the modern environment these works of art tend to crack and important cultural artifacts are threatened. Conservators use barium to preserve and restore such art objects. A solution of barium nitrate may be sprayed over the fresco and is absorbed by the cavities in the surface. Then an additional spraying is carried out with an ammonia solution. This raises the pH, and barium hydroxide $Ba(OH)_2$ is formed in cracks and other defective parts of the fresco. In the course of time the water evaporates and carbon dioxide from the air reacts with the hydroxide, forming white, insoluble barium carbonate. The surface of the fresco is saved and so are its delicate colors.

16.4.3.3 Ultrasound in Factory and Hospital

In 1880, Pierre Curie and his brother Jacques made the first observation of the *piezoelectric effect*. What they found was that some crystals, e.g. quartz, are deformed mechanically when an electrical voltage is applied to them. An AC electric potential might thus cause vibration. This made possible the generation and reception of ultrasound (a sound with such a high frequency, more than 15 000 Hz = 15 kHz, so that the human ear cannot hear it). For technical and medical uses of ultrasound, still higher frequencies, over 1 MHz, are often used. For modern ultrasound equipment, effective piezoelectric crystals have to be used. The ceramics *barium titanate* and *lead zirconate titanate* have been introduced and have made it possible to make transducers with improved sensitivity.

When ultrasound is used, a probe containing both transmitting and receiving transducers is placed on the object to be investigated (for materials testing; Figure 16.2) or above the patient's bed (for medical use).

Ultrasound is sound and, as such, can only be transmitted by matter, unlike electromagnetic radiation, which can pass through a vacuum. As soon as the transducer has emitted an ultrasound pulse it is automatically changed to a receiver. When the sound returns as an echo the piezoelectric crystal transforms the oscillations to electrical impulses, which are recorded on the screen of the oscilloscope. The time used by the sound for its "journey" forward and back is automatically calculated by the equipment. If the speed of the sound in the actual material is known, the time – also automatically – can be recalculated to distance.

Ultrasound testing is important as a diagnostic tool in medicine. It is used mainly in obstetrics and gynecology but also for examining the heart and blood vessels.

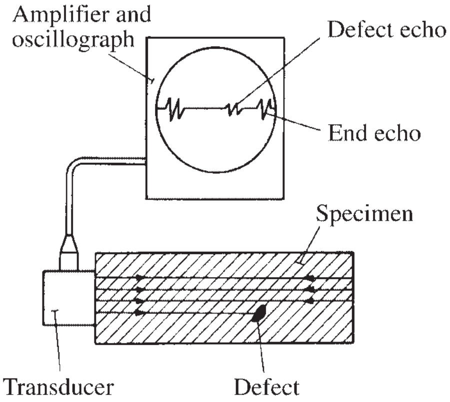

Figure 16.2 The principle of materials testing with ultrasound. A flaw or a pore in a weld may be detected and the position of the defect is shown. (From B. A. Gustafsson, *Materiallära*, Almqvist & Wiksell, Stockholm, 1992. With permission.)

16.4.3.4 **Metallic Barium**

Barium metal is only sparsely used. Because of its great chemical reactivity, however, it is used as a "trap" for different gases, e.g. oxygen and moisture, in TV tubes. Barium metal reacts so readily with air that it is almost impossible to work it into shape without working in a vacuum system. However, an alloy of 55% barium with aluminum, which is inert enough to permit deformation, can be used. After installing the component and evacuation and sealing of the tube, the alloy is heated inductively. Barium metal, which is volatile at high temperatures, vaporizes and is condensed as a very thin layer on the inner surfaces of the tube. This layer frees the evacuated tube from the last residues of oxygen and moisture.

16.5
Colors and Sparks in Fireworks

Pyrotechnics were used for different ceremonial and religious purposes in China and India in the first centuries AD. A mixture of saltpeter, sulfur and charcoal was used. The Chinese made war rockets and explosives as early as the 6th century, and the craft spread to Arabia in the 7th century. The Arabs called the rockets "Chinese arrows". Chinese chronicles mention the use of war rockets against the Mongol invaders in 1279. Perhaps the Mongols introduced gunpowder and rockets into Europe in the middle of the 13th century. This would be consistent with the date of the first records of their use in Europe.

By the 17th century, elaborate displays of traditional fireworks accompanied important celebrations. In the 18th century, however, many new substances became available, materials with distinct flame colors. This opened up new possibilities for artistic fireworks. The basic phenomena of flame and color production became well established, but novel effects and novel materials still continue to be discovered. Color was given to the fire by incorporating compounds of various metals (Table 16.1). Using the names *Chinese* and *Bengal lights* retain the connection with the origin of fireworks components.

Metals with low heat conductivity are inclined to form sparks. Titanium and zirconium have very low values, 22 and 23 W m^{-1} K^{-1} respectively (compared with iron 84, aluminum 236). Therefore Ti and Zr are used in modern fireworks in order to produce sparks.

In contrast, copper has a very high heat conductivity, 400 W m^{-1} K^{-1}. Because of this, strong copper alloys such as beryllium copper or aluminum bronzes are used in *sparkless kneading tools* for the preparation of dynamite.

Table 16.1 Color effects in fireworks

Substance	Color
Sodium salt	Yellow
Strontium salt	Brilliant red
Barium salt	Green
Copper salt	Blue
Magnesium metal	Intensely white
Mg-Al alloy	Twinkling effects

Potassium nitrate (saltpeter) was the essential oxygen donor in most fireworks, while substances such as charcoal and sulfur combined with oxygen, producing heat and light. Shortly after 1800, potassium chlorate or perchlorate, still used in most fireworks mixtures, replaced potassium nitrate. Chlorine strengthens the emission of colored light and increases the effects. In the second half of the 19th century, the chlorate technique was applied in the Orient, leading to the rapid expansion and artistic development of firework production in China and Japan. In place of charcoal and sulfur, different inflammable substances, such as starch and various petroleum derivatives, are frequently used in the mixture.

Pyrotechnic devices are widely used in fireworks for celebration and entertainment. They are also much used for different warning devices. Military applications include tracer ammunition, signal rockets and marine distress signals.

16.6
Biological Roles

Strontium is quite common in seawater. Some organisms use strontium sulfate as a skeletal material. Strontium is added to the water in aquariums, as the decorative stony corals need it. Strontium has no function in the human body. (It is the most abundant element in the human body without a known function there.) Nor is barium essential for life; indeed it is toxic. The symptoms of barium poisoning are colic, diarrhoea, vomiting and paralysis. The content of barium in food plants is as a rule low (part per million levels) but there is an exception: Brazil nuts may contain as much as 1% barium. The metabolism is stimulated by barium, but to such a high degree that the heart begins to beat erratically (ventricular fibrillation). Barium salts are thus toxic to humans, but the use of barium sulfate as an X-ray contrast medium is accepted because of its very low solubility.

Barium is not essential for humans but there are species for which this element is vital. A type of single-celled algae, *desmids*, seem to use the weight of barium sulfate as a sensor for orientation of their position in the sea. If barium is not present they stop growing.

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17

Scandium, Yttrium, Lanthanum and the 14 Lanthanides – Rare Earth Metals (REMs)

The complete group of rare earth metals consists of the three elements scandium Sc, yttrium Y and lanthanum La and the fourteen lanthanides cerium to lutetium. The total number of REMs is thus 17. They are, for practical reasons, divided into two subgroups, the cerium group with the lighter elements and the yttrium group with the heavier ones (Table 17.1).

Table 17.1 Two groups of rare earth metals

The cerium group **The lighter elements**				**The yttrium group** **The heavier elements**			
Atomic number	**Density g/cm^3**	**Element**	**Symbol**	**Atomic number**	**Density g/cm^3**	**Element**	**Symbol**
21	2.99	Scandium	Sc	39	4.47	Yttrium	Y
57	6.15	Lanthanum	La	64	7.90	Gadolinium	Gd
58	6.69	Cerium	Ce	65	8.23	Terbium	Tb
59	6.77	Praseodymium	Pr	66	8.55	Dysprosium	Dy
60	7.00	Neodymium	Nd	67	8.80	Holmium	Ho
61	7.22	Promethium	Pm	68	9.07	Erbium	Er
62	7.52	Samarium	Sm	69	9.32	Thulium	Tm
63	5.24	Europium	Eu	70	6.97	Ytterbium	Yb
				71	9.84	Lutetium	Lu

Encyclopedia of the Elements. Per Enghag

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17.1 Sc
Facts about Scandium

17.1.1 Sc
The Element

Symbol:	Sc
Atomic number:	21
Atomic weight:	44.96
Ground state electron configuration:	[Ar]$3d^1 4s^2$
Crystal structure:	Hexagonal hcp with $a = 3.31$ Å and $c = 5.27$ Å

17.1.2 Sc
Discovery and Occurrence

Discovery: Lars Fredrik Nilson discovered scandium in Uppsala in 1879. The discovery confirmed Mendelejev's prediction that eka-boron would be found.

Most important mineral: Scandium is present in a large number of minerals. There are, however, only a few in which the Sc content is high. Most important are *thortveitite*, $(Sc,Y)_2Si_2O_7$ and *kolbeckite*, $ScPO_4·2H_2O$, the only known pure scandium mineral (Figure M26).

Ranking in order of abundance in earth crust:	31
Mean content in earth crust:	22 ppm (g/tonne)
Mean content in oceans:	$6 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	$40 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Sc
Chemical Characterization

Scandium is a soft, silvery white metal, which tarnishes in air to a slightly yellowish or pinkish color. Scandium has an unexpectedly high melting point, 1541°C compared to 661 for Al. In aluminum alloys 0.3% Sc is reported to prevent grain growth during casting or welding and to increase strength by precipitation of Al3Sc particles. The Soviet MIG 29 and 31 aircraft used alloys of this type.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Sc^{III} as in Sc_2O_3, ScF_3, and Sc_2S_3	$Sc(g) \rightarrow Sc^+(g) + e^-$	633	$Sc(g) + e^- \rightarrow Sc^-(g)$ –18.1
	$Sc^+(g) \rightarrow Sc^{2+}(g) + e^-$	1235	
	$Sc^{2+}(g) \rightarrow Sc^{3+}(g) + e^-$	2389	
	$Sc^{3+}(g) \rightarrow Sc^{4+}(g) + e^-$	7091	

Standard reduction potential: $Sc^{3+}(aq) + 3e^- \rightarrow Sc(s)$ $E^0 = -2.03$ V

Electronegativity (Pauling): 1.36

Radii of atoms and ions: (WebElements™)		
	Atomic:	160 pm
	Covalent:	144 pm
	Sc^{3+} (6-coordinate, octahedral):	88.5 pm
	Sc^{3+} (8-coordinate):	101 pm

17.1.4 Sc

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 25 °C**
2989 kg m^{-3} 2.99 g cm^{-3}	15.04 cm^3	1814 K 1541 °C	3104 K 2831 °C	567 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
15	16	–	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
–	505 (550 at 298 K)	750	1150	1670	1980

Coefficient of linear expansion at 298 K	$10.2 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$88 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
74 GPa	29 GPa	55 GPa	0.28

17.1.5 Sc
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	16.0 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	315 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	378 $kJmol^{-1}$
Entropy S^0 at 298 K	34.64 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
–	25.52	26.5	28.3	33.5	33.5

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3Sc + O_2 \rightarrow 2/3Sc_2O_3$	–1206	–1160	–1047	–935	–

17.1.6 Sc
Nuclear Properties and X-ray

Isotope range, natural and artificial 40–52

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{45}Sc	Stable	100	7/2–	4.756

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
20	Ca	3.688
21	Sc	4.086
22	Ti	4.505

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	181
17.37 keV ($MoK\alpha_2$)	21.1

Neutron absorption	**Thermal neutron capture cross section**	25 barns

17.1 Y
Facts about Yttrium

17.1.1 Y
The Element

Symbol:	Y
Atomic number:	39
Atomic weight:	88.91
Ground state electron configuration:	[Kr]$4d^1 5s^2$
Crystal structure:	Hexagonal hcp with $a = 3.65$ Å and $c = 5.73$ Å

17.1.2 Y
Discovery and Occurrence

Discovery: The Finnish chemist Johan Gadolin discovered the oxide of the new metal in 1794. He made the discovery when he investigated the black stone "ytterbite" (gadolinite) that Arrhenius had found in 1787 in the feldspar quarry at Ytterby outside Stockholm.

Most important mineral: Yttrium has given the name to the heavy REM-group, the yttrium group. Minerals typical for this group are *euxenite* $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$. Figure M18.

Ranking in order of abundance in earth crust:	29
Mean content in earth crust:	33 ppm (g/tonne)
Mean content in oceans:	$1.3 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Y
Chemical Characterization

Yttrium is a silvery white, rather unreactive metal. Turnings, however, ignite in air. Yttrium oxysulfide, doped with europium, is used in phosphors to give red colors in television screens. Yttrium is also one of the components in the superconducting ceramic $Ba_2YCu_3O_7$.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Y^{III} as in Y_2O_3, YCl_3, and $YNbO_4$	$Y(g) \rightarrow Y^+(g) + e^-$	600	$Y(g) + e^- \rightarrow Y^-(g)$ –29.6
	$Y^+(g) \rightarrow Y^{2+}(g) + e^-$	1180	
	$Y^{2+}(g) \rightarrow Y^{3+}(g) + e^-$	1980	
	$Y^{3+}(g) \rightarrow Y^{4+}(g) + e^-$	5847	

Standard reduction potential:	$Y^{3+}(aq) + 3e^- \rightarrow Y(s)$ $E^0 = -2.37$ V	
Electronegativity (Pauling):	1.22	
Radii of atoms and ions: (WebElements™)	Atomic:	180 pm
	Covalent:	162 pm
	Y^{3+} (6-coordinate, octahedral):	104 pm
	Y^{3+} (8-coordinate):	116 pm

17.1.4 Y

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
4472 kg m^{-3} 4.47 g cm^{-3}	19.88 cm^3	1795 K 1522 °C	3618 K 3345 °C	298 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
16.5	17	–	–	–

Resistivity nΩm 78 K	273 K	298 K	573 K	973 K	1473 K
155	550	570	–	–	–

Coefficient of linear expansion at 298 K	$10.6 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$27.0 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
65 GPa	26 GPa	43 GPa	0.25

17.1.5 Y
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	17.2 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	385 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	421 kJmol^{-1}
Entropy S^0 at 298 K	44.43 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

100 K	298 K	600 K	1000 K	2000 K	2500 K
–	26.53	26.4	28.1	33.5	33.5

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3Y + O_2 \rightarrow 2/3Y_2O_3$	–1210	–1172	–1078	–985	–895

17.1.6 Y
Nuclear Properties and X-ray

Isotope range, natural and artificial 78–109

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{89}Y	Stable	100	1/2–	–0.1374

Characteristic X-radiation

Z	Element	Kα_2 keV
38	Sr	14.098
39	Y	14.882
40	Zr	15.692

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	125
17.37 keV (MoKα_2)	98.0

Neutron absorption	**Thermal neutron capture cross section**	1.3 barns

17.1 La
Facts about Lanthanum

17.1.1 La
The Element

Symbol:	La
Atomic number:	57
Atomic weight:	138.91
Ground state electron configuration:	[Xe]$5d^16s^2$
Crystal structure:	Hexagonal hcp with $a = 3.77$ Å and $c = 12.14$ Å

17.1.2 La
Discovery and Occurrence

Discovery: Carl Gustaf Mosander in Stockholm discovered the new element, hidden in cerium, in 1839.

Most important mineral: Lanthanum belongs to the light REM-group, the cerium group. Minerals typical for this group are monazite $(Ce,La,Nd,Th)(PO_4,SiO_4)$, Figure M25 and bastnaesite, $(Ce,La)CO_3(F,OH)$, Figure M22.

Ranking in order of abundance in earth crust:	28
Mean content in earth crust:	39 ppm (g/tonne)
Mean content in oceans:	$3.4 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 La
Chemical Characterization

Lanthanum is a metal, soft enough to be cut with a knife, and one of the most reactive of the rare earth metals. It oxidizes rapidly when exposed to air and is attacked by hot water. It is a component of mischmetall, used for cigarette-lighter flints. The intermetallic compound LaNi5 is the negative electrode, MH (metal hydride), in the modern Ni-MH alkaline battery. It is an ecofriendly alternative to the nickel–cadmium battery.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
La^{III} as in La_2O_3, $LaCl_3 \cdot 3H_2O$, and LaH_3	$La(g) \rightarrow La^+(g) + e^-$	538	$La(g) + e^- \rightarrow La^-(g)$
	$La^+(g) \rightarrow La^{2+}(g) + e^-$	1067	−48
	$La^{2+}(g) \rightarrow La^{3+}(g) + e^-$	1850	
	$La^{3+}(g) \rightarrow La^{4+}(g) + e^-$	4819	

Standard reduction potential: $La^{3+}(aq) + 3e^- \rightarrow La(s)$ $E^0 = -2.38$ V

Electronegativity (Pauling): 1.10

Radii of atoms and ions: (WebElements™)	Atomic:	195 pm
	Covalent:	169 pm
	La^{3+} (6-coordinate, octahedral):	117 pm
	La^{3+} (8-coordinate):	130 pm

17.1.4 La

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
6146 kg m^{-3} 6.15 g cm^{-3}	22.60 cm^3	1194 K 921 °C	3730 K 3457 °C	195 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
12	13	14.5	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1123 K
–	540 (570 at 298 K)	660	830	1050	1260

Coefficient of linear expansion at 298 K	$5.0 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+11 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
37 GPa	14 GPa	28 GPa	0.28

17.1.5 La
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	10.0 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	400 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	431 kJmol^{-1}
Entropy S^0 at 298 K	56.9 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	23.6	27.1	27.1	27.8	28.0	28.0

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$4/3La + O_2 \rightarrow 2/3La_2O_3$	–1185	–1147	–1054	–	–

17.1.6 La
Nuclear Properties and X-ray

Isotope range, natural and artificial 120–150

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half-life**	**Decay mode**	**Decay energy Q**
^{139}La	Stable	99.91	7/2+	2.783	–	–	–
^{138}La	Active	0.09	5+	3.714	$1.1 \cdot 10^{11}$ y	β^-	1.044 MeV
						EC or β^+	1.738 MeV

Characteristic X-radiation

Z	**Element**	**Kα_2 keV**
56	Ba	31.817
57	La	33.034
58	Ce	34.279

X-ray radiation absorbed by the element

Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	350
17.37 keV (MoKα_2)	45.4

Neutron absorption **Thermal neutron capture cross section** 8.9 barns

17.1 Ce
Facts about Cerium

17.1.1 Ce
The Element

Symbol:	Ce
Atomic number:	58
Atomic weight:	140.12
Ground state electron configuration:	$[\mathrm{Xe}]4f^2 6s^2$
Crystal structure:	Hexagonal hcp with $a = 3.62$ Å and $c = 5.99$ Å

17.1.2 Ce
Discovery and Occurrence

Discovery: Cronstedt discovered “the heavy stone from Bastnaes” in 1751. Berzelius and Hisinger in Sweden identified a new silicate in it and called it *cerite* after the newly discovered small planet Ceres. In 1803 Berzelius isolated the oxide of the new metal *cerium*. Klaproth in Berlin investigated the same mineral and also identified a new metal.

Most important mineral: Cerium has given its name to the light REM group, the cerium group. Minerals typical for this group are monazite $(\mathrm{Ce,La,Nd,Th})(\mathrm{PO_4,SiO_4})$), Figure M25 and bastnaesite $(\mathrm{Ce,La})\mathrm{CO_3}(\mathrm{F,OH})$) Figure M22.

Ranking in order of abundance in earth crust:	25
Mean content in earth crust:	66.5 ppm (g/tonne)
Mean content in oceans:	$1.2 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	$50 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man’s body (weight 70 kg):	–

17.1.3 Ce

Chemical Characterization

Cerium is the most abundant and, except for europium, the most reactive of the rare earth elements. It is an iron-gray malleable metal that oxidizes readily at room temperature, especially in moist air. Mischmetall is an alloy containing about 50% Ce. Alloyed with iron, mischmetall is used for flints in cigarette lighters. This application has gradually been substituted by the piezoelectric cigarette lighter. 1–2% cerium oxide is added to glass for aerospace windows and television sets. This glass absorbs UV radiation.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ce^{III} as in Ce_2O_3, $CeCl_3$, and CeN	$Ce(g) \rightarrow Ce^{+}(g) + e^{-}$	534	$Ce(g) + e^{-} \rightarrow Ce^{-}(g)$
Ce^{IV} as in CeO_2, CeF_4, $(NH_4)_4(CeF_8)$,	$Ce^{+}(g) \rightarrow Ce^{2+}(g) + e^{-}$	1050	–50
and $[Ce(NO_3)_6]^{2-}$	$Ce^{2+}(g) \rightarrow Ce^{3+}(g) + e^{-}$	1949	
	$Ce^{3+}(g) \rightarrow Ce^{4+}(g) + e^{-}$	3547	
	$Ce^{4+}(g) \rightarrow Ce^{5+}(g) + e^{-}$	6325	

Standard reduction potential:	$Ce^{4+}(aq) + e^{-} \rightarrow Ce^{3+}(aq)$	$E^0 = +1.76$ V
	$Ce^{3+}(aq) + 3e^{-} \rightarrow Ce(s)$	$E^0 = -2.34$ V
Electronegativity (Pauling):	1.12	
Radii of atoms and ions:	Atomic:	185 pm
(WebElements™)	Ce^{3+} (6-coordinate, octahedral):	115 pm
	Ce^{3+} (8-coordinate):	128 pm
	Ce^{4+} (6-coordinate, octahedral):	101 pm
	Ce^{4+} (8-coordinate):	111 pm

17.1.4 Ce

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
6689 kg m^{-3} 6.69 g cm^{-3}	20.95 cm^3	1071 K 798 °C	3700 K 3427 °C	192 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
8	11	13	16	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1053 K
–	730	800	920	1100	1230

Coefficient of linear expansion at 298 K	$6.3 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$217 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
37 GPa	15 GPa	23 GPa	0.23

17.1.5 Ce

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	8.9 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	(350) $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	423 $kJmol^{-1}$
Entropy S^0 at 298 K	72.0 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	26.94	27.0	33.9	40.6	33.5	33.5

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Ce + O_2 \rightarrow CeO_2$	–1025	–983	–882	–	–

17.1.6 Ce

Nuclear Properties and X-ray

Isotope range, natural and artificial 123–152

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{136}Ce	Stable	0.19	0+	–	–	–	–
^{138}Ce	Stable	0.25	0+	–	–	–	–
^{140}Ce	Stable	88.48	0+	–	–	–	–
^{142}Ce	Active	11.08	0+	–	$5 \cdot 10^{16}$ y	–	–

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
57	La	33.034
58	Ce	34.279
59	Pr	35.550

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	370
17.37 keV ($MoK\alpha_2$)	48.2

Neutron absorption **Thermal neutron capture cross section** 0.7 barns

17.1 Pr
Facts about Praseodymium

17.1.1 Pr
The Element

Symbol:	Pr
Atomic number:	59
Atomic weight:	140.91
Ground state electron configuration:	[Xe]$4f^3 6s^2$
Crystal structure:	Hexagonal hcp with $a = 3.67$ Å and $c = 11.84$ Å

17.1.2E
Discovery and Occurrence

Discovery: Carl Gustaf Mosander in Stockholm discovered didymium, “the twin”, in 1840. Carl Auer von Welsbach in Vienna discovered in 1885 that didymium is composed of two elements. One of them he called praseodymium “the green twin”, the other neodymium “the new twin”.

Most important mineral: Praseodymium belongs to the light REM group, the cerium group. Minerals typical for this group are monazite $(Ce,La,Nd,Th)(PO_4,SiO_4))$, Figure M25, and bastnaesite $(Ce,La)CO_3(F,OH)$, Figure M22.

Ranking in order of abundance in earth crust:	39
Mean content in earth crust:	9.2 ppm (g/tonne)
Mean content in oceans:	$6.4 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man’s body (weight 70 kg):	–

17.1.3 Pr
Chemical Characterization

Praseodymium is a soft, silvery metal with a yellowish tinge. It corrodes in moist air and develops a green oxide. It also forms green trivalent salts. “Didymium glass”, containing praseodymium and neodymium, absorbs infrared heat radiation and is used in goggles for people working with components at high temperature, for instance welders and glass blowers.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
Pr^{III} as in Pr_2O_3 and $PrCl_3$	$Pr(g) \rightarrow Pr^{+}(g) + e^{-}$	527	$Pr(g) + e^{-} \rightarrow Pr^{-}(g)$
Pr^{IV} as in $Pr(NO_3)_4$	$Pr^{+}(g) \rightarrow Pr^{2+}(g) + e^{-}$	1020	–50
	$Pr^{2+}(g) \rightarrow Pr^{3+}(g) + e^{-}$	2086	
	$Pr^{3+}(g) \rightarrow Pr^{4+}(g) + e^{-}$	3761	
	$Pr^{4+}(g) \rightarrow Pr^{5+}(g) + e^{-}$	5551	

Standard reduction potential:	$Pr^{4+}(aq) + e^{-} \rightarrow Pr^{3+}(aq)$	$E^0 = 3.2$ V
	$Pr^{3+}(aq) + 3e^{-} \rightarrow Pr(s)$	$E^0 = -2.35$ V
Electronegativity (Pauling):	1.13	
Radii of atoms and ions:	Atomic:	185 pm
(WebElements™)	Covalent:	–
	Pr^{3+} (6-coordinate, octahedral):	113 pm
	Pr^{3+} (8-coordinate):	127 pm
	Pr^{4+} (6-coordinate, octahedral):	99 pm
	Pr^{4+} (8-coordinate):	110 pm

17.1.4 Pr
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
6773 kg m^{-3} 6.77 g cm^{-3}	20.80 cm^3	1204 K 931 °C	3793 K 3520 °C	193 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
9.9	12	13.4	–	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1123 K
–	650 (680 at 298 K)	780	960	1180	1340

Coefficient of linear expansion at 298 K	$6.7 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+447 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
37 GPa	15 GPa	29 GPa	0.28

17.1.5 Pr
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	10.0 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	333 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	356 $kJmol^{-1}$
Entropy S^0 at 298 K	73.2 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	27.20 $JK^{-1}mol^{-1}$

17.1.6 Pr
Nuclear Properties and X-ray

Isotope range, natural and artificial 121–154

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{141}Pr	Stable	100	5/2+	4.136

Characteristic X-radiation

Z	Element	Kα_2 keV
58	Ce	34.279
59	Pr	35.550
60	Nd	36.847

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	391
17.37 keV (MoKα_2)	51.3

Neutron absorption **Thermal neutron capture cross section** 11.5 barns

17.1 Nd
Facts about Neodymium

17.1.1 Nd
The Element

Symbol:	Nd
Atomic number:	60
Atomic weight:	144.24
Ground state electron configuration:	[Xe]4f^{4}6s^2
Crystal structure:	Hexagonal hcp with $a = 3.66$ Å and $c = 11.80$ Å

17.1.2 Nd
Discovery and Occurrence

Discovery: Carl Gustaf Mosander in Stockholm discovered didymium, "the twin", in 1840. Carl Auer von Welsbach in Vienna discovered in 1885 that didymium is composed of two elements. One of them he called praseodymium "the green twin", the other neodymium "the new twin".

Most important mineral: Neodymium belongs to the light REM group, the cerium group. Minerals typical for this group are monazite $(Ce,La,Nd,Th)(PO_4,SiO_4)$, Figure M25, and bastnaesite $(Ce,La)CO_3(F,OH)$, Figure M22.

Ranking in order of abundance in earth crust:	27
Mean content in earth crust:	41.5 ppm (g/tonne)
Mean content in oceans:	$2.8 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Nd
Chemical Characterization

Neodymium is a silvery metal with a yellowish tinge. It is very reactive and tarnishes in air. It forms trivalent salts, which are rose-red or reddish-violet in color. Mischmetall contains 18% neodymium. Neodymium's greatest use is for preparing an intermetallic compound with iron and boron. This is ferromagnetic and gives the strongest commercial permanent magnets available.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Nd^{III} as in Nd_2O_3 and $NdCl_3$	$Nd(g) \rightarrow Nd^+(g) + e^-$	533	$Nd(g) + e^- \rightarrow Nd^-(g)$
	$Nd^+(g) \rightarrow Nd^{2+}(g) + e^-$	1040	−50
	$Nd^{2+}(g) \rightarrow Nd^{3+}(g) + e^-$	2130	
	$Nd^{3+}(g) \rightarrow Nd^{4+}(g) + e^-$	3900	

Standard reduction potential: $Nd^{3+}(aq) + 3e^- \rightarrow Nd(s)$ $E^0 = -2.32$ V

Electronegativity (Pauling): 1.13

Radii of atoms and ions: (WebElements™)		
	Atomic:	185 pm
	Covalent:	–
	Nd^{3+} (6-coordinate, octahedral):	112 pm
	Nd^{3+} (8-coordinate):	125 pm

17.1.4 Nd
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
7003 kg m^{-3} 7.00 g cm^{-3}	20.60 cm^3	1294 K 1021 °C	3347 K 3074 °C	190 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
–	16.5	16.7	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1183 K
–	610 (640 at 298 K)	740	930	1200	1380

Coefficient of linear expansion at 298 K	$6.9 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+490 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
41 GPa	16 GPa	32 GPa	0.28

17.1.5 Nd
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	7.1 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	284 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	328 $kJmol^{-1}$
Entropy S^0 at 298 K	71.5 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	27.45 $JK^{-1}mol^{-1}$

17.1.6 Nd
Nuclear Properties and X-ray

Isotope range, natural and artificial	127–156

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment µ	Half-life	Decay mode	Decay energy Q
^{142}Nd	Stable	27.13	0+	–	–	–	–
^{143}Nd	Stable	12.18	7/2–	–1.065	–	–	–
^{145}Nd	Stable	8.30	7/2–	–0.656	–	–	–
^{146}Nd	Stable	17.19	0+	–	–	–	–
^{148}Nd	Stable	5.76	0+	–	–	–	–
^{144}Nd	Active	23.80	0+	–	$2.3 \cdot 10^{15}$ y	α	1.905 MeV
^{150}Nd	Active	5.64	0+	–	$1.1 \cdot 10^{19}$ y	$\beta^-\beta^-$	–

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
59	Pr	35.550
60	Nd	36.847
61	Pm	38.171

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient µ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	406
17.37 keV (Mo$K\alpha_2$)	53

Neutron absorption	**Thermal neutron capture cross section**	50 barns

17.1 Pm
Facts about Promethium

17.1.1 Pm
The Element

Symbol:	Pm
Atomic number:	61
Atomic weight:	145
Ground state electron configuration:	[Xe]$4f^5 6s^2$
Crystal structure:	–

17.1.2 Pm
Discovery and Occurrence

Discovery: Charles D. Coryell, Jacob A. Marinsky and Lawrence E. Glendenin discovered Pm in fission products from a nuclear reactor at Oak Ridge, Tennessee in 1945 (1943). Pm was isolated by the ion-exchange technique. It was the last discovery of a rare earth element.

Most important mineral: Promethium minerals do not occur naturally.

Ranking in order of abundance in earth crust:	89–92
Mean content in earth crust:	–
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Pm
Chemical Characterization

As a consequence of its radioactivity great care is required when handling the element. Several promethium compounds have been prepared but very little is known about the properties of the metal itself. The isotope ^{147}Pm is, however, commercially available and has been tested in miniature batteries for guided missiles. The useful battery life is about five years.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Pm^{III} as in Pm_2O_3 and $PmBr_3$	$Pm(g) \rightarrow Pm^+(g) + e^-$	540	$Pm(g) + e^- \rightarrow Pm^-(g)$
	$Pm^+(g) \rightarrow Pm^{2+}(g) + e^-$	1050	–50
	$Pm^{2+}(g) \rightarrow Pm^{3+}(g) + e^-$	2150	
	$Pm^{3+}(g) \rightarrow Pm^{4+}(g) + e^-$	3970	

Standard reduction potential: $Pm^{3+}(aq) + 3e^- \rightarrow Pm(s)$ $E^0 = -2.29$ V

Electronegativity (Pauling): –

Radii of atoms and ions: (WebElements™)		
	Atomic:	185 pm
	Covalent:	–
	Pm^{3+} (6-coordinate, octahedral):	111 pm
	Pm^{3+} (8-coordinate):	123 pm

17.1.4 Pm
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
7220 kg m^{-3} 7.22 g cm^{-3} (refers to ^{147}Pm)	20.1 cm^3	1315 K 1042 °C	3273 K 3000 °C	–

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	298 K	373 K	573 K	973 K
–	17.9	18.4	–	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1473 K
–	500	640	890	1260	–

Coefficient of linear expansion at 298 K	$11 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	–
Magnetic characterization	–

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
46 GPa	18 GPa	35 GPa	0.28

17.1.5 Pm
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	(10) $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	(290) $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	(325) $kJmol^{-1}$
Entropy S^0 at 298 K	–
Molar heat capacity Cp at 298 K	27 $JK^{-1}mol^{-1}$

17.1.6 Pm
Nuclear Properties and X-ray

Isotope range, natural and artificial 130–158

Naturally occurring isotopes

Nuclide	Half-life	Naturally occuring (N)	Nuclear spin	Magnetic moment μ	Decay		
					Mode	Reaction	Energy Q
^{145}Pm	17.7 y	–	5/2+	–	EC or β^+	$^{145}\mathrm{Pm}\rightarrow^{145}\mathrm{Nd}$	0.163 MeV
^{146}Pm	5.53 y	–	3–	–	EC or β^+	$^{146}\mathrm{Pm}\rightarrow^{146}\mathrm{Nd}$	1.472 MeV
					β^-	$^{146}\mathrm{Pm}\rightarrow^{146}\mathrm{Sm}$	1.542 MeV
^{147}Pm	2.62 y	–	7/2+	2.6	β^-	$^{147}\mathrm{Pm}\rightarrow^{147}\mathrm{Sm}$	0.224 MeV

Characteristic X-radiation

Z	Element	Kα_2 keV
60	Nd	36.847
61	Pm	38.171
62	Sm	39.523

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	428
17.37 keV (MoKα_2)	56.9

Neutron absorption **Thermal neutron capture cross section** 8400±1680 barns

17.1 Sm
Facts about Samarium

17.1.1 Sm
The Element

Symbol:	Sm
Atomic number:	62
Atomic weight:	150.36
Ground state electron configuration:	[Xe]$4f^6 6s^2$
Crystal structure:	Rhombohedral with $a = b = c = 9.00$ Å

17.1.2 Sm
Discovery and Occurrence

Discovery: Paul-Émile Lecoq de Boisbaudran in Paris discovered a new element in didymium in 1879. He gave it the name *samarium* after the mineral *samarskite*.

Most important mineral: Samarium belongs to the light REM group, the cerium group. Minerals typical for this group are monazite $(Ce,La,Nd,Th)(PO_4,SiO_4)$, Figure M25, and bastnaesite $(Ce,La)CO_3(F,OH)$, Figure M22.

Ranking in order of abundance in earth crust:	40
Mean content in earth crust:	7.05 ppm (g/tonne)
Mean content in oceans:	$4.5 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Sm
Chemical Characterization

Samarium is a hard and brittle metal. It is reasonably stable in air but ignites at 150°C. The intermetallic compound $SmCo_5$ has markedly ferromagnetic properties and is used in magnets for small electric motors. The radioactive samarium isotope ^{147}Sm with a half-life of $1.06 \cdot 10^{11}$ years is used to determine the age of minerals and rocks.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Sm^{III} as in Sm_2O_3 and SmF_3	$Sm(g) \rightarrow Sm+(g) + e^-$	544.5	$Sm(g) + e^- \rightarrow Sm^-(g)$
Sm^{II} as in SmO and $SmSO_4$	$Sm^+(g) \rightarrow Sm^{2+}(g) + e^-$	1070	–50
	$Sm^{2+}(g) \rightarrow Sm^{3+}(g) + e^-$	2260	
	$Sm^{3+}(g) \rightarrow Sm^{4+}(g) + e^-$	3990	

Standard reduction potential:	$Sm^{2+}(aq) + 2e^- \rightarrow Sm(s)$	$E^0 = -2.67$ V
	$Sm^{3+}(aq) + 3e^- \rightarrow Sm(s)$	$E^0 = -2.30$ V

Electronegativity (Pauling): 1.17

Radii of atoms and ions:	Atomic:	185 pm
(WebElements™)	Covalent:	–
	Sm^{2+} (8-coordinate):	141 pm
	Sm^{3+} (6-coordinate, octahedral):	110 pm
	Sm^{3+} (8-coordinate):	122 pm

17.1.4 Sm
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
7520 kg m^{-3} 7.52 g cm^{-3}	20.00 cm^3	1347 K 1074 °C	2067 K 1794 °C	196 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
10	13	13	14	–

Resistivity nΩm

78 K	273 K	298 K	573 K	973 K	1473 K
660	914	940	–	–	–

Coefficient of linear expansion at 298 K	$12.7 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+152 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
50 GPa	20 GPa	38 GPa	0.27

17.1.5 Sm
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	11.0 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	192 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	207 $kJmol^{-1}$
Entropy S^0 at 298 K	69.6 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	29.54 $JK^{-1}mol^{-1}$

17.1.6 Sm
Nuclear Properties and X-ray

Isotope range, natural and artificial 131–160

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{144}Sm	Stable	3.1	0+	–	–	–	–
^{150}Sm	Stable	7.4	0+	–	–	–	–
^{152}Sm	Stable	26.7	0+	–	–	–	–
^{154}Sm	Stable	22.7	0+	–	–	–	–
^{147}Sm	Active	15.0	7/2–	−0.8149	$1.1 \cdot 10^{11}$ y	α	2.311 MeV
^{148}Sm	Active	11.3	0+	–	$7 \cdot 10^{15}$ y	α	1.986 MeV
^{149}Sm	Active	13.8	7/2–	−0.6718	$2 \cdot 10^{15}$ y	–	–

Characteristic X-radiation

Z	Element	Kα_2 keV
61	Pm	38.171
62	Sm	39.523
63	Eu	40.902

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	436
17.37 keV (MoKα_2)	58.5

Neutron absorption **Thermal neutron capture cross section** 5800 barns

17.1 Eu
Facts about Europium

17.1.1 Eu
The Element

Symbol:	Eu
Atomic number:	63
Atomic weight:	151.96
Ground state electron configuration:	[Xe]$4f^7 6s^2$
Crystal structure:	Cubic bcc with $a = 4.58$ Å

17.1.2 Eu
Discovery and Occurrence

Discovery: Samarium was supposed to be a pure element. At the turn of the century 1900 Eugène-Anatole Demarçay in Paris found a companion in it and separated it. He called the new element europium.

Most important mineral: Europium belongs to the light REM group, the cerium group. Minerals typical for this group are monazite (Ce,La,Nd,Th)(PO4,SiO4), Figure M25, and bastnaesite (Ce,La)CO3(F,OH), Figure M22.

Ranking in order of abundance in earth crust:	52–53
Mean content in earth crust:	2 ppm (g/tonne)
Mean content in oceans:	$1.3 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Eu
Chemical Characterization

Europium is the most reactive of the rare earth metals. It is quickly oxidized in air and ignites at about 150°C. Yttrium oxysulfide, doped with europium, is used in phosphors to give red colors in television screens.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Eu^{III} as in Eu_2O_3 and EuI_3	$Eu(g) \rightarrow Eu^+(g) + e^-$	547	$Eu(g) + e^- \rightarrow Eu^-(g)$
Eu^{II} as in EuO, EuS	$Eu^+(g) \rightarrow Eu^{2+}(g) + e^-$	1085	–50
	$Eu^{2+}(g) \rightarrow Eu^{3+}(g) + e^-$	2404	
	$Eu^{3+}(g) \rightarrow Eu^{4+}(g) + e^-$	4120	

Standard reduction potential:	$Eu^{3+}(aq) + e^- \rightarrow Eu^{2+}(aq)$	$E^0 = -0.35$ V
	$Eu^{2+}(aq) + 2e^- \rightarrow Eu(s)$	$E^0 = -2.80$ V
	$Eu^{3+}(aq) + 3e^- \rightarrow Eu(s)$	$E^0 = -1.99$ V

Electronegativity (Pauling): –

Radii of atoms and ions:	Atomic:	185 pm
(WebElements™)	Covalent:	–
	Eu^{2+} (6-coordinate, octahedral):	131 pm
	Eu^{2+} (8-coordinate):	139 pm
	Eu^{3+} (6-coordinate, octahedral):	109 pm
	Eu^{3+} (8-coordinate):	121 pm

17.1.4 Eu
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
5244 kg m^{-3} 5.24 g cm^{-3}	28.98 cm^3	1095 K 822 °C	1802 K 1529 °C	182 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
–	14	–	–	–

Resistivity nΩm

78 K	273 K	298 K	573 K	973 K	1473 K
600	890	900	–	–	–

Coefficient of linear expansion at 298 K	$35 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+2810 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
18 GPa	8 GPa	8 GPa	0.14

17.1.5 Eu
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	10.4 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	176 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	175 $kJmol^{-1}$
Entropy S^0 at 298 K	77.78 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	27.66 $JK^{-1}mol^{-1}$

17.1.6 Eu
Nuclear Properties and X-ray

Isotope range, natural and artificial 131–162

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{151}Eu	Stable	47.8	5/2+	3.472
^{153}Eu	Stable	52.2	5/2+	1.533

Characteristic X-radiation Z	 Element	 Kα_2 keV
62	Sm	39.523
63	Eu	40.902
64	Gd	42.309

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	395
17.37 keV (MoKα_2)	61.6

Neutron absorption	**Thermal neutron capture cross section**	4100 barns

17.1 Gd
Facts about Gadolinium

17.1.1 Gd
The Element

Symbol:	Gd
Atomic number:	64
Atomic weight:	157.25
Ground state electron configuration:	[Xe]4f^{7}5d^{1}6s^2
Crystal structure:	Hexagonal hcp with $a = 3.64$ Å, $c = 5.78$ Å

17.1.2 Gd
Discovery and Occurrence

Discovery: Jean-Charles Gallisard de Marignac in Geneva in 1880 investigated the mineral samarskite and found, as he thought, two new rare earth metals. Spectral analysis showed that one was samarium; the other, however, was new. He gave it a provisional name. With Marignac's assent Boisbaudran gave the new element the name *gadolinium* in 1886. The intention was to emphasize the great importance of the original RE mineral gadolinite.

Most important mineral: Gadolinium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	41
Mean content in earth crust:	6.2 ppm (g/tonne)
Mean content in oceans:	$7 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Gd
Chemical Characterization

Gadolinium is a silvery white metal, malleable and ductile, with a white oxide and colorless salts. It is relatively stable in dry air but tarnishes in moist air and reacts slowly with water. Gadolinium has the highest thermal neutron capture cross-section of any element and is used as a component of control rods in nuclear reactors. It is ferromagnetic and used in equipment for magnetic cooling.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Gd^{III} as in Gd_2O_3 and $GdCl_3 \cdot 6H_2O$	$Gd(g) \rightarrow Gd^+(g) + e^-$	593	$Gd(g) + e^- \rightarrow Gd^-(g)$
	$Gd^+(g) \rightarrow Gd^{2+}(g) + e^-$	1170	–50
	$Gd^{2+}(g) \rightarrow Gd^{3+}(g) + e^-$	1990	
	$Gd^{3+}(g) \rightarrow Gd^{4+}(g) + e^-$	4250	

Standard reduction potential: $Gd^{3+}(aq) + 3e^- \rightarrow Gd(s)$ $E^0 = -2.28$ V

Electronegativity (Pauling): 1.20

Radii of atoms and ions: (WebElements™)		
	Atomic:	180 pm
	Gd^{3+} (6-coordinate, octahedral):	108 pm
	Gd^{3+} (8-coordinate):	119 pm

17.1.4 Gd
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
7901 kg m^{-3} 7.90 g cm^{-3}	19.90 cm^3	1586 K 1313 °C	3546 K 3273 °C	236 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
12	10	–	–	–

Resistivity nΩm 78 K	273 K	298 K	573 K	973 K	1473 K
200	1260	1300	–	–	–

Coefficient of linear expansion at 298 K	$9.4 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$60\,300 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
55 GPa	22 GPa	38 GPa	0.26

17.1.5 Gd
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	15.5 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	310 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	398 $kJmol^{-1}$
Entropy S^0 at 298 K	68.1 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	37.03 $JK^{-1}mol^{-1}$

17.1.6 Gd
Nuclear Properties and X-ray

Isotope range, natural and artificial 137–164

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{154}Gd	Stable	2.18	0+	–	–	–	–
^{155}Gd	Stable	14.80	3/2–	−0.2591	–	–	–
^{156}Gd	Stable	20.47	0+	–	–	–	–
^{157}Gd	Stable	15.65	3/2–	−0.3399	–	–	–
^{158}Gd	Stable	24.84	0+	–	–	–	–
^{160}Gd	Stable	21.86	0+	–	–	–	–
^{152}Gd	Active	0.20	0+	–	$1.1 \cdot 10^{14}$ y	α	2.205 MeV

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
63	Eu	40.902
64	Gd	42.309
65	Tb	43.744

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	403
17.37 keV ($MoK\alpha_2$)	63.3

Neutron absorption **Thermal neutron capture cross section** 49 000 barns

17.1 Tb
Facts about Terbium

17.1.1 Tb
The Element

Symbol:	Tb
Atomic number:	65
Atomic weight:	158.93
Ground state electron configuration:	[Xe]$4f^96s^2$
Crystal structure:	Hexagonal hcp with $a = 3.60$ Å and $c = 5.69$ Å

17.1.2 Tb
Discovery and Occurrence

Discovery: Carl Gustaf Mosander in Stockholm in 1842–43 found that Gadolin's yttrium, the first rare earth metal discovered, was composed of three elements. One was allowed to keep the name yttrium, while the two others became *terbium* and *erbium*. Thus these new elements also got their names from Ytterby.

Most important mineral: Terbium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	58–59
Mean content in earth crust:	1.2 ppm (g/tonne)
Mean content in oceans:	$1.4 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Tb
Chemical Characterization

Terbium is a silvery gray metal, ductile and soft enough to be cut with a knife. It is fairly unreactive in air. Terbium (and dysprosium) find considerable use in magnetostrictive materials. Magnetostriction is the dimension change caused by magnetization. The material *Terfenol-D*, has the largest room-temperature strain of any commercially produced magnetostrictive material. Its name is derived from terbium (TER), iron (FE), Naval Ordinance Labs (NOL), and dysprosium-D. *MiniDiscs* with a magnetic recording layer of *terbium–iron–cobalt* or *terbium–gadolinium–iron–cobalt* have been developed.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Tb^{III} as in Tb_2O_3 and Tb_2S_3	$Tb(g) \rightarrow Tb^+(g) + e^-$	566	$Tb(g) + e- \rightarrow Tb-(g)$
Tb^{IV} as in TbF_4	$Tb^+(g) \rightarrow Tb^{2+}(g) + e^-$	1110	–50
	$Tb^{2+}(g) \rightarrow Tb^{3+}(g) + e^-$	2114	
	$Tb^{3+}(g) \rightarrow Tb^{4+}(g) + e^-$	3839	

Standard reduction potential: $Tb^{4+}(aq) + e^- \rightarrow Tb^{3+}(aq)$ $E^0 = +3.1$ V
$Tb^{3+}(aq) + 3e^- \rightarrow Tb(s)$ $E^0 = -2.31$ V

Electronegativity (Pauling): –

Radii of atoms and ions: (WebElements™)		
	Atomic:	180 pm
	Tb^{3+} (6-coordinate, octahedral):	106 pm
	Tb^{3+} (8-coordinate):	118 pm
	Tb^{4+} (6-coordinate, octahedral):	90 pm
	Tb^{4+} (8-coordinate):	102 pm

17.1.4 Tb
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
8225 kg m^{-3} 8.225 g cm^{-3}	19.32 cm^3	1629 K 1356 °C	3503 K 3230 °C	182 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
11	10.5	–	–	–

Resistivity nΩm 78 K	273 K	298 K	573 K	973 K	1473 K
270	1130	1160	–	–	–

Coefficient of linear expansion at 298 K	$10.3 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$11\,500 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
56 GPa	22 GPa	41 GPa	0.27

17.1.5 Tb
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	(15) $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	(390) $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	390 $kJmol^{-1}$
Entropy S^0 at 298 K	73.22 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	28.91 $JK^{-1}mol^{-1}$

17.1.6 Tb
Nuclear Properties and X-ray

Isotope range, natural and artificial 140–165

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{159}Tb	Stable	100	3/2+	2.014

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV
64	Gd	42.309
65	Tb	43.744
66	Dy	45.208

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	310
17.37 keV ($MoK\alpha_2$)	66.5

Neutron absorption **Thermal neutron capture cross section** 30 barns

17.1 Dy
Facts about Dysprosium

17.1.1 Dy
The Element

Symbol:	Dy
Atomic number:	66
Atomic weight:	162.50
Ground state electron configuration:	$[Xe]4f^{10}6s^2$
Crystal structure:	Hexagonal hcp with $a = 3.59$ Å and $c = 5.65$ Å

17.1.2 Dy
Discovery and Occurrence

Discovery: Paul-Émile Lecoq de Boisbaudran in France in 1886 found a new element in the REM holmium, earlier discovered by Cleve. The discovery was hard work (*dysprositos* in Greek), so the new element was given the name *dysprosium*.

Most important mineral: Dysprosium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	42
Mean content in earth crust:	5.2 ppm (g/tonne)
Mean content in oceans:	$9.1 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man’s body (weight 70 kg):	–

17.1.3 Dy
Chemical Characterization

Dysprosium is a metal with bright silver luster, relatively stable in air at room temperature. The element has a very high magnetic susceptibility, which means that it is markedly paramagnetic. For dysprosium there are only few applications. One important is its use, together with terbium, in magnetostrictive materials.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Dy^{III} as in Dy_2O_3, $DyCl_3$, and $Dy(NO_3)_3 \cdot 5H_2O$	$Dy(g) \rightarrow Dy^+(g) + e^-$	573	$Dy(g) + e^- \rightarrow Dy^-(g)$ –50
	$Dy^+(g) \rightarrow Dy^{2+}(g) + e^-$	1130	
	$Dy^{2+}(g) \rightarrow Dy^{3+}(g) + e^-$	2200	
	$Dy^{3+}(g) \rightarrow Dy^{4+}(g) + e^-$	3990	

Standard reduction potential: $Dy^{3+}(aq) + 3e^- \rightarrow Dy(s)$ $E^0 = -2.29$ V

Electronegativity (Pauling): 1.22

Radii of atoms and ions: (WebElements™)	Atomic:	175 pm
	Dy^{3+} (6-coordinate, octahedral):	105 pm
	Dy^{3+} (8-coordinate):	117 pm

17.1.4 Dy
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
8550 kg m^{-3} 8.55 g cm^{-3}	19.00 cm^3	1685 K 1412 °C	2840 K 2567 °C	173 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	298 K	573 K	973 K
9	10.5	10.7	–	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1473 K
260	890	1030	1240	1565	1840

Coefficient of linear expansion at 298 K	$9.9 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+8000 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
61 GPa	25 GPa	41 GPa	0.25

17.1.5 Dy
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	(15) $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	290 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	290 $kJmol^{-1}$
Entropy S^0 at 298 K	74.77 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	28.16 $JK^{-1}mol^{-1}$

17.1.6 Dy
Nuclear Properties and X-ray

Isotope range, natural and artificial 141–169

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{156}Dy	Stable	0.06	0+	–
^{158}Dy	Stable	0.10	0+	–
^{160}Dy	Stable	2.34	0+	–
^{161}Dy	Stable	18.9	5/2+	−0.4806
^{162}Dy	Stable	25.5	0+	–
^{163}Dy	Stable	24.9	5/2–	0.6726
^{164}Dy	Stable	28.2	0+	–

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
65	Tb	43.744
66	Dy	45.208
67	Ho	46.699

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	324
17.37 keV (MoKα_2)	69.0

Neutron absorption **Thermal neutron capture cross section** 90 barns

17.1 Ho
Facts about Holmium

17.1.1 Ho
The Element

Symbol:	Ho
Atomic number:	67
Atomic weight:	164.93
Ground state electron configuration:	[Xe]$4f^{11}6s^2$
Crystal structure:	Hexagonal hcp with $a = 3.58$ Å, $c = 5.62$ Å

17.1.2 Ho
Discovery and Occurrence

Discovery: During 1878–79, Per T. Cleve in Uppsala discovered that erbium contained two other elements. He named them thulium after the old Roman name *Thulia* for the Furthest North and *holmium* after Stockholm. Delafontaine and Soret in Switzerland had in fact found lines of a foreign element during the spectral analysis of erbium in 1878. This element, erbium-X or element-X, appeared to be identical with holmium. In tables of discoverers Delafontaine and Soret are mentioned alongside Cleve.

Most important mineral: Holmium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are euxenite, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and fergusonite $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	56
Mean content in earth crust:	1.3 ppm (g/tonne)
Mean content in oceans:	$2.2 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Ho
Chemical Characterization

Holmium is a silvery metal, soft and malleable, and stable in dry air at room temperature. However, it oxidizes rapidly in moist air and at elevated temperature. Holmium has almost no commercial applications, although it has unusual magnetic properties. These are utilized in pole pieces of superconducting research magnets (Tallahassee, Florida).

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ho^{III} as in Ho_2O_3 and $HoCl_3$	$Ho(g) \rightarrow Ho^+(g) + e^-$	581	$Ho(g) + e^- \rightarrow Ho^-(g)$ –50
	$Ho^+(g) \rightarrow Ho^{2+}(g) + e^-$	1140	
	$Ho^{2+}(g) \rightarrow Ho^{3+}(g) + e^-$	2204	
	$Ho^{3+}(g) \rightarrow Ho^{4+}(g) + e^-$	4100	

Standard reduction potential: $Ho^{3+}(aq) + 3e^- \rightarrow Ho(s)$ $E^0 = -2.33$ V

Electronegativity (Pauling): 1.23

Radii of atoms and ions: (WebElements™)		
	Atomic:	175 pm
	Ho^{3+} (6-coordinate, octahedral):	104 pm
	Ho^{3+} (8-coordinate):	115.5 pm

17.1.4 Ho
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
8795 kg m^{-3} 8.795 g cm^{-3}	18.75 cm^{3}	1747 K 1474 °C	2973 K 2700 °C	165 J K^{-1} kg^{-1}

Thermal conductivity Wm^{-1}K^{-1} 173 K	273 K	373 K	573 K	973 K
14	16	17	–	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1473 K
340	900	1050	1340	1750	2030

Coefficient of linear expansion at 298 K	11.2 · 10^{-6} K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	+5490 · 10^{-9} m^{3} kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
65 GPa	26 GPa	40 GPa	0.23

17.1.5 Ho
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	17.1 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	260 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	301 kJmol^{-1}
Entropy S^0 at 298 K	75.3 JK^{-1}mol^{-1}
Molar heat capacity Cp at 298 K	27.15 JK^{-1}mol^{-1}

17.1.6 Ho
Nuclear Properties and X-ray

Isotope range, natural and artificial 141–172

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{165}Ho	Stable	100	7/2–	4.173

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
66	Dy	45.208
67	Ho	46.699
68	Er	48.221

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	126
17.37 keV (Mo$K\alpha_2$)	72.1

Neutron absorption **Thermal neutron capture cross section** 65 barns

17.1 Er
Facts about Erbium

17.1.1 Er
The Element

Symbol:	Er
Atomic number:	68
Atomic weight:	167.26
Ground state electron configuration:	[Xe]$4f^{12}6s^2$
Crystal structure:	Hexagonal hcp with $a = 3.56$ Å, $c = 5.59$ Å

17.1.2 Er
Discovery and Occurrence

Discovery: Carl Gustaf Mosander in Stockholm in 1842–43 found that Gadolin's yttrium, the first discovered rare earth metal, was composed of three elements. One was allowed to keep the name yttrium, while the two others became *terbium* and *erbium*. Thus these new elements also got their names from Ytterby.

Most important mineral: Erbium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	43–44
Mean content in earth crust:	3.5 ppm (g/tonne)
Mean content in oceans:	$8.7 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Er
Chemical Characterization

Erbium is a soft and malleable metal with a bright, silvery luster. Erbium oxide Er_2O_3 is a rose-red compound, soluble in acids, forming a series of rose-colored salts. Recently erbium doping of silicon has been tested for special LEDs (light emitting diodes). The special feature of erbium is that it has an electron transition in the f-subshell, corresponding to the wavelength 1.54 mm, a standard wavelength for telecommunications.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Er^{III} as in Er_2O_3 and $ErCl_3 \cdot 6H_2O$	$Er(g) \rightarrow Er^+(g) + e^-$	589	$Er(g) + e^- \rightarrow Er^-(g)$ –50
	$Er^+(g) \rightarrow Er^{2+}(g) + e^-$	1150	
	$Er^{2+}(g) \rightarrow Er^{3+}(g) + e^-$	2194	
	$Er^{3+}(g) \rightarrow Er^{4+}(g) + e^-$	4120	

Standard reduction potential: $Er^{3+}(aq) + 3e^- \rightarrow Er(s)$ $E^0 = -2.32$ V

Electronegativity (Pauling): 1.24

Radii of atoms and ions: (WebElements™)		
	Atomic:	175 pm
	Er^{3+} (6-coordinate, octahedral):	103 pm
	Er^{3+} (8-coordinate):	114 pm

17.1.4 Er
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
9066 kg m^{-3} 9.07 g cm^{-3}	18.45 cm^3	1802 K 1529 °C	3141 K 2868 °C	168 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
14	15	–	–	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1473 K
410	810	1030	1350	1830	2160

Coefficient of linear expansion at 298 K	$12.2 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+3330 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
70 GPa	28 GPa	44 GPa	0.24

17.1.5 Er
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	17.2 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	292 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	317 kJmol^{-1}
Entropy S^0 at 298 K	73.18 J$K^{-1}$$mol^{-1}$
Molar heat capacity Cp at 298 K	28.12 J$K^{-1}$$mol^{-1}$

17.1.6 Er
Nuclear Properties and X-ray

Isotope range, natural and artificial 145–175

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{162}Er	Stable	0.14	0+	–
^{164}Er	Stable	1.61	0+	–
^{166}Er	Stable	33.6	0+	–
^{167}Er	Stable	22.95	7/2+	−0.5665
^{168}Er	Stable	26.8	0+	–
^{170}Er	Stable	14.9	0+	–

Characteristic X-radiation

Z	Element	Kα_2 keV
67	Ho	46.699
68	Er	48.221
69	Tm	49.973

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	132
17.37 keV (MoKα_2)	75.3

Neutron absorption	Thermal neutron capture cross section	0.16 barns

17.1 Tm
Facts about Thulium

17.1.1 Tm
The Element

Symbol:	Tm
Atomic number:	69
Atomic weight:	168.93
Ground state electron configuration:	[Xe]4f^{13}6s^2
Crystal structure:	Hexagonal hcp with $a = 3.54$ Å, $c = 5.55$ Å

17.1.2 Tm
Discovery and Occurrence

Discovery: During 1878–9 Per T. Cleve in Uppsala discovered that erbium contains two other elements. He named them *thulium* after the old Roman name *Thulia* for the Furthest North and *holmium* after Stockholm. With the exception of promethium, thulium is the rarest of the rare earth elements and is about as rare as silver or gold.

Most important mineral: Thulium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	62
Mean content in earth crust:	0.52 ppm (g/tonne)
Mean content in oceans:	$1.7 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Tm
Chemical Characterization

Thulium is a silver-gray, ductile metal, unreactive in air if protected from moisture. Thulium has almost no practical applications. The γ-radiation from the radioactive isotope ^{170}Tm has, however, been examined for use in materials testing and as a portable X-ray source for medical use.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Tm^{III} as in Tm_2O_3 and TmI_3	$Tm(g) \rightarrow Tm^+(g) + e^-$	597	$Tm(g) + e^- \rightarrow Tm^-(g)$ –50
	$Tm^+(g) \rightarrow Tm^{2+}(g) + e^-$	1160	
	$Tm^{2+}(g) \rightarrow Tm^{3+}(g) + e^-$	2285	
	$Tm^{3+}(g) \rightarrow Tm^{4+}(g) + e^-$	4120	

Standard reduction potential: $Tm^{3+}(aq) + 3e^- \rightarrow Tm(s) \quad E^0 = -2.32$ V

Electronegativity (Pauling): 1.25

Radii of atoms and ions: (WebElements™)	Atomic:	175 pm
	Tm^{3+} (6-coordinate, octahedral):	102 pm
	Tm^{3+} (8-coordinate):	113 pm

17.1.4 Tm
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
9321 kg m^{-3} 9.32 g cm^{-3}	18.12 cm^3	1818 K 1545 °C	2223 K 1950 °C	160 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
16	17	–	–	–

Resistivity nΩm

78 K	273 K	298 K	573 K	973 K	1473 K
310	670	700	–	–	–

Coefficient of linear expansion at 298 K	$13.3 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+1900 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
75 GPa	31 GPa	43 GPa	0.2

17.1.5 Tm
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	18.4 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	250 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	232 $kJmol^{-1}$
Entropy S^0 at 298 K	74.01 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	27.03 $JK^{-1}mol^{-1}$

17.1.6 Tm
Nuclear Properties and X-ray

Isotope range, natural and artificial 146–177

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{169}Tm	Stable	100	1/2+	−0.2316

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
68	Er	48.221
69	Tm	49.773
70	Yb	51.354

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	138
17.37 keV (Mo$K\alpha_2$)	78.8

Neutron absorption	Thermal neutron capture cross section	115 barns

17.1 Yb
Facts about Ytterbium

17.1.1Yb
The Element

Symbol:	Yb
Atomic number:	70
Atomic weight:	173.04
Ground state electron configuration:	[Xe]$4f^{14}6s^2$
Crystal structure:	Cubic fcc with a = 5.49 Å

17.1.2 Yb
Discovery and Occurrence

Discovery: J.-C. Marignac in Switzerland discovered Ytterbium in 1878. He investigated erbium and found that the element was not homogenous but contained a new rare earth metal. Once again Ytterby's name was invoked.

Most important mineral: Ytterbium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	45
Mean content in earth crust:	3.2 ppm (g/tonne)
Mean content in oceans:	$8.2 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Yb
Chemical Characterization

Ytterbium is a soft, malleable metal with a bright, silvery luster. It is fairly unreactive but needs to be kept in closed containers to protect it from air and moisture. Ytterbium fluoride is non-toxic and inert. It is not transparent to X-rays. Because of that the compound has been tested as an additive to composite dental plastic fillings. Traces of fluoride ions are continuously set free, giving protection against caries.

Oxidation states:	**Ionization energy (kJ mol⁻¹):**		**Electron affinity (kJ mol⁻¹):**
Yb^{III} as in Yb_2O_3 and YbF_3	$Yb(g) \rightarrow Yb^+(g) + e^-$	603	$Yb(g) + e^- \rightarrow Yb^-(g)$
Yb^{II} as in YbO and $YbCO_3$	$Yb^+(g) \rightarrow Yb^{2+}(g) + e^-$	1175	–50
	$Yb^{2+}(g) \rightarrow Yb^{3+}(g) + e^-$	2417	
	$Yb^{3+}(g) \rightarrow Yb^{4+}(g) + e^-$	4203	

Standard reduction potential:	$Yb^{2+}(aq) + 2e^- \rightarrow Yb(s)$	$E^0 = -2.8$ V
	$Yb^{3+}(aq) + 3e^- \rightarrow Yb(s)$	$E^0 = -2.22$ V
	$Yb^{3+}(aq) + e^- \rightarrow Yb^{2+}(aq)$	$E^0 = -1.05$ V

Electronegativity (Pauling): –

Radii of atoms and ions:	Atomic:	175 pm
(WebElements™)	Yb^{3+} (6-coordinate, octahedral):	101 pm
	Yb^{3+} (8-coordinate):	112.5 pm
	Yb^{2+} (6-coordinate, octahedral):	116 pm
	Yb^{2+} (8-coordinate):	128 pm

17.1.4 Yb
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
6965 kg m^{-3} 6.965 g cm^{-3}	24.84 cm^3	1092 K 819 °C	1469 K 1196 °C	155 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
–	35.4	34.3	–	–

Resistivity nΩm 78 K	273 K	298 K	573 K	973 K	1473 K
130	277	290	–	–	–

Coefficient of linear expansion at 298 K	$26.3 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+18.1 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
24 GPa	9.9 GPa	14 GPa	0.21

17.1.5 Yb
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	9.2 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	160 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	152 $kJmol^{-1}$
Entropy S^0 at 298 K	59.87 $JK^{-1}mol^{-1}$
Molar heat capacity at 298 K	26.74 $JK^{-1}mol^{-1}$

17.1.6 Yb
Nuclear Properties and X-ray

Isotope range, natural and artificial 151–180

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{168}Yb	Stable	0.13	0+	–
^{170}Yb	Stable	3.05	0+	–
^{171}Yb	Stable	14.3	1/2–	0.4919
^{172}Yb	Stable	21.9	0+	–
^{173}Yb	Stable	16.12	5/2–	−0.6776
^{174}Yb	Stable	31.8	0+	–
^{176}Yb	Stable	12.7	0+	–

Characteristic X-radiation

Z	Element	Kα_2 keV
69	Tm	49.773
70	Yb	51.354
71	Lu	52.965

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	143
17.37 keV (MoKα_2)	81.3

Neutron absorption **Thermal neutron capture cross section** 37 barns

17.1 Lu
Facts about Lutetium

17.1.1 Lu
The Element

Symbol:	Lu
Atomic number:	71
Atomic weight:	174.97
Ground state electron configuration:	[Xe]4f^{14}5d^{1}6s^2
Crystal structure:	Hexagonal hcp with $a = 3.50$ Å, $c = 5.55$ Å

17.1.2 Lu
Discovery and Occurrence

Discovery: Three scientists, G. Urbain in France, C. Auer von Welsbach in Austria and C. James in the USA investigated ytterbium carefully. In 1907, independently of each other, they discovered a new metal. Urbain called the new element *lutecium* after an old name for Paris. Auer wanted to use the name *cassiopeium*. In 1909 it was decided that the name should be *lutetium*.

Most important mineral: Lutetium belongs to the heavy REM group, the yttrium group. Minerals typical for this group are *euxenite*, $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and *fergusonite* $Y(Nb,Ta)O_4$, Figure M19.

Ranking in order of abundance in earth crust:	61
Mean content in earth crust:	0.8 ppm (g/tonne)
Mean content in oceans:	$1.5 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

17.1.3 Lu
Chemical Characterization

Lutetium is a silvery white metal, relatively stable in air. There are few applications for lutetium. The availability is poor and the price high. If the Lu atom is activated by thermal neutrons its nucleus emits a pure β-radiation. In this form the metal can be used as a catalyst for cracking and polymerization.

Oxidation states:	**Ionization energy (kJ mol⁻¹):**		**Electron affinity (kJ mol⁻¹):**
Lu^{III} as in Lu_2O_3 and $LuBr_3$	$Lu(g) \rightarrow Lu^+(g) + e^-$	523.5	$Lu(g) + e^- \rightarrow Lu^-(g)$
	$Lu^+(g) \rightarrow Lu^{2+}(g) + e^-$	1340	–50
	$Lu^{2+}(g) \rightarrow Lu^{3+}(g) + e^-$	2022	
	$Lu^{3+}(g) \rightarrow Lu^{4+}(g) + e^-$	4370	

Standard reduction potential: $Lu^{3+}(aq) + 3e^- \rightarrow Lu(s)$ $E^0 = -2.28$ V

Electronegativity (Pauling): 1.27

Radii of atoms and ions: (WebElements™)		
	Atomic:	175 pm
	Covalent:	160 pm
	Lu^{3+} (6-coordinate, octahedral):	100 pm
	Lu^{3+} (8-coordinate):	112 pm

17.1.4 Lu

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 25 °C
9840 kg m^{-3} 9.84 g cm^{-3}	17.78 cm^3	1936 K 1663 °C	3675 K 3402 °C	154 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
18	17	–	–	–

Resistivity nΩm 78 K	273 K	298 K	573 K	973 K	1473 K
160	540	790	–	–	–

Coefficient of linear expansion at 298 K	$8.3 \cdot 10^{-6}$ K^{-1}
Mass magnetic susceptibility χ_{mass} at 293 K	$+1.3 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
69 GPa	27 GPa	52 GPa	0.28

17.1.5 Lu

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	19.2 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	425 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	428 $kJmol^{-1}$
Entropy S^0 at 298 K	50.96 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	26.86 $JK^{-1}mol^{-1}$

17.1.6 Lu
Nuclear Properties and X-ray

Isotope range, natural and artificial 150–184

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{175}Lu	Stable	97.41	7/2+	2.233	–	–	–
^{176}Lu	Active	2.59	7–	3.19	$3.8 \cdot 10^{10}$ y	β^-	1.193 MeV

Characteristic X-radiation

Z	Element	Kα_2 keV
70	Yb	51.354
71	Lu	52.965
72	Hf	54.611

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	150
17.37 keV (MoKα_2)	85.0

Neutron absorption **Thermal neutron capture cross section** 75 barns

17.2
Rare Earth Metals in the Periodic Table – and in Nature

17.2.1
A Very Special Place in the Periodic Table

In the periodic table, Figure 17.1, all the elements belonging to groups 3–12 are called *transition elements*. Many of them are important in technical applications as for instance alloying elements in steels and superalloys.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	**57** **La**	**72** **Hf**	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104	105	106	107	108	109									

Figure 17.1 An incomplete periodic table of the elements.

In group 3, we find scandium, Sc, yttrium, Y, and lanthanumm, La, the latter with atomic number 57. One step to the right we expect to find the atomic number 58. But instead there is number 72, Hf. 14 elements are missing! This chapter is devoted to the exciting story of discovery and discoverers, and descriptions of the modern uses of these high-tech elements Sc, Y, La and lanthanides.

The discoveries started with the findings in Ytterby and Bastnaes. With the final results available (Figure 17.2) we can say that the 14 elements all belong to group 3 and period 6. They constitute a subgroup of elements, all so similar to lanthanum that they are called *the lanthanides*.

6	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Figure 17.2 Lanthanides, the 14 elements between lanthanum and hafnium (Period 6, group 3).

The two outer electron shells in neutral atoms of each lanthanide element have the same number of valence electrons as lanthanum, 2 and 1 respectively. This is the reason for the great similarities between them. And this is also the background to the enormously difficult discovery and separation work, characteristic of the lanthanides. But there are in fact some differences. In the third shell, the numbers of the so-called f-electrons differ. Lanthanum itself has no f-electron, the first lanthanide, cerium Ce, has 1, the second, praseodymium Pr, has 2 and the fourteenth, lutetium Lu, has 14 (see below, section 17.5.1).

17.2.2

Rare – But Common

The designation *rare* is rather inappropriate. The RE metals *are* rare compared to the alkaline earth metals, calcium, magnesium and so on, but are not especially rare in general. Cerium, the RE metal with the highest mean content in earth crust is more common than copper. Thulium, the rarest RE metal (with the exception of promethium) is more common in the earth's crust than is silver.

In one way, however, the REMs are rare. They are markedly dispersed in the crust. 160 RE minerals are known, most of them evenly distributed and thus not workable. In particular, scandium is present in almost all of the crust minerals. Its atom has a very low weight, small radius and a high charge. According to the principles outlined in Chapter 4 Geochemistry, an ion of this type is favored during the crystallization of stone melts as aggregates of solid phase grow. In two minerals, however, *thortveitite* and *kolbeckite*, high contents of scandium are present.

RE metals other than scandium are very similar and occur with each other in the crust. From among the large number of minerals a few are mentioned with their formulas in Tables 17.2 and 17.3.

Table 17.2 Some cerium group minerals

Mineral	Formula
Thortveitite	$(Sc,Y)_2Si_2O_7$
Kolbeckite Figure M26	$ScPO_4 \cdot 2H_2O$
Monazite Figure M25	$(Ce,La,Nd,Th)(PO_4,SiO_4)$
Bastnaesite Figure M22	$(Ce,La)CO_3(F,OH)$
Cerite Figure M23	$(Ca,Mg)_2(Ce)_8\,[Si(O,F)_4]_7 \cdot 3H_2O$

Table 17.3 Some yttrium group minerals

Mineral	Formula
Gadolinite Figure M18	$Be_2FeY_2Si_2O_{10}$
Fergusonite Figure M19	$Y(Nb,Ta)O_4$
Yttrotantalite	$(Y,U,Fe)(Ta,Nb)O_4$
Thalenite Figure M21	$Y_2Si_2O_7$.
Euxenite	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$
Xenotime Figure M20	YPO_4
Samarskite	$(Y,Ce,U,Ca,Fe,Pb,Th)(Nb,Ta,Ti,Sn)_2O_6$

Of these minerals mainly monazite and bastnaesite are mined. In fact monazite is an important yttrium raw material although yttrium is not part of the mineral formula. Monazite contains thorium and because of that is slightly radioactive.

17.3
Many Complex Turns

17.3.1
They did it

Discoverers are briefly presented by name in Table 17.4. More details are given in section 17.4.

Table 17.4 Discoverers and discoveries

Discoverer	Discovery	Year	Note
Carl Axel Arrhenius, Stockholm; Johan Gadolin, Finland (Åbo) and Uppsala	Gadolinite. Yttrium	1787; 1794	The black stone, "ytterbite", gadolinite found in Ytterby
Wilhelm Hisinger, Jöns Jacob Berzelius, Stockholm	Cerite. Cerium	1803	The mineral cerite found in Bastnaes
Carl Gustaf Mosander, Stockholm	Lanthanum Didymium Erbium Terbium	1839 1840 1842 1843	Lanthanum was discovered in cerium, didymium in lantha-num. Erbium and terbium were discovered in yttrium
Per T. Cleve, Uppsala Marc Delafontaine, Geneva Louis Soret, Geneva	Holmium	1878	Spectroscopy was invented about 1850. It was of great benefit in REM discoveries
Jean-Charles Gallisard de Marignac, Geneva	Ytterbium Gadolinium	1878 1880	
Lars Fredrik Nilson, Uppsala	Scandium	1879	Mendelejev's eka-boron
Per T. Cleve, Uppsala	Thulium	1879	
Paul-Émile Lecoq de Boisbaudran, Paris	Samarium Dysprosium	1879 1886	
Carl Auer von Welsbach, Vienna	Praseodymium Neodymium	1885 1885	He separated Mosander's didymium
Eugène-Anatole Demarçay, Paris	Europium	1901	
Georges Urbain, Paris Carl Auer von Welsbach, Vienna Charles James, New Hampshire, USA	Lutetium	1907	

17.3.2
Schedule and naming

It is difficult to construct a satisfactory outline of the many complex turns in the discovery of the RE metals. One element, discovered at a certain point of time, might after further research with improved separation and analysis methods be shown to consist of two or three elements. After a subdivision of the element of this type one of the elements would keep the older name, while new names were given to the other elements. This became almost an unwritten law, followed in all cases but one (see section 17.4.10.1). Reading about the RE discoveries is made easier if done in conjunction with the diagram in Figure 17.3.

From the two minerals gadolinite and cerite, with their main elements yttrium and cerium, knowledge developed like two genealogical trees. Principally, knowledge of the cerium group elements “grew“ on the “cerium plant“, and knowledge of the yttrium group elements grew on the “yttrium plant“.

Separation and purification were exceptionally difficult. Most discoveries were made using time-consuming and labor-intensive methods involving fractional crystallization.

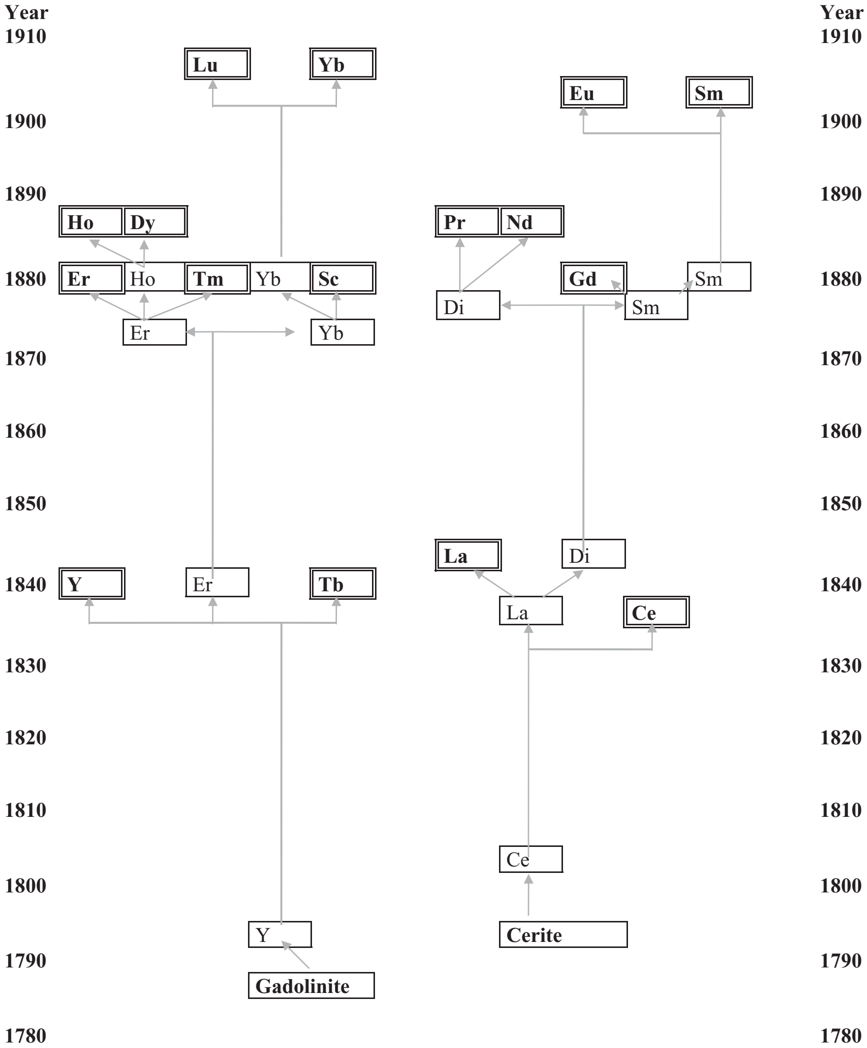
17.4
The Long Story of Discovery

From Figure 17.3 it is clear that the history of discoveries falls into three different periods. The first, about 1800, was the time for the basic discoveries, yttrium and cerium; the second, around 1840, resulted in four new elements, erbium, terbium, lanthanum and didymium. Not until the introduction of the spectroscopy in the middle of the 19th century and the development of improved separation techniques did the discoveries enter the third period, 1870–1910. Yet, the last REM, promethium, was not discovered until 1945. Some biographical information about the actual discoverers is given along with the different discovery descriptions below.

17.4.1
The Discovery of Gadolinite in Ytterby – The Beginning

17.4.1.1 A Quartz and Feldspar Quarry

Ytterby was a quartz and feldspar quarry on the island of Resarö, 3 km north of Vaxholm in the Stockholm archipelago. Quarrying began in the second half of the 18th century. There was nothing special about this deposit. However, the pottery manufacturers in Sweden, who needed these minerals as raw material, valued the quartz and feldspar mined there. Geologically the mine is situated in coarse-grained granite, a *pegmatite formation*. The Ytterby pegmatite was composed mainly of light-gray quartz, grayish-white oligoclase (sodium feldspar), and red microcline (potassium feldspar) with biotite (dark mica). Complex pegmatites are often the last



Symbols:

La Indicates that the metal is discovered but not yet a single element.

La Indicates that the pure element now exists

Figure 17.3 Rare earth metals – two genealogical trees with their roots in the minerals gadolinite and cerite.

magmas to solidify during rock formation and, because of that, contain many rare elements.

This was especially true for the pegmatite in Ytterby. In 1787, Carl Axel Arrhenius, an artillery officer interested in mineralogy, found a black mineral that had obviously been previously overlooked. He gave it the name “ytterbite“, soon changed to *gadolinite* (Figure M18) after the Finnish chemist Johan Gadolin, who made the first chemical analysis of it. It was later said of that mineral that it had played a bigger role in the development of inorganic chemistry than any other mineral.

What elements did gadolinite contain? An exciting history of discovery started about 1790 and did not end until 1945.

The black gadolinite, a silicate containing iron, beryllium and rare earth metals, was not the sole remarkable mineral in Ytterby. Brown *fergusonite* (Figure M19), containing yttrium, niobium and tantalum as well as *yttrotantalite*, the mineral in which the element tantalum was discovered, were also present. At that time – in the 1790s – the elements were of mainly academic interest. Nowadays the minerals and their content are of very great technical importance. Is Ytterby then a mining place for these rare metals? Not at all! The interesting minerals seem to have been concentrated in the superficial layers of the pegmatite and most of the discoveries were made at the beginning of mining. Then quarrying for quartz and feldspar ended and the installations fell into decay. However, students of chemistry at universities throughout the world read with wonder about the striking village outside Stockholm, whose name is given to the elements *yttrium, ytterbium, erbium* and *terbium*. In addition, *gadolinium* is named after the original black Ytterby mineral. As a logical consequence of its unique position in the history of element discoveries, in 1990 the American Society for Metals, ASM, declared Ytterby to be a *Historical Landmark*. Ytterby was the sixth place in Europe to be honored in this way.

17.4.1.2 Carl Axel Arrhenius

Carl Axel Arrhenius, Figure 17.4, made Ytterby familiar to the chemical world. He was born in 1757, became an artillery officer and took an active part in the Swedish war against Russia. As an artilleryman he was interested in technical matters, and was given an assignment to investigate the gunpowder used by the artillery and the army. He thus came in contact with Peter Jacob Hjelm and Bengt Reinhold Geijer in the Laboratorium Chymicum. Presumably he got competent assistance. More important, and of great consequence for the whole history of the discovery of elements, was that the young lieutenant’s interest in chemistry and mineralogy was awakened by contact with the experienced masters. He also gained a fundamental education in the two subjects. To practice he was sent to the Ytterby quarry. He was supposed to find and identify lovely white and red stones. So he did but he also found a black one.

With his interest in minerals, Arrhenius had taken the first step to open the way to an exploration of the rare earth metals. That development gradually absorbed prominent chemists in different parts of the world. But lieutenant Arrhenius could have known nothing of that when he found his black stone in Ytterby.

Without having passed any academic examination in science the lieutenant, interested in chemistry as he was, came to play another important role for Swedish chemistry in the paradigm shift in the latter part of the 18th century. Through a journey to Paris in 1787–1788 he made Lavoisier’s ac-

Figure 17.4 Carl Axel Arrhenius (1757–1824). (Reprinted from *Svenskt Biografiskt Lexikon*, Albert Bonnier, Stockholm.)

quaintance, and on his return to Sweden he became an eager advocate against the phlogiston theory and for the modern chemical theory.

His military career continued and Arrhenius became a lieutenant colonel. His interest in chemistry, however, remained and in 1816 he was made supervisor of all gunpowder manufacture in the country. Almost to the end of his life he attended Berzelius' lectures on chemistry.

17.4.2
The Element Yttrium

17.4.2.1 Discovery and Naming

A sample of Arrhenius's black Ytterby stone was sent to Martin Heinrich Klaproth in Berlin. The quantity was, however, too small for the famous German chemist to analyze. The Finnish chemist Johan Gadolin made the first complete analysis. He reported in 1794 [17.1] the result: "31 parts silica, 19 parts alumina, 12 parts iron oxide and 38 parts of an unknown earth". These 38 parts placed Ytterby on the map of the chemical world.

Ekeberg in Uppsala published the first confirmation of Gadolin's analysis in 1797 (according to P. Pyykko and O. Orama, in ref. [17.9]). His result was "25 parts silica, 41/2 parts aluminum oxide, 18 parts iron oxide, and 471/2 parts of the new oxide". Ekeberg had got a sample, almost free from feldspar, from Arrhenius. Because of that, his values for silica and aluminum oxide were low compared to Gadolin's. That the mineral really contained an oxide of an unseen element also was quickly confirmed by N.-L. Vauqelin and R.-J. Haüy in Paris, and by M. H. Klaproth in Berlin. They changed the mineral name from ytterbite to *gadolinite*. The new oxide was called *yttria* and the corresponding element *yttrium*.

17.4.2.2 Johan Gadolin

Åbo Akademi was founded in 1640 in Finland, then an integral part of Sweden. Even today it is designated Finland's Swedish University. A professorship of chemistry was created in 1761 and the first holder of the chair was *Per Adrian Gadd*. He was a professor to the taste of the authorities, interested mainly in serving the Finnish trade and industry. He lectured on chemistry until 1787. One of his students was *Johan Gadolin*, Figure 17.5. He was to make a pioneering contribution to the history of element discoveries.

Figure 17.5 Johan Gadolin (1760–1852). (Reprinted from R. Tigerstedt, Acta Societatis Scientarium Fennicae, Helsingfors, 1910.)

Gadolin was born in 1760 and, as mentioned, gained his first academic education in chemistry from Per Adrian Gadd. At the age of 19 he moved to Uppsala and became one of Professor Torbern Bergman's students. From 1785 he had professorial positions in Åbo but he cooperated continuously with colleagues in Uppsala and Stockholm.

During his active time in Uppsala and Åbo, Gadolin worked in different branches of chemistry. His investigation of the black mineral from Ytterby and his discovery of the new element yttrium made him well known throughout the world. Gadolin's university education as a chemist occurred just as the old phlogiston theory was being replaced. Originally Gadolin, like his former teacher Bergman, accepted the phlogiston theory, but gradually he changed his mind. In a booklet *"Inledning till Chemien" (Introduction to Chemistry),* edited in Åbo in 1798, he described a chemistry without phlogiston. It was probably the first chemistry textbook in the Swedish language to express the role of oxygen in combustion in a modern way.

17.4.3
Bastnaes' Contributions to REM Development

17.4.3.1 The Heavy Stone From Bastnaes

The Bastnaes field is a region rich in minerals, situated at Riddarhyttan in the province of Westmanland in Central Sweden. Iron and copper ores have been mined there for hundreds of years.

Axel Fredrik Cronstedt, the discoverer of nickel, investigated different minerals in the Bastnaes field. In 1751 he described a heavy stone that he simply called "heavy stone from Bastnaes". This stone worried the Swedish geologists, as they did not know its composition. In 1782 a sample was sent to Carl Wilhelm Scheele for analysis. This celebrated chemist reported that this "tungsten" contained no tungsten, but he could not find any new element in it. After Arrhenius' finding of his black stone and Gadolin's discovery of the element yttrium Hisinger, an ironworks proprietor in Sweden and at the same time a recognized scientist, put a question to himself and to his young colleague Berzelius: Might the elusive heavy stone contain yttrium? If so, it could explain why even Scheele failed to discover the metal, so different is it from other elements. The two colleagues started an investigation and found no yttrium in the "heavy stone", but early in 1803 they discovered another element. They gave it the name *cerium* after the minor planet Ceres, discovered in 1801. The mineral was named *cerite* (Figure M23). The discovery was not only the birth of a new element but also the first important appearance of a new great scientist, Jöns Jacob Berzelius, then 24 years of age.

17.4.3.2 **A New Scientist and a Bitter Quarrel**

The new oxide, *ceria*, was investigated energetically by Berzelius. He found that – unlike yttria – it had two different oxidation states corresponding, in today's nomenclature, to Ce_2O_3 and CeO_2 (oxidation states 3 and 4 respectively). In the lower oxidation state the element gave colorless solutions, in the higher yellowish-red ones. Berzelius saw something special in the new element and found it difficult to place its oxide among the proper earths. Today we know what is really special about cerium – it is the first lanthanide.

Berzelius and Hisinger very soon sent a paper about the discovery for publication in the German Journal *Neues Allgemeines Journal der Chemie*. The editor answered to Berzelius:

(a) We accept your paper for publishing in number 4 this year.
(b) In number 3, which is now being printed, we publish a paper, written by M. H. Klaproth. It also deals with the discovery of a new element in a heavy stone from Bastnaes in Sweden.

Klaproth had named the oxide he had discovered *ockroite* after its yellowish-brown color. Now a big scientific struggle started. The two Swedes would in fact have accepted shared priority with Klaproth, the most distinguished analytical chemist in Europe. The accusations did not come from Berzelius but from Klaproth. The background was this [17.2]:

> After having read the two publications, N.-L. Vauquelin in Paris wrote his own paper in which, for some inscrutable reason, he asserted that the two Swedes had made the cerium discovery, informed Klaproth about it, and also sent a sample of the heavy stone from Bastnaes. Klaproth had then published the investigation in his own name. This was a terrible accusation, which naturally made Klaproth very indignant. That a young unknown *Herr Berzelius,* 24 years of age and without experience, should compete with

> Klaproth for an element discovery was bad enough. An accusation of scientific dishonesty was far beyond the limit of what could be accepted! On July 10th 1805, Berzelius got a furious letter from Klaproth demanding to know whether he really had given the untruthful information to Vauquelin. In the letter, Klaproth informed Berzelius that in 1788 he had obtained a sample of the heavy stone from Bastnaes from the Prussian ambassador at the Swedish court, Count von Lepel who had got it from the Swedish mine-inspector Geijer1). At the turn of the century he had analyzed it, found the new oxide and sent his discovery for publication.
>
> Berzelius answered respectfully and with a humble spirit "... that he, newly entered upon a scientific career, had not had a correspondent in Paris and had not talked or written to anyone about this subject, but had first heard about it from Klaproth's letter". He also declared that both he himself and Hisinger respected Klaproth too much to spread such a falsehood. Berzelius never received a reply.

Nicolas-Louis Vauquelin, however, verified Hisinger's and Berzelius' result, and the name cerium was before long accepted.

17.4.3.3 Bastnaesite From Bastnaes

Cerite was very important for the history of science and the growing knowledge of the rare earth elements. Another mineral discovered in Bastnaes has, however, been of much greater technical importance. In 1838 Wilhelm Hisinger discovered a mineral, a carbonate containing fluorine, that later on appeared to be a rich source of rare earth metals. The mineral was given its name *bastnaesite* (Figure M22) by a French mineralogist in 1841. It has been found in many localities all over the world, in China as well as in Mountain Pass Mine in California.

17.4.4

Ironworks Proprietor and Scientist

> Wilhelm Hisinger's talent and working capacity were obviously sufficient for two great missions in life. He was born in 1766, son of the ironworks proprietor Wilhelm Hising. He himself followed his father in the profession and successfully modernized his own iron industry, Skinnskatteberg in Central Sweden. He was raised to the nobility in 1784, took the name Hisinger and became a man of importance in parliament, banking and the country's finances. He died in 1852.
>
> Hisinger was representative of the Swedish leaders who were active in the iron works at the start of the industrial era. Many were learned men, bold and versatile characters. Times of prosperity gave them economic independence and the possibility for activities beyond direct management.

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1) The description is typical of the situation in Sweden at the end of the 18th century. Torbern Bergman and Carl Wilhelm Scheele were dead. Who could examine new mineral findings? Johan Gadolin had returned to Finland and J. J. Berzelius was only 21 years of age at the turn of the century.

Hisinger was a prominent scientist. He had studied chemistry in Uppsala under Professor Torbern Bergman and for some time he had worked at the Bergskollegium (The Board of Mining and Metallurgy). When he took over the management at Skinnskatteberg from his father, he built a laboratory in the garden of his country house, in which he could work at mineralogy and the chemical analysis of minerals. In winter he often stayed in Stockholm, working in the Laboratorium Chymicum (see section 30.2.4) and co-operating with P. J. Hjelm, manager of the laboratory in the period 1794–1813. At the turn of the century, Hisinger began to experiment with the voltaic pile and, together with J. G. Gahn, he founded a galvanic society. It was in this connection that he became acquainted with Berzelius. He wrote in a letter to Gahn in 1802 (Hisinger was then 36, Berzelius 23) that he had succeeded in acquiring a co-worker: "a young medicus, Berzelius, who has a good knowledge of modern chemistry and particularly good dexterity in galvanic experiments".

The friendship that now began became important for Berzelius from both scientific and economic standpoints. Hisinger owned a property in Stockholm called *The house of the German baker*. There a well-equipped laboratory was placed at Berzelius' disposal, giving him good working conditions. His collaboration with Hisinger, starting in Bastnaes and being completed in the new Stockholm laboratory, resulted in the discovery of cerium, the first lanthanide. Figures 17.6 and 17.7.

Hisinger was one of Sweden's most eminent mineralogists and geologists. He became known for his great work (in 1808) *Mineralogisk geographie öfver Sverige (Mineralogical Geography of Sweden)*. Friedrich Wöhler translated it into German.

In his *Early collections of a chemist* Wöhler gave a charming picture of Hisinger's home: "After a five-day stay at Fahlun we drove to Skinnskatteberg, Hisinger's estate, and we found Berzelius there. The venerable, genial

Figure 17.6 "The house of the German baker" with Berzelius' living space and laboratory. (Reprinted from H. G. Söderbaum, *Jac. Berzelius* Vol. 2, Uppsala, 1929.)

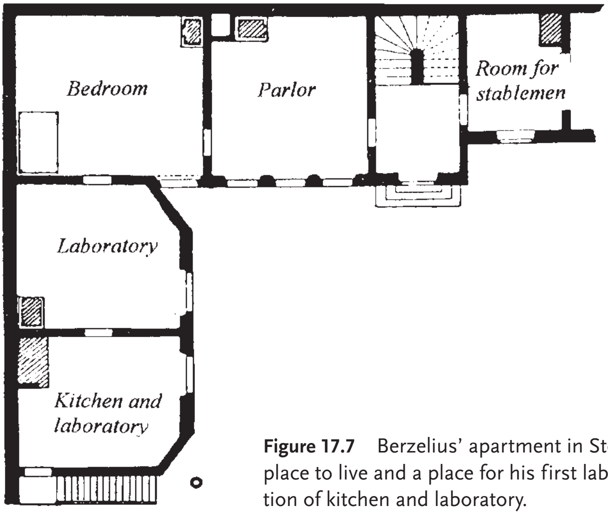

Figure 17.7 Berzelius' apartment in Stockholm 1809–1819, with a place to live and a place for his first laboratory. Notice the combination of kitchen and laboratory.

> Hisinger, so well known through the liberality with which he had supported Berzelius, lived here, a very rich man on a princely estate, surrounded by magnificent forests, gardens, and iron mines. In company with Berzelius and Hisinger we made an excursion to the mines of Riddarhyttan and Bastnaes. At the mouth of this mine, which at that time had already been abandoned, we collected in the scorching sun hundreds of specimens of cerite."
>
> (Cited from Mary Weeks, *Discovery of the Elements*.)

In this simple house and laboratory Berzelius lived and worked in the 1810s when he introduced the new, internationally accepted element designations, Fe, O, S, and so on and here he started the accurate determinations of atomic weights. These were a prerequisite for the developing periodic system of the elements.

17.4.5
Jöns Jacob Berzelius – Chemist and Mineralogist

17.4.5.1 A Hard Childhood – A Happy Youth

The important mineral discovery at Ytterby occurred in 1787. Shortly before this, two of Sweden's most eminent chemists had passed away: Torbern Bergman in 1784 and Carl Wilhelm Scheele in 1786. At the time of the discovery in Ytterby, Jöns Jacob Berzelius was a fatherless boy, living at Väversunda in the countryside of Central Sweden. For the small boy, 8 years old, the big occurrence in 1787 was not the finding of a black stone in Ytterby. Instead it was a devastatingly black sorrow: his mother died. Jöns Jacob now was parentless and he had a hard childhood and adolescence. An uncle helped him to a place in the high school in Linköping. There he had an excellent teacher, C. F. Hornstedt, who taught young Jacob to identify the species of plants and insects, and this started his interest in natural science.

Periodically, however, he had to break off his schooling and work for a living. But in 1796 he was able to move to Uppsala although even here he had to combine study at the university with practical work. Yet he found that the practical work could be valuable and even stimulating to his academic career. During a period of work in a pharmacy he learned glass blowing from an Italian. After that he could make himself equipment for the laboratory such as thermometers and flasks. In 1800 he worked as a doctor without salary at the Medevi mineral spring and took the opportunity to make many water analyses. The results became the basis for his Master of Science dissertation.

Berzelius did not find the chemistry teaching in Uppsala stimulating. The phlogiston theory was still dominant and the stream of new ideas from France, which the young students were interested in, were rejected. For one teacher of chemistry, however, the assistant Anders Gustaf Ekeberg, he felt great respect. In 1801 Berzelius graduated as Bachelor of Medicine and the year after as Licentiate. He was then appointed teacher at the Surgical School of Stockholm, today the Karolinska Institute. In 1807, at the age of 28, he was appointed professor of medicine and pharmacology. The orphan boy had at last made good. He now began the work in inorganic and organic chemistry that took Sweden back into a leading position in the chemical world, similar to the situation in the 18th century.

17.4.5.2 Berzelius and Mineralogy

Berzelius had not been interested in mineralogy during his time of study. Contacts with Wilhelm Hisinger and Johan Gottlieb Gahn in Falun awakened his interest. It is astonishing to see how rapidly Berzelius learned mineralogy, which was almost new to him, and how absorbed he became in the subject. A powerful contribution was, of course, that in 1803, at the age of 24, he discovered the mineral cerite and the element cerium. In fact he also soon introduced a new, scientific mineralogical system, based on the laws of chemical proportions and electrochemical theories.

During the 1810s Berzelius often went to Gahn in Falun in the summer. He experienced great pleasure on these occasions. A great advantage of these “summer excursions“ was that he got a valuable training in identifying minerals and a knowledge of how to use the blowpipe for mineral analysis. He had also the opportunity to collect many specimens for further examination in his laboratory in Stockholm. All these contacts and activities contributed to Berzelius’ own element discoveries: cerium (1803), selenium (1817), silicon (1824) and thorium (1829).

17.4.5.3 A Model Laboratory

In the early nineteenth century the laboratory had many practical problems, such as ventilation, the heating of furnaces and the supply of water. Modern scientists and their assistants do not need to worry about such things. In addition it was a big problem to procure pure chemicals for analytical work and to build equipment for weighing and for determination of gas volumes and pressures. Berzelius seems to have been a pioneer in creating laboratory techniques and a laboratory environment.

A Scottish agricultural chemist, J. F. W. Johnston, visited Berzelius in 1829. Berzelius by then had a new laboratory at his disposal, in a house owned by the Academy of Sciences, whose secretary he had been since 1818. The laboratory impressed the Scottish visitor, who wrote in his traveling report [17.3]:

> A visitor will recognize from various utensils in the first room that it is part of a chemical laboratory. He needs, however, not fear those emanations, which, in most laboratories, affect so painfully the organs of respiration. Here a system of ventilation, planned with the greatest care[2], makes them disappear immediately. After having glanced at the blowpipe, the large lamp, and all the objects near it, he will come to the sandbath. He will look in vain for furnaces of brick or stone. They are useless in the delicate operations of analysis. In the second room the first object one notices is a glass case standing on a table. It is the balance. How much light this fragile, simple instrument has shed on the natural sciences! Not far from there are the little lead weights, which are the exact counterpoises, or tares, of all the crucibles and small platinum utensils in the laboratory, so that each of them can be balanced in an instant. Berzelius is always busy. He works twelve to fourteen hours every day. But in spite of all he has done for experimental chemistry, one must not think that he works without respite in his laboratory. Often, when he is composing, he stops for months at a time.
>
> Everything in Berzelius' laboratory is conspicuously clean and in admirable order; everything is in its place, ready for immediate use.... He also uses many ingenious machines, which facilitate or shorten his operations, the invention of which he attributes to assessor Gahn. But many of them he has made by himself.

This laboratory, described with such great insight by Johnston, certainly influenced the development of laboratories and examination techniques in other parts of Europe. The fact that the famous German chemist Friedrich Wöhler frequently worked as a visiting scientist in the laboratory also contributed to its influence. Carl Gustaf Mosander's substantial work with rare earths around 1840 was also performed here. This led to the discovery of the elements lanthanum, didymium, erbium and terbium.

17.4.6
To Separate the Almost Inseparable

17.4.6.1 Dare I Say that Berzelius is Wrong?

It was Carl Gustaf Mosander (Figure 17.8), from 1836 Berzelius' successor as professor of chemistry, who started the great work of separating the almost inseparable. As Berzelius' student from 1820 he soon came into his service. He prepared cerium sulfide and let it react with chlorine. Anhydrous cerium chloride $CeCl_3$, was formed, from which he prepared metallic cerium by reduction with potassium metal. This was in about 1825. With all his work with different cerium compounds he began to

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[2] The chapter "The Laboratory in the 19th Century" in Jan Trofast, *Excellensen och Berzelius*, Atlantis, Stockholm, 1988, describes how ventilation hoods are placed over furnaces and sandbaths and connected to the upper part of the stove.

question whether cerium really was one single metal. Was there something else hidden in it? In 1838 he discovered the concealed stranger. With great intuition he treated cerium oxide with chlorine water in such slightly acid conditions that the oxide ought not to be attacked. But in fact this treatment extracted the chloride of a different metal. A similar result was obtained after treatment with dilute nitric acid. When he examined these chloride and nitrate solutions he observed that the new metal could not be oxidized or reduced. Unlike cerium it only had a single oxidation number. Mosander did not make a great fuss about his discovery. At the beginning he did not even tell Berzelius, although they worked in the same laboratory and met almost every day. Perhaps it was a delicate subject to point out that what Berzelius and Hisinger had discovered was not a pure element but a mixture of two, and that the great chemist had not been aware of that for 35 years after the discovery of cerium. At the end of 1838, however, Berzelius was informed and he confirmed that Mosander's discovery was correct. With his usual generosity towards students and colleagues, he made publicized Mosander's discovery in the chemical world. But why the name lanthanum? It was Berzelius' proposal, accepted by Mosander. For a third of a century the element had hidden from Berzelius. The Greek word *lanthanein*, "to be hidden", was a suitable name.

Figure 17.8 Carl Gustaf Mosander (1797–1858). (Reprinted from N. Sjöberg, *Svenska Läkare och Apotekare (Swedish Doctors and Pharmacists)*. Svenska Läkaresällskapet, Vol. III, Stockholm, 1910.)

17.4.6.2 **Lanthanum Has a Twin Sister!**

Mosander continued to study the properties of lanthanum and determined its atomic weight. During this work he made some observations that confused him. The oxide was brick-red but the color altered from experiment to experiment. In 1840 Mosander made some very important investigations of the amethyst-colored solution of lanthanum sulfate. He discovered that the sulfate was more soluble in cold water than in warm. He prepared a concentrated solution at 9°C. When he heated this solution to 40°C, pale amethyst-colored crystals precipitated. He dissolved these in water at 9°C, again heated the solution to 40°C, separated the precipitate and dissolved it in a fresh amount of water at 9°C. He repeated the procedure 15 times and at the end of this long experiment the precipitated crystals were colorless. The oxide prepared from this sulfate was not brick-red but white. Mosander concluded that this was pure lanthanum oxide. From the amethyst-colored solution red crystals could be obtained and from these a new oxide could be prepared, reddish-brown to black. Mosander named the metal in this oxide *didymium,* "the twin", because of its very close relationship to lanthanum. This discovery was at first kept secret, but became known through publications in 1842–43 [17.5] and [17.6]. The name didymium was severely criticized by Wöhler and did not last long, although it did not disappear because of Wöhler's criticism but because Auer von Welsbach in Austria was able to split the element in two, giving new names to both the twins (see section 17.4.10).

17.4.6.3 More Hidden Elements Found

After the discovery of didymium, many scientists thought that the new element might also be found in yttrium isolated from the mineral gadolinite. In the autumn of 1842, Mosander was convinced that yttrium in fact was a mixture and not a pure element. But he did not find didymium in it. Its oxide was found to contain white yttrium oxide (giving colorless salts) and also a yellow oxide, hitherto unknown (giving amethyst-colored salts). At first Mosander intended to give the new element the name *odinium* after the god Woden in Scandinavian mythology, but before this was published continued experiments showed that "yttrium oxide" in fact contained three oxides. They could be separated by fractional crystallization of their oxalates. The most basic gave a white oxide and colorless solutions. It was allowed to keep the name *yttrium*. The oxide of the least basic element was yellow. It was given the name *erbium* after Ytterby. An element of intermediate basicity was responsible for the amethyst coloring of solutions. It was given the name *terbium*, also after Ytterby.

17.4.6.4 "The Breadth of his Activities Detrimentally Influences the Depth"

Carl Gustaf Mosander was born in Kalmar in southern Sweden in 1797. At the age of 23, after an education in pharmacy, he applied for admission to the medical school in Stockholm, at which Berzelius was the chemistry teacher. It was a decisive step for his scientific development. Later, he was employed by his teacher and, under his guidance, made various chemical investigations. However, alongside this apparently straightforward development, Mosander's biography gives a startling impression. The section title is in fact a comment that was made about him. He worked at different times as an assistant at the mineralogical department of the Museum of Natural History, as a surgeon in the navy, as a teacher of pharmaceutics and as the owner of a spa in Stockholm. Such a division of energy must be a hindrance to fundamental achievements and does not seem suitable as a preparation for a place in the history of science. Nevertheless, Mosander is firmly established in the history of element discoveries, in spite of his many occupations. But his main occupation was working for and together with Berzelius. The two were very different. Berzelius was interested in theories, always ready for talk and discussion and had an open and generous nature. When Mosander developed an interest in a subject he was very private and not at all communicative. This was perhaps the reason for his nickname "Pater Moses", used by both Berzelius, his senior by 18 years, and by Wöhler, who was the same age as Mosander. Yet Wöhler and Mosander were good friends and took long walks together in the area around Stockholm when his German colleague visited Berzelius' laboratory. Mosander also helped Wöhler with a mineral collection to bring home. In the autumn of 1824, Mosander withdrew to prepare to take his doctorate. Berzelius informed Wöhler in a letter, saying that he now missed his company in the laboratory. Wöhler answered in the following summer: "I suppose that Moses now is Herr Doctor Pater Moses. Congratulations."

Berzelius had a great knack of creating a good atmosphere in the circle of students and colleagues around him. Mosander's nickname was surely an expression of kindness and sympathy. However, we may suspect a degree of underestimation. In 1825, neither Berzelius nor Wöhler expected that 15 years later Mosander would astonish the world by discovering four new elements.

In 1836, at the age of 57, Berzelius retired from his professorship and was succeeded by Carl Gustaf Mosander. Berzelius, however, continued with active work almost to his death in 1848.

The great discoveries in the REM field around 1840 are all the result of Mosander's work. Because of his achievement the number of members of the REM family increased from two (yttrium and cerium) to six (yttrium, cerium, lanthanum, didymium, terbium and erbium).

17.4.7
Mosander's Discoveries Checked. Were They Correct?

17.4.7.1 Confirmation or Not?

The 35 years after 1840 were uneventful regarding the discovery of rare earth elements. Berzelius had died in 1848, Mosander in 1858. Inorganic chemistry was under pressure from the growing organic chemistry. The introduction of a new analytical technique, spectroscopy, however, aroused new interest and opened new approaches. The gradual separation of one element from another could be followed. This was very valuable in the many and time-consuming fractional crystallizations.

There seemed to be no doubt about the existence of lanthanum and didymium. Around 1850, *Marignac* in Switzerland determined their atomic weights and carefully investigated the chemistry of the two elements.

Regarding erbium and terbium, however, learned disputes arose, a struggle that is known as the *terbium debate*. *Delafontaine*, also in Switzerland, made a very careful examination in the mid-1860s. His experiments supported the existence of erbium as a separate element but the results for terbium were ambiguous. In Germany, Robert Bunsen and his assistant Johan Bahr repeated Mosander's original experiment by examining gadolinite. After dissolving the mineral in hydrochloric acid and removing the silica, they precipitated the metals in the cerium group with oxalic acid. The precipitate was dissolved in nitric acid and the precipitation was repeated. The process was repeated many times until the solution ought to have contained only elements from the yttrium group: yttrium, erbium and terbium. Spectral analysis indicated erbium and yttrium but not terbium. On the contrary, the presence of cerium, lanthanum and didymium was indicated in spite of the exhaustive separation work. Spectral analysis is a sensitive method!

Bunsen's investigation seemed to show that terbium does not exist. But the argument is dubious. Spectroscopy was in its infancy and the method was very empirical. The wavelengths in the spectrum of an element X were recorded by investigating a sample of pure X. To find out if an unknown sample contained element X, the sample's spectrum was examined for lines from element X. If Bunsen had never seen the element terbium he could know nothing about its spectrum. Bunsen and Bahr's investigations had little value as evidence in the terbium debate.

Although Delafontaine did not succeed in confirming the existence of terbium he did continue to support Mosander's terbium discovery. However, he muddled up the terminology. In fact he discovered an element in the mineral samarskite, an element that he asserted to be identical with terbium. He named it *mosandrium*. Now Marignac protested: Let the element keep the name terbium! And so it remained. Marignac also made a check analysis of gadolinite and in 1878 confirmed terbium's existence as a real element. The English spectroscopist *H. E. Roscoe* gave a final ratification in 1882, when he reported 194 specific lines in the spectrum of terbium. Mosander's discoveries 40 years earlier had finally been accepted. Erbium, terbium, lanthanum and didymium existed. But were they really elemental or were they composed of two or more, still unknown, rare earth metals? It was necessary to go further.

17.4.7.2 Jean-Charles Marignac

Jean-Charles de Marignac (1817–1894) belonged to a Huguenot family that had escaped from Languedoc in France at the beginning of the 18th century and settled in Switzerland. Jean-Charles was born in Geneva. At the age of 16 he became a student at the École Polytechnique in Paris and finished his education by study tours to Sweden and Germany. After working in the porcelain factory in Sèvres he returned to Switzerland and became professor at the university in his native town. He taught and carried on research in both chemistry and mineralogy.

He made important contributions to the solution of the controversy over niobium and tantalum that will be described in Chapters 22 and 23. He also co-operated with Berzelius over atomic weight determinations and got the highest endorsement of the Swedish master for his accurate scientific work. His research activities in the field of rare earth elements led to the discovery of ytterbium in 1878 and gadolinium in 1880.

17.4.7.3 Marc Delafontaine and Louis Soret

Two other Swiss, also from Geneva, had considerable achievements in the discovery of rare earth elements. They were *Louis Soret* (1827–1890) and *Marc Delafontaine* (1837–1911). The former was professor of physics at the university; the latter was a chemist who had studied under Marignac and for some time taught chemistry at the university in Geneva. Having worked with the terbium problem in the 1860s he moved to Chicago in 1870 and worked there teaching and carrying out research in the field of spectroscopy. As a specialist in chemical analysis he also worked for the Chicago police. In 1878, back in Switzerland, he investigated erbium oxide in cooperation with Soret and found a new element, "erbium-X" Later this appeared to be identical with holmium, discovered by *Per. T. Cleve*.

17.4.8
A Research Leap in 1880 – Bold New Goals

17.4.8.1 Many New Discoveries

To avoid too many details of the complicated discovery story, Table 17.5 summarizes the position in 1880, listing the elements, homogeneous and mixed, that were then known (see also Figure 17.3).

Table 17.5 The situation in 1875

Real elements		**Mixtures of elements**	
The yttrium group	**The cerium group**	**The yttrium group**	**The cerium group**
Yttrium Terbium	Cerium Lanthanum	Erbium	Didymium

Marignac investigated erbium precipitates and found that they were not homogeneous. Two elements were present. One formed red salts with a characteristic absorption spectrum, while compounds of the other element were colorless. The element with the red color kept the name erbium, the other he called ytterbium. The discovery was made in 1878 and separation was possible by addition of hyposulfurous acid to chloride solutions. The erbium precipitated but not the ytterbium. The two elements erbium and ytterbium also appeared to be mixed, and research had to continue.

Cleve in Sweden concentrated on the erbium that remained after the separation of ytterbium. He carried out extensive separation work in 1878–9 and obtained three fractions. Using spectroscopy he found that one was erbium but the other two contained new elements. He called these *thulium*, after *Thulia*, the old Roman name of the uttermost North, and *holmium*, after *Holmia*, the Latin name of Stockholm. As already mentioned, Delafontaine and Soret had in fact found lines of a foreign element during the spectral analysis of an erbium sample they had obtained from Marignac. This element, erbium-X or element-X, appeared to be identical with holmium. In tables of discoverers, Delafontaine and Soret are mentioned alongside Cleve.

Boisbaudran in France made an extensive investigation of the chemistry of holmium. He dissolved gadolinite and carried out more than 50 precipitations. The fractions were examined spectroscopically. Then he found that yet another element was present in Cleve's holmium. He isolated this the new one in 1886. The goal had been difficult to reach, and the discoverer decided that the Greek word *dysprositos* (difficult to arrive at) would be a suitable designation. The element's name became *dysprosium*.

In 1878 Delafontaine made an important observation. He isolated didymium both from cerite and from the mineral samarskite[3]. Absorption spectra obtained during examination of the two didymium samples were different. To Delafontaine this was an indication that didymium was not a homogenous element. This interested Boisbaudran in France. Unlike Delafontaine he used emission and not absorption spectroscopy. He found lines showing the presence of a previously unknown element. In 1879 he announced the discovery with the information that its name was *samarium* after the mineral.

Marignac in 1880 also examined the mineral samarskite. Fractional precipitation using potassium sulfate and oxalate gave two different elements. He thought that both were new. Soret analyzed both fractions spectroscopically. He observed that one element was samarium but the other was previously unknown. In 1886 Marignac named it *gadolinium* after the mineral gadolinite.

Eugène-Anatole Demarçay in Paris just before the end of the 19th century carried out a series of fractional crystallization experiments, using double nitrates of magnesium and samarium. During these experiments *europium* was discovered.

17.4.8.2 Per Theodor Cleve – The Versatile Professor of Chemistry

Per T. Cleve (1840–1905), Figure 17.9, was examined on his doctoral thesis in chemistry at the University of Uppsala in 1863. In 1874 he became professor there. Cleve resumed the Swedish research about rare earth elements that

Figure 17.9 Per T. Cleve (1840–1905). (Reprinted from the 1903 yearbook of the Swedish Academy of Sciences.

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[3] This mineral, with the complicated formula (Y, Ce, U, Ca, Fe, Pb, Th) (Nb, Ta, Ti, Sn)$_2$O$_6$, was discovered by G. Rose in the USA in 1839 but got its name from V. Samarsky, a Russian colonel and mining engineer, who had found it in the 1860s in the Ural Mountains. In the USA the mineral was rediscovered in 1878 and attracted much interest as a potential source of new elements.

had been so successfully started by Gadolin, Berzelius and Mosander during the first half of the 19th century.

Cleve is known as the discoverer of the rare elements *holmium* and *thulium*. He is also mentioned, alongside William Ramsay, as the discoverer of *helium*. He wrote chemistry textbooks that attracted much attention.

Cleve's deep knowledge of chemistry and his broad scientific interests guided him, at the end of his active life, into fields quite other than inorganic chemistry. He carried out important research on freshwater algae and described many species of them. He studied plankton organisms and developed methods for investigating water circulation in the sea.

17.4.8.3 Paul Lecoq de Boisbaudran

Lecoq de Boisbaudran (1838–1912) was the very first to confirm the Mendelejev system when in 1875 he identified eka-aluminum and named it gallium, from *Gallia*, the Roman name for his native country, France. He was born in the Cognac district into a family descended from an earlier Protestant upper class. When Paul grew up, his family had their own cognac firm, in which his father and brothers were distillers. From his mother, a well-educated woman, Paul learned foreign languages and history. This made it possible for him to apply for admission into the École Polytechnique in Paris. When accepted there he chose to study his favorite subjects, physics and chemistry. All his family supported him, even later, in his scientific work. An uncle provided capital for a small private laboratory. In this he discovered the element gallium. Lecoq also discovered the rare earth metals samarium and dysprosium.

17.4.8.4 Eugène-Anatole Demarçay

The man, who discovered the rare earth element europium was E. A. Demarçay (1852–1903). He studied chemistry and geology at the École Polytechnique in Paris. Perhaps his interest in rare earth elements was awakened when he also studied under and cooperated with Lecoq de Boisbaudran.

In his career, before the discovery of europium in 1901, he had developed spectroscopy in order to make it more effective for the identification of RE metals. He used a special induction coil, which generated a very high spark temperature. The material of the electrodes was especially pure platinum. Thus all foreign spectral lines except those of platinum were eliminated. With this spectroscope Demarçay made a special contribution to science. Pierre Curie had brought to him a sample of barium, in which lines of radium could be observed for the first time (see Chapter 52 The Radioactive Elements). After the discovery of europium Demarçay had only a few years to live. He died in 1903. In ref. [17.19] James and Virginia Marshall have described the life of Demarçay and his discovery of europium.

17.4.9
Scandium – eka-Boron

17.4.9.1 A Missing Element – With a Detailed Description

Lars Fredrik Nilson was professor of chemistry in Uppsala and cooperated with Per. T. Cleve over rare earth metals. In 1879 he attempted to verify Marignac's ytterbium and isolated erbium from gadolinite. He used the method described by Marignac and verified the existence of ytterbium within two months.

In 1840, the mineralogist *Theodor Scheere*, educated at the Bergakademie Freiberg and active in Christiania (Oslo), obtained an unknown mineral from Arendal in southern Norway. When it was analyzed he found oxides of tantalum, titanium, yttrium, uranium, cerium and lanthanum. It is today described by the complicated formula $(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$ and given the mineral name *euxenite*. It is always mingled with other REMs besides yttrium and cerium. Scheere had found lanthanum. Could the Institution of Chemistry at the University of Uppsala investigate and perhaps find known or unknown rare earth elements in it? In 1879, a sample of the mineral arrived with Lars Fredrik Nilson. One of his aims was to isolate ytterbium oxide from this source. After using similar separation methods to those that gave ytterbium from erbium, he also isolated a quantity of ytterbium from euxenite. On adding oxalic acid to a solution of ytterbium he obtained a precipitate. After heating this precipitate he found to his amazement that he had a previously unknown oxide in his crucible. The atomic weight of the new metal was so startlingly low compared to ytterbium that a mistake was impossible. Nilson proposed the name *scandium*, as the new element had been found in Scandinavian rocks.

Having obtained 10 kg of euxenite from Norway, Nilson could prepare oxides of both ytterbium and scandium in quantities large enough for atomic weight determinations. His values were 173 for ytterbium and 44 for scandium. Modern atomic weights are 173.04 and 44.96 respectively.

The oxide of scandium was white and its solutions were colorless. In the spectroscope around 30 distinct lines were visible, easily separated from the lines of ytterbium and other metals.

According to Szabadvary and Evans, pp 55–66 in ref. [17.9] the importance of Nilson's discovery of scandium surpassed an "ordinary" element discovery, as it verified the occurrence of the element to which Mendelejev had given the name eka-boron.

When, around 1870, the astute Mendelejev arranged the elements known at that time according to their atomic weights his notes could have looked like Table 17.6. In modern chemistry this became the upper left-hand corner of the periodic table. The atomic weights are put in brackets. There is an obvious empty place between calcium and titanium, where Mendelejev's eka-boron is situated. Its atomic weight ought to be 44–45. It was this missing element that Nilson had discovered.

Table 17.6 Mendelejev's notes about a missing element

H							
	(1)						
Li		Be		B		C	
(7)		(9)		(11)		(12)	
	Na		Mg		Al		Si
	(23)		(24)		(27)		(28)
K		Ca		?		Ti	
(39)		(40)		(?)		(48)	

In Table 17.7 Mendelejev's predictions for eka-boron are compared with Nilson's and Cleve's findings after the discovery of scandium.

Table 17.7 Comparison between Mendelejev's forecast for eka-boron and results obtained for scandium by Nilson and Cleve

Property	Eka-boron, (EB), according to forecast by Mendelejev	Scandium, Sc, according to examinations by Nilson and Cleve
Atomic weight	44	44
Oxides, Oxide characteristics	An oxide $(EB)_2O_3$, more basic than Al_2O_3 but less basic than Y_2O_3 and MgO. The oxide density 3.5 g/cm^3. The oxide will be infusible. After heating to high temperature it will be difficult to dissolve in acids.	One single oxide Sc_2O_3 , more basic than Al_2O_3, less basic than Y_2O_3 and MgO. The density of the oxide is 3.86 g/cm^3. The ignited oxide dissolves only with difficulty in acids.
Salts	Crystallizes with difficulty. The salts are colorless. On addition of potassium hydroxide gelatinous precipitates are formed. In solution, containing sulfuric acid and alkali sulfate, no alum is formed. The anhydrous chloride is decomposed by water evolving hydrogen chloride gas.	Sc-sulfate crystallizes only with difficulty. On addition of potassium hydroxide to scandium solutions gelatinous precipitates are formed. The double salt with alkali is not an alum. Crystals of scandium chloride are decomposed by heating giving HCl gas

Details taken from D. Mendelejev, Liebigs Ann. Chem. Suppl. Bd. 8 1872, 133–229; L.F. Nilson, Ber. Deutsche Chem. Ges. 1880, 13, 1439–1450; P. Cleve, Compt. Rend. 1879, 89, 419–422. (Cited from Gmelin's Handbuch.)

17.4.9.2 **Lars Fredrik Nilson – Scandium and Agricultural Chemistry**

Lars Fredrik Nilson (Figure 17.10) was born in 1840. His parents were originally farmers in Östergötland, southern Sweden. Later, when Lars Fredrik was about 15 they moved to the island of Gotland in the Baltic Sea. At 19 he began to study chemistry and other scientific subjects at the university in Uppsala. The chemical laboratory, in which Lars Fredrik was to work with such great success, was quite new when he embarked on his academic career (Figure 17.11).

In 1866 he became a doctor of chemistry and associate professor. Nilson was a practical chemist and a clever experimentalist. He could blow glass and made himself much of the equipment he needed for his research. In 1874 he was appointed professor of general chemistry and agricultural chemistry. During the first part of his time as professor he had important achievements regarding different compounds within inorganic chemistry. Together with Otto Pettersson he carried out experiments with the gemstone emerald, which attracted much attention. They fused emeralds with potassium car-

Figure 17.10 Lars Fredrik Nilson 1840–1899.

Figure 17.11 The new institution for chemistry in Uppsala 1850. (Reprinted from Olof Beckman, *Ångström, Father and Son*, Acta Universitatis Upsaliensis. Series C60, 1997.)

bonate and prepared beryllium oxide. In a steel bomb they reduced the oxide with metallic potassium.

Nilson is, however, best known for the discovery of the element scandium.

One particular research activity was a cooperation with Swedish metallurgists regarding high-phosphorus slag, obtained in the Thomas process for steel production. Nilson showed experimentally that the slag is very suitable as fertilizer for soils lacking phosphorus.

At the end of his life Alfred Nobel had made his big bequest for literature and science. Lars Fredrik Nilson became engaged in discussing and planning how it should be used, for prizes and for the Nobel Institutes for research.

17.4.10
Splitting of the Twin

17.4.10.1 The Element Didymium is Two!

Auer von Welsbach in Austria developed a new separation method. If a mixture of RE oxides is attacked by nitric acid the most basic oxides dissolve, while the less basic will be enriched in the insoluble residue. By using this method he was able, in 1884, to separate lanthanum (the more basic) from didymium. He continued to apply the same method to the didymium fraction and carried out more than 100 fractional crystallizations, each taking two days. In this way didymium was separated into two main fractions. In 1885, spectroscopic studies confirmed that two different elements were present. Auer called the green-colored one *praseodymium*, “the green twin“, while the other got the name *neodymium*, “the new twin“. This naming has been accepted, although it involved a deviation from the earlier rule that when a supposedly pure RE metal is divided in two, one of the elements shall keep the older name, while the other is given a new name by the discoverer.

Mosander’s didymium was banished to a backyard of chemistry, which depreciates his enormous contribution to element discovery. Instead Auer is credited with both the twin elements associated with his name, as shown in Table 17.8

Table 17.8 Accepted names for the three first lanthanides

Element	58 Ce Cerium	59 Pr Praseodymium	60 Nd Neodymium
Discoverer	Berzelius/Hisinger Klaproth	Auer von Welsbach	Auer von Welsbach

Mosander’s priority to didymium has never been questioned, not even by Auer von Welsbach, but it is no longer among the elements. The background described would justify a change as outlined in Table 17.9. The naming in this table agrees with the principle once formulated by Berzelius and Mosander when lanthanum was discovered.

Table 17.9 The names the elements ought to bear

Element	58 Ce Cerium	59 Di Didymium	60 Nd Neodymium
Discoverer	Berzelius/Hisinger Klaproth	Mosander	Auer von Welsbach

The names praseodymium and neodymium are however so established that it is certainly impossible to make a motivated change.

17.4.10.2 Auer von Welsbach

Auer was born in Vienna in 1858 and died in 1929. He studied chemistry in the University of Vienna and continued in Heidelberg for two or three years in the early 1880s. While studying inorganic chemistry, he became especially interested in the rare earth metals and was encouraged by Robert Bunsen to choose this field of activity. Even if his time in Heidelberg was short, Auer kept close contact right up to Bunsen's death in 1899.

Auer had two main interests. One was science, characterized by discoveries of rare elements; the other was industrial management. Auer headed enterprises founded on his own inventions. The motto he had formulated for his activity – *Plus lucis* (more light) – he realized literally by introducing the incandescent mantle. He had learned from Bunsen that the light of a gas burner could be enhanced by having metal oxides in contact with the flame. In Auer's invention, announced in 1886, a cotton fabric was steeped in a solution of rare earth nitrates. After burning, a net-like structure of oxides remained, which, when put over the burner flame, markedly increased the emission of white light. Examination of different oxides showed that a mixture of lanthanum oxide and zirconium oxide gave the best result. He manufactured lanthanum nitrate by fractional crystallization and sent the Zr–La nitrate solution, without revealing its composition, to the licensees who produced the mantles for sale. They rapidly became successful, but problems followed. The mantles did not last long enough and were too expensive, a situation that was aggravated by growing competition from electric light. Another quality problem was that the light was too green.

Auer needed other and cheaper sources of raw material and found them in monazite sand, containing thorium and rare earth elements, from the United States and Brazil. Auer isolated thorium and made mantles of its oxide. He found, however, that impure thorium oxide was better than pure. By energetic and systematic work he found that the optimal condition was thorium oxide mixed with 1% cerium oxide. And now he could go out to capture the market. The new dazzling light was introduced in the fall darkness outside the Opern Cafe in Vienna on 4th November 1891. The new oxide mixture became a worldwide success. Almost 100 000 Auer mantles were sold within nine months. The aura of mysticism that had been associated with the rare earth elements increased rather than disappeared, although Auer had found and demonstrated the first industrial application for the metals. Many cities introduced public lightning with Auer lamps and the railway companies used the light to a large extent, mainly, however, indoors in railroad cars.

To people used to candles and paraffin lamps, the long-lasting and odourless light of the incandescent mantle seemed like a miracle. The carbon filament lamp, invented by Edison in 1879, was no serious threat to Auer's light, as the new lamp was very expensive to use. In fact Auer himself started to develop Edison's idea, and in 1893 he was granted a patent for the osmium filament lamp.

About Auer von Welsbach it must be said that he – as a scientist, inventor and industrialist – improved the living conditions for people of his time. By his achievement with the metal filament lamp he also exerted a great influence on the welfare of following generations.

17.4.11
Lutetium and Ytterbium

17.4.11.1 Controversies With a Streak of Political Antagonism

The element scandium had been discovered in ytterbium. That element was, however, not yet emptied of its hidden content. The last efforts to create clarity lead to a bitter struggle.

Around 1900, Auer von Welsbach attempted to solve the ytterbium mystery. He dissolved 500 kg yttrium oxide, obtained from monazite sand. In a series of experiments he added ammonium oxalate and obtained precipitates of double (RE,NH_4) oxalates. According to the excess of added oxalate the solubility of the different double oxalates varied in a systematic way. With this method he could separate erbium and thulium from ytterbium. On further fractionation he observed a gradual change in the emission spectra of ytterbium in the residues. At last he got a fairly constant spectrum, different from that of the original incompletely separated ytterbium. Auer asserted that he had split Marignac's ytterbium into two new elements. He reported this conclusion to the Vienna Academy in March 1905. In a more complete report on 19th December 1907 he attached information about observed wavelengths as proof of the existence of two elements in ytterbium. He admitted that he had not been able to isolate the two but nevertheless he proposed two new names: Marignac's ytterbium he called *cassiopeium* Cp, the new element *aldebaranium* Ad.

Intensive work with ytterbium was going on in Paris at the same time. *Georges Urbain* reported to the Paris Academy of Science on 4th November 1907 (44 days before Auer's second report to the Vienna Academy) that he had performed a total of 800 fractionations of ytterbium nitrates, prepared from the mineral xenotime. Now he announced that he had divided ytterbium into two elements, for which he proposed the names *neo-ytterbium* Ny and *lutecium* Lu. The former was Marignac's element, now purified, the latter named after an old name for Paris, *Lutetia Parisorum*.

A bitter struggle arose between Auer and Urbain, a struggle to which the growing political antagonism between Austria-Hungary and France formed a background, obstructing compromises.

The international committee for atomic weights decided in 1909 to give Urbain the priority, but changed the name neoytterbium to ytterbium and lutecium to *lutetium*. The committee thus accepted the principle of Berzelius and Mosander regarding naming. It is satisfactory that Auer's cassiopeium did not gain a hearing. Otherwise Marignac's ytterbium would have been deported to the backyard in chemical history, where Mosander's didymium is waiting to obtain redress. Helge Kragh has made a thorough exposition of the priority situation in connection with the discovery of lutetium in ref. [17.9].

At the same time as Auer and Urbain were fractionating and separating in their respective countries, intensive work in the same field was going on in North America. At the university in New Hampshire, USA, *Charles James* used a method he himself had developed. It was a fractional crystallization of (RE,Mg) nitrates. In the summer of 1907 he had separated considerable amounts of ytterbium's companion. Of the three scientists, he was certainly the one who had made most progress. When he was just about to announce his results he learned about Urbain's work and claim, so he abandoned any public claim for his own pioneer work. Had he been less discreet and more aggressive he could have had priority for the element discovery.

An American chemist, Theodore William Richards, had made it his mission in life to make very careful atomic weight determinations. In 1911 he performed 15 000 recrystallizations of lutetium bromide, obtaining a very pure lutetium compound that made an accurate atomic weight determination possible.

17.4.11.2 **Georges Urbain**

The Frenchman Georges Urbain was born in 1872. He was professor of chemistry at the Sorbonne University from 1899. In Chapter 20 Hafnium his efforts to find element 72 (hafnium) are described and also how he failed. With rare earth metals he was more successful. He was originally inspired to research in this field by Lecoq de Boisbaudran, among others. Even if he had to sustain bitter fights with Auer, they ended with a recognized priority for the discovery of the element lutetium.

17.4.11.3 **Charles James**

Charles James, Figure 17.12, was born in 1880 at Earls Barton near Northampton, England and died in 1928 in New Hampshire, USA. He studied at University College, London, under Sir William Ramsay and graduated from the Institute of Chemistry in 1904. He moved to USA and the University of New Hampshire in 1906. There he developed new fractional crystallization techniques for separating rare earth elements. He was the first to separate large amounts of lutetium from ytterbium.

In his continuous work he separated and characterized large quantities – at the kilogram level – of pure rare earths. His highly purified samples were in great demand by research laboratories around the world. James became recognized as an international expert on REM and together with colleagues he published more than 60 papers between 1907 and 1931, mainly in the *Journal of the American Chemical Society*.

Figure 17.12 Charles James (1880–1928). (Reprinted with permission from Milne Special Collections and Archives Department, University of New Hampshire Library, Durham, NH, USA.)

On 29th October 1999 the American Chemical Society designated New Hampshire University as a *National Historic Chemical Landmark* because of Charles James and his achievements [17.4]. At the ceremony it was said by Clarence J. Murphy:

As a matter of fact the rare earth group was commonly supposed to be a group of elements without practical importance and of monotonous chemical behavior. But the investigation of the magnetic properties of the rare earth ions showed that this monotony does not extend to their physical properties. The rare earth ions have similar properties because the external electron shell for each ion is the same – a group of eight electrons just like the inert gases – but the differences in the rare earth ions are found in their uncompleted fourth shell of electrons that lies beneath the outer fifth shell. … Today the rare earths are used in color television picture tubes, glass polishes, ceramic glasses, protective goggles, lasers, superconductors, and diagnostic imaging, among other applications … .

17.4.11.4 Theodore William Richards

Theodore William Richards was born in Germantown, Pennsylvania in 1868 and died at Cambridge, Massachusetts in 1928. After taking his Ph.D. at Harvard University, Cambridge, MA in 1888, he spent one year in Germany where he studied under Victor Meyer, among others. He returned to the USA and Harvard and was appointed professor in 1901. About half of Richards' original work was concerned with atomic weights. By 1912 he had redetermined, with the highest accuracy, the atomic weights of over thirty important elements. In 1911 he received the Nobel Prize in chemistry *"in recognition of his accurate determinations of the atomic weight of a large number of chemical elements"*.

17.4.12
The Lanthanides and the Periodic Table

17.4.12.1 The Lanthanides Are Homeless

It was 1907. The situation for discovered rare earth elements is shown in Table 17.10. Using modern terminology, 16 REMs had been discovered, of which 13 were lanthanides. The existence of still more rare earth elements was a possibility that continued to attract the interest of many chemists. It resulted in searches – sometimes unplanned – along several sidetracks. Elements were discovered and given different imaginative names before they were excluded. That part of the history is also excluded also from this account. Well-reputed chemists like Auer and Urbain in fact presented new findings, sometimes rather obscure. How many additional elements could actually be expected? A theoretical understanding and pattern were lacking and the situation tended to be chaotic.

Table 17.10 Discoveries of the rare earth elements in chronological order up to 1907.

Discovery No	1	2	3	3A		5	6
Discovery Year	1794	1803	1839	1840		1842	1843
Element	Y	Ce	La	Didymium		Er	Tb

Discovery No	7	8	9	10	11	12	13	14	15	16
Discovery Year	1878	1879	1879	1879	1885	1885	1886	1886 (1880)	1901	1907
Element	Ho	Tm	Sc	Sm	Pr	Nd	Dy	Gd	Eu	Lu

Development stopped in 1843 and did not resume until 1878, after spectroscopy had been invented.

17.4.12.2 Order Instead of Chaos

All these discoveries, especially those that had been confirmed, led to problems for Mendelejev's periodic table. Yet, scandium had become a proof of the validity of the system and yttrium and lanthanum fitted well into group 3. But where should the lanthanides be located? No natural place was available. Different proposals for an extensive modification of the system were submitted.

Carl Benedicks [17.7] in Uppsala carried out some research that contributed to "saving" the periodic system in its original form. At that time, in 1903, the molar volumes of the lanthanides were not known. Not all the elements had even been discovered. Benedicks put together values of known molar volumes for oxides, chlorides, sulfates, and so on. The results were very irregular, because it was difficult to get the samples free from included water and thus difficult to get the right weights. Yet he could trace some distinct tendencies: the molar volumes of the compounds decreased with increasing atomic weight of the metal. He concluded that the molar volumes of the metals themselves could be expected to vary in a similar manner to other elements, which Lothar Meyer had already shown around 1870. If so, the molar volumes of the lanthanide metals should, Benedicks postulated, follow a straight line, drawn from cerium Ce to tungsten W in the atomic weight/molar volume diagram. Benedicks diagram is shown in Figure 17.13.

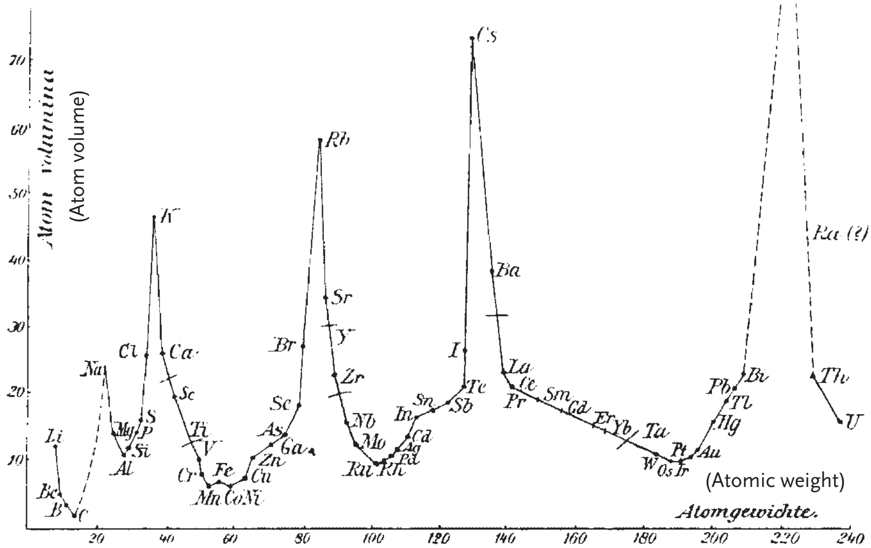

Figure 17.13 The periodicity in molar volumes of the elements, including values for lanthanides, according to Benedicks.

Benedicks concluded, as other scientists did also, that the elements cerium to ytterbium, the lanthanides known at that time, ought to be collected in *one* place in the system. After them, tantalum follows in a new place. A stroke in the figure between Yb and Ta marks the link between the position of the lanthanides and the position of tantalum. In today's system, this link is situated between Lu (discovered in 1907) and Hf (discovered in 1923).

This approach has been accepted. Group 3 in the periodic table is unique. In the place defined for group 3 and period 6 not just one but several elements are present. The lanthanides follow lanthanum like a "collateral branch". But how many lanthanides could be expected in this branch? That was the main question, whose answer might bring order into the work of discovery.

In the 1910s a revolution in atomic physics occurred, which made it possible to answer the question. Niels Bohr's atomic theory presented a new model of the atom according to which it became quite clear that there are fourteen lanthanides, neither more nor less. Thirteen were discovered, the fourteenth was missing. In the same decade G. J. Moseley's X-ray spectroscopy created a method to make a definitive decision whether a discovered rare earth metal is a real element or not. This is described in Chapter 10 about spectroscopy. The complete, modern periodic table could be built up, as already shown in Chapter 1, Figure 1.1.

17.4.13
The Fourteenth and Last Lanthanide

17.4.13.1 Discovery in an Unexpected Environment

As just mentioned, thirteen lanthanides had been discovered but, according to the new knowledge of the atom, one was missing. In 1914, Moseley confirmed that there must be an element with atomic number 61 between neodymium and samarium. Where was that element in nature? Astronomical studies indicated that it is present on the surface of star HR[465] in the Andromeda galaxy. But all attempts to find it on earth failed. The search had to take quite different paths than had been common in the whole history of lanthanide discovery.

Within the Manhattan project during World War II, a process was developed to produce the isotopes ^{235}U and ^{240}Pu for the first atomic bomb. In 1943 a nuclear chemistry group was moved from the metallurgical laboratory at the University of Chicago to the new Clinton Laboratories at Oak Ridge in Tennessee. Uranium was bombarded with neutrons in a graphite-moderated reactor and fission products were examined. A very small side issue in the gigantic research project was to investigate if element 61 was present among the fission products. A small quantity of residue from a neutron–uranium reaction was analyzed. 15 mg lanthanum was added as a carrier. All the lanthanides present were then separated from uranium. Element 61, if present, was supposed to follow lanthanum. Cerium was oxidized to tetravalent state and precipitated as cerium iodate $Ce(IO_3)_4$. The filtrate, free from cerium, was heated with potassium carbonate. Then a fine crystalline, mixed carbonate, $K_5(RE)(CO_3)_4$, was precipitated, in which RE consisted of La, Pr, Nd and element 61, if present. The precipitate was dissolved and the precipitation with carbonate was repeated many times to completely remove yttrium, europium and samarium. When the laborious processing was regarded as complete the solution was introduced into cation exchanger Amberlite IR-1 of the sulfonated formaldehyde type, which adsorbs all the lanthanides. Elution was performed with a solution containing 5% ammonium citrate, pH 2.75. The radioactivities for the different metals in the elutions were measured. The order of elution of the rare earth elements was established in a series of experiments, using radioactive cerium, lanthanum, europium and yttrium produced in fission and radioactive praseodymium and europium produced by slow-neutron activation of pure oxides. The results of these experiments showed clearly that the order of elution of the rare earth metals is the reverse of that of the atomic numbers. Thus a tool was available to identify an unknown element with specified atomic number.

The elution fractions from the unknown lanthanide mixture were collected and the respective γ and β activities of the different isotopes were measured. The result is shown in Figure 17.14. The last lanthanide had been discovered in 1943. For security reasons the discovery was kept secret. It was not made public until a meeting of the American Chemical Society in 1947.

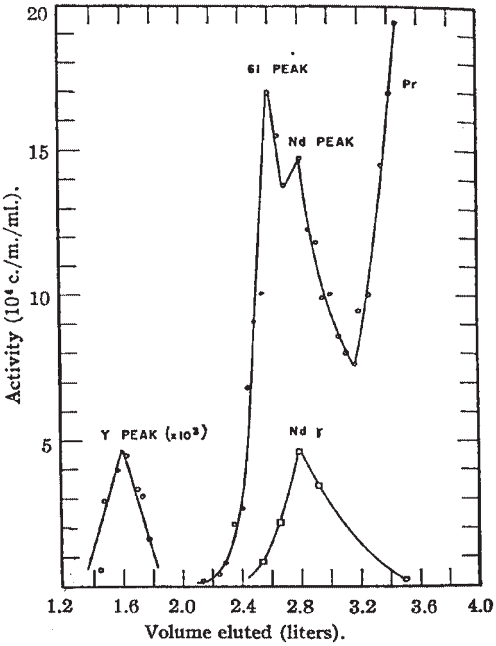

Figure 17.14 Activity results for different elution fractions. The upper curve (symbols o shows, from right, β-activities from praseodymium (atomic number 59) and neodymium (atomic number 60) and then a peak for an unknown element. This was element 61 [17.8].

17.4.13.2 Charles D. Coryell, Jacob A. Marinsky and Lawrence E. Glendenin

Charles D. Coryell was the leader of a radiochemical group that moved from the University of Chicago to Oak Ridge in 1943. In March 1944, Jacob Marinsky was one of eighteen soldier students at Purdue University, selected from at least 1000, to be transferred to Oak Ridge. There was a shortage of scientists at that time and the group of eighteen was assigned to the Special Engineering Detachment (SED). After being interviewed by professor Coryell himself Marinsky was chosen to join his research program. “I was the last member of the group to be assigned, but the luckiest” (J. A. Marinsky, The Search for Element 61) in ref. [17.9]. Together with the more experienced instructor, Lawrence E. Glendenin, he was given the task of using the ion-exchange technique, new at that time, to separate the fission products of uranium. After the testing technique, described above, had been developed it was time for the final, decisive test. In this experiment, the elution required the continuous attention of the researcher, as no automatic control had yet been provided. After having spent more than 30 hours with the experiment, Marinsky was so exhausted that Glendenin sent him to sleep and took over. Some hours later Marinsky was awakened with the news that element 61 had been discovered.

There was no question about the fact that Marinsky and Glendenin were the discoverers. Their superior, Professor Coryell, declined to be included in the discovery group on the grounds that he had not been active enough in the actual research work. He also pointed out that his name might distract attention from the two who really did the job. He was, however, persuaded by his co-workers, as his inspiring leadership had been of such great importance for the success of the research.

Marinsky beat a record for element discoverers. Only one year after his bachelor degree he took his place in the discovery history of the elements.

The whole trio, Coryell, Marinsky and Glendenin, were officially given the credit for the discovery by IUPAC at the conference in Amsterdam in 1949. On that occasion the name of element 61 was also established.

17.4.13.3 Fire From the Gods Arrived ...

Different proposals for naming had been considered. *Phoenicium* was one, as the element had risen like a phoenix from the ashes in the atomic reactor. Another was *Clintonium* after the Clinton laboratory. Professor Coryell's wife Grace Mary had her own proposal. The Titan Prometheus stole the fire from the gods and gave it to humans. That could be seen as a model for element 61. It had been brought to the earth from the interior of a nuclear reactor. *Promethium* was her proposal, which was accepted and established by IUPAC in 1949.

17.4.13.4 .... But Not the Nobel Prize

Alfred Nobel was born in Stockholm in 1833 and died in San Remo, Italy, on December 10, 1896. When his will was read it came as a surprise that his fortune was to be used for prizes in physics, chemistry, physiology or medicine, literature and peace. The Royal Swedish Academy of Sciences was entrusted with the nomination and selection of Nobel laureates in physics and chemistry. The awards are presented every year on the anniversary of Alfred Nobel's death, 10th December.

The first Nobel Prizewinners were honored in 1901 and the prizes in chemistry and physics in the first four years are listed in Table 17.11. Lord Rayleigh was rewarded "for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies". Ramsay got the prize *"in recognition of his services in the discovery of the inert gaseous elements in air and his determination of their place in the periodic system"*.

Table 17.11 Nobel prizes for chemistry and physics in the four first years of their existence

Year	Chemistry	Physics
1901	J. van't Hoff	W. Röntgen
1902	E. Fischer	H. Lorentz, P. Zeeman
1903	S. Arrhenius	Marie and Pierre Curie, A. Becquerel
1904	Sir William Ramsay	Lord Rayleigh

Discoveries of the rare earth elements ended in 1907 (apart from promethium).

Many discoverers of rare earth metals from 1880 and later were dead when the nomination process began. Some, however, were still active (the year of death is given in parentheses): *Demarçay* (1904), *Cleve* (1905), *Delafontaine* (1911), *Boisbaudran* (1912), *James* (1928), *Auer* (1929), *and Urbain* (1938). Auer and Urbain were seriously discussed for the prize. Auer was nominated 10 times between 1908 and 1929, Urbain 56 times between 1912 and 1936. None of them, however, was awarded the prestigious prize [17.10].

17.5
The Special Nature of the Lanthanide Elements

17.5.1
Electron Configuration and Chemistry

The electron configuration for the lanthanides and the two preceding and two following elements are shown in Table 17.12.

Table 17.12 The idealized electron configurations of the lanthanides, the two preceding and the two following elements in period 6

No	Group	Element	Shell 1 K	Shell 2 L	Shell 3 M	Shell 4 N		Shell 5 O			Shell 6 P
			s	s + p	s + p + d	s + p + d	f	s	p	d	s
55	1	Cs	2	8	18	18	0	2	6	0	1
56	2	Ba	2	8	18	18	0	2	6	0	2
57	3	La	2	8	18	18	**0**	2	6	**1**	**2**
58	3	Ce	2	8	18	18	**1**	2	6	**1**	**2**
59	3	Pr	2	8	18	18	**2**	2	6	**1**	**2**
60	3	Nd	2	8	18	18	**3**	2	6	**1**	**2**
61	3	Pm	2	8	18	18	**4**	2	6	**1**	**2**
62	3	Sm	2	8	18	18	**5**	2	6	**1**	**2**
63	3	Eu	2	8	18	18	**6**	2	6	**1**	**2**
64	3	Gd	2	8	18	18	**7**	2	6	**1**	**2**
65	3	Tb	2	8	18	18	**8**	2	6	**1**	**2**
66	3	Dy	2	8	18	18	**9**	2	6	**1**	**2**
67	3	Ho	2	8	18	18	**10**	2	6	**1**	**2**
68	3	Er	2	8	18	18	**11**	2	6	**1**	**2**
69	3	Tm	2	8	18	18	**12**	2	6	**1**	**2**
70	3	Yb	2	8	18	18	**13**	2	6	**1**	**2**
71	3	Lu	2	8	18	18	**14**	2	6	**1**	**2**
72	4	Hf	2	8	18	18	14	2	6	2	2
88	5	Ta	2	8	18	18	14	2	6	3	2

For all lanthanides the outermost shell 6 (K) has 2 s-electrons and the number of 5d-electrons is also formally the same, namely 1, in all the elements. That is the background to the chemical similarity between the different lanthanides and the very hard separation and discovery work, described above. The picture is, however, not quite so simple. The energy of the sole 5d-electron within the lanthanide atoms is almost the same as for the 4f-electrons. Spectroscopic examination indicates a modified electronic configuration as shown in Table 17.13 [17.11].

Table 17.13 The real number of 4f, 5 d, and 6s electrons in the ground state according to spectroscopic studies

Element	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4f	1	3	4	5	6	7	7	9	10	11	12	13	14	14
5d	1	0	0	0	0	0	1	0	0	0	0	0	0	1
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2

The valence electrons of the neutral lanthanide elements are distributed among the 4f, 5d and 6s orbitals. When three electrons have been removed no electrons remain in 5d and 6s orbitals but the remaining 4f electrons are stabilized as a group. Thus the +3 oxidation state is by far the most common. This is quantitatively expressed by the fact that the sum of the first three ionization energies is rather low while, in all cases, the fourth ionization energy is higher than this sum. The extra energy required to remove a fourth electron is so great that the oxidation state +4 is almost impossible to reach. Some exceptions to this rule do exist, however. Owing to the special situation at the beginning of the lanthanide series, cerium can for instance show valencies of both +3 and +4.

17.5.2
Electron Configuration and Color

Several lanthanide ions have a characteristic color in water solutions, as shown in Table 17.14. The color for an element ion with *n* f-electrons is very similar to those element ions that have (14 – *n*) electrons. In the table the colors of powdered common oxides are shown.

Table 17.14 The colors of trivalent lanthanum and lanthanide ions in water solution and of common oxide powders

Atomic Number	Element	Ion	Color	Number of f-electrons	Oxide	
					Formula	Color
57	Lanthanum	La^{3+}	Colorless	0	La_2O_3	White
58	Cerium	Ce^{3+}	Colorless	1	Ce_2O_3; CeO_2	White
59	Praseodymium	Pr^{3+}	Green	2	Pr_6O_{11}[a]	Dark brown
60	Neodymium	Nd^{3+}	Lilac	3	Nd_2O_3	Pale white
61	Promethium	Pm^{3+}	Pink	4	–	–
62	Samarium	Sm^{3+}	Yellow	5	Sm_2O_3	Yellowish
63	Europium	Eu^{3+}	Pale pink	6	Eu_2O_3	Light pink
64	Gadolinium	Gd^{3+}	Colorless	7	Gd_2O_3	White
65	Terbium	Tb^{3+}	Pale pink	8	Tb_4O_7[a]	Dark brown
66	Dysprosium	Dy^{3+}	Yellow	9	Dy_2O_3	Light pink
67	Holmium	Ho^{3+}	Yellow	10	Ho_2O_3	Light yellow
68	Erbium	Er^{3+}	Rose pink	11	Er_2O_3	Rose pink
69	Thulium	Tm^{3+}	Pale green	12	Tm_2O_3	–
70	Ytterbium	Yb^{3+}	Colorless	13	Yb_2O_3	White
71	Lutetium	Lu^{3+}	Colorless	14	Lu_2O_3	White

[a] Non-stoichiometric oxides are dark-colored. Pr_6O_{11} is $Pr_2O_3 \cdot 4PrO_2$; Tb_4O_7 is $Tb_2O_3 \cdot 2TbO_2$.

Normally the electrons in an ion are situated in orbitals corresponding to the lowest energy. The ion is then in its *ground state*. When an electron gains a quantum of energy it moves to a higher level and the ion is in an *excited state*. Such excitation can be caused by absorption of energy from electromagnetic radiation. If an ion can absorb in the visible region, the energy absorbed is missing when white light is transmitted. If a frequency corresponding to red is absorbed, the solution may appear blue and so on. Electronic absorption spectroscopy studies the interactions between photons and matter. The method has been extensively used to investigate f-element compounds. The electronic transactions connected with excitation of 3-valent lanthanide ions only involve a redistribution of electrons within the 4f subshell. Consequently the colors are very little influenced by the ligands and change only slightly from compound to compound. The color is characteristic for the actual element. Glass containing neodymium and praseodymium ions (didymium glass) absorb sodium light so specifically and so strongly that it can be used in goggles for glass blowers. An additional great benefit is that it also absorbs in the infrared region, thus protecting the eyes from heat radiation.

Standard filters for calibrating optical instruments also utilize the sharp absorption bands of lanthanide ions.

17.5.3
Electron Configuration and Magnetic Properties

17.5.3.1 Diamagnetism and Paramagnetism

The magnetic properties of chemical substances result from the fact that each moving electron is itself a magnet. The electron may influence the magnetic behavior in two ways: by its *spin* and by its *orbital motion*. All the electrons present co-operate to give the substance its magnetic properties. Placed in a magnetic field the substance aligns itself either counteracting or strengthening the applied field. Substances with the former behavior are *diamagnetic* and their susceptibilities are negative. Substances with the latter behavior are *paramagnetic* with positive susceptibility values. All the REM elements are paramagnetic as metals, but for their ions the situation is more complex.

Table 17.15 gives some information about the magnetic properties of the trivalent ions of yttrium, lanthanum and the lanthanides.

Table 17.15 Permanent magnetic moments (Bohr magnetons mB) for yttrium, lanthanum and lanthanide ions

Ion	Number of unpaired electrons	Magnetic moment. Bohr magnetons μ_B		
		Calculated	Observed	
			In $Ln_2(SO_4)_3 \cdot 8H_2O$	In $Ln(C_5H_5)_3$
Y^{3+}	0	0	0	–
La^{3+}	0	0	–	0
Ce^{3+}	1	2.56	–	2.46
Pr^{3+}	2	3.62	3.47	3.61
Nd^{3+}	3	3.68	3.52	3.63
Pm^{3+}	4	2.83	–	–
Sm^{3+}	5	1.55–1.65	1.58	1.54
Eu^{3+}	6	3.40–3.51	3.54	–
Gd^{3+}	7	7.94	7.9	7.98
Tb^{3+}	6	9.7	9.6	–
Dy^{3+}	5	10.6	10.3	10.0
Ho^{3+}	4	10.6	10.4	–
Er^{3+}	3	9.6	9.4	9.45
Tm^{3+}	2	7.6	7.0	–
Yb^{3+}	1	4.5	4.3	4.00
Lu^{3+}	0	0	–	–

Ln stands for Y, La and Ce–Lu. $Ln(C_5H_5)_3$ is an organometallic compound of the metal and cyclopentadienyl ligands C_5H_5. Values taken from ref. [17.12].

The ions Y^{3+}, La^{3+} and Lu^{3+} are diamagnetic, as are Yb^{2+} and Ce^{4+} also. All the other lanthanide ions are paramagnetic. Owing to the shielding of the 4f-electrons from the chemical environment, complexing groups or anions bound to paramagnetic lanthanide ions have little effect upon the magnetic moments. The lanthanides are thus very special in respect of their magnetic properties, which makes them useful in many high-tech applications.

The high values of the permanent magnetic moments of gadolinium and the following elements depend on the additive behavior of spin and orbital moments. These moments are in opposition for the elements before gadolinium.

17.5.3.2 Ferromagnetism

The three paramagnetic elements iron, nickel and cobalt are special because they are *ferromagnetic*. This is dealt with in Chapter 30 Cobalt. It might be expected that rare earth metals, with their unique magnetic properties, would also be ferromagnetic. That is true for some of them although their Curie temperatures are very low, as shown for terbium and dysprosium in Table 17.16. However, different intermetallic compounds with such high Curie temperatures that they are ferromagnetic at and above room temperature can be prepared.

Table 17.16 Curie temperatures for metals and intermetallic compounds

Material	Fe	Tb	Dy	$TbFe_2$	$DyFe_2$	$SmFe_2$
Curie temp. °C	770	–43	–188	431	362	415

The intermetallic compound $SmCo_5$, with markedly ferromagnetic properties, was invented in the 1970s. Rare earth metals are nowadays very much used in magnetic alloys, for instance samarium–cobalt in quartz watches and other miniaturized systems. Still better is the compound Sm_2Co_{17} with a certain content also of iron, copper and zirconium. For heavier magnets, alloys of neodymium, iron and boron are used.

17.6
Occurrence of Rare Earth Metals

17.6.1
Geochemistry Is a Guide

The occurrence of lanthanides follows *Harkin's rule*. This states that elements with even atomic numbers are more common than their nearest neighbors with odd numbers. As stated in Chapter 4 Geochemistry, cations with similar ionic radii (in stone melts) have a tendency to follow each other in crystallizations during geological processes. Among the rare earths, the radii of the trivalent ions decrease with increasing atomic number (the lanthanide contraction). The lighter elements – with low atomic numbers and large radii – thus favor certain host minerals, while the heavier elements are enriched in others. This has resulted in the formation of different RE-mineral types, constituting the cerium group and the yttrium group respectively, see Tables 17.2, 17.3, 17.17 and 17.18.

Table 17.17 Minerals containing rare earths metals

Group	Mineral	Type[a]	Composition	
			General	Specific examples
Cerium Group	Monazite Figure M25	RE phosphate	50–75% of the Ce group oxides 1–4% of the Y group oxides 5–9% thorium oxide	*Monazite from Australia* La_2O_3 23% CeO_2 46% Nd_2O_3 18%
	Bastnaesite Figure M22	RE fluoro carbonate	65–70% of the Ce group oxides < 1% of Y group oxides	*Bastnaesite from California* La_2O_3 32% CeO_2 49% Nd_2O_3 14%
Yttrium Group	Euxenite	(RE,Nb,Ta,Ti) oxide	15–35% of the Y group oxides 2–8% of the Ce group oxides 20–23% TiO_2 25–35% $(Nb,Ta)_2O_5$	
	Xenotime Figure M20	Y phosphate	55–65% of the Y group oxides 0.1% of the Ce group oxides 0–3% ThO_2 0–3,5% U_3O_8 2–3% ZrO_2	*Xenotime from Malaysia:* Y_2O_3 61% Dy_2O_3 9% Er_2O_3 5% Yb_2O_3 6%
	Gadolinite Figure M18	RE silicate, containing Be	35–50% of the Y group oxides 2–17% of the Ce group oxides 0–12% Be oxide	

a The chemical formulas are given in Tables 17.2 and 17.3.

Table 17. 18 Typical contents of lanthanide elements (percentage of metal) in monazite and bastnaesite ores

Ore/Element	**La**	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Monazite	20	43	4	16	0	2.5	0.1	1.5	.05	0.6	.005	0.2	.02	0.1	.02
Bastnaesite	33	49	4	12	0	0.8	0.1	0.2	.016	.03	.005	.004	.001	.0005	.0001

Source: ref. [17.18].

17.6.2

Monazite and Bastnaesite in Many Places ...

The important raw material for cerium, monazite, is also the most important mineral source for thorium. As this metal was desirable it initially supported and accelerated the extraction of rare earth elements from monazite. The radioactivity of thorium has, however, created environmental problems for monazite. Nowadays, minerals free from radioactive components are favored for the extraction of REMs.

The exploitable monazite resources are as a rule alluvial[4] and occur mainly as monazite *sand*. Seashore deposits at Travancore in India contain very large quantities of monazite. Other important sources are located on the Atlantic coast in Bahia, Brazil. In Australia, monazite is obtained as a by-product when seashore sand is treated for extraction of ilmenite. Even yttrium group metals are extracted from monazite, in spite of the low original content. At Mountain Pass in California large deposits of bastnaesite have been found. Euxenite is worked in Idaho for extraction of niobium and tantalum. Then REMs are obtained as by-products.

17.6.3
… But China Has Most of It

China has the largest supply in the world of REMs. The recoverable resources account for near 75% of the world's total reserves. The description in this section is based on W. Minggin and D.Xuehong in ref. [17.9] and L. F. Trueb in ref. [17.13].

17.6.3.1 Complex Ores in Inner Mongolia

At Baiyunebo in Inner Mongolia, 135 km from Baotou, RE minerals are found together with minerals of iron, titanium and niobium. The deposit is worked for iron, which keeps the costs low for production of the RE metals. Both monazite and bastnaesite are mined and, because of that, the mine is very important as a source of the cerium group metals. The bastnaesite has a higher content of samarium and europium than the Californian ore in Mountain Pass. As the monazite is low in thorium and free from uranium its radioactivity is low, which is a benefit for ore handling.

17.6.3.2 Simple Bastnaesite in the Shandung and Sichuan Provinces

Mineral veins rich in bastnaesite have been found in mines in Weishan (Shandung) and in Mianning (Sichuan). These deposits give ores from which the rare earths are much easier to separate than from the Baiyunebo mixed minerals, favoring high yield and low cost.

17.6.3.3 Monazite and Xenotime as By-products in Placers

Coastal and river placer deposits in Guandong and Hainan provinces have been worked for ilmenite and zircon, giving monazite and xenotime as by-products. Owing to the high content of thorium and uranium in the material – giving safety problems – these ores have gradually been replaced by others for the extraction of REMs.

17.6.3.4 Unique Ion Adsorption Deposits in Jiangxi

The ion-exchange clays in the Southern Chinese province Jiangxi are curious. When granites with above average RE content weathered during geological epochs and in tropical climatic conditions, clays were formed. Sodium aluminosilicate in these clays acted as an ion exchange material, a zeolite. RE ions, which had been dissolved by humic acids and water, were separated by ion exchange in the zeolite. Ions of heavy

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[4] The designation alluvial is used for a placer formed by the action of running water.

and medium-heavy RE metals were adsorbed and enriched while other ions, cerium above all, passed on. The actual clays, Longman clays, have a RE content of 0.05–0.15%. Cerium that has passed the Longman clays is found in other deposits.

The occurrence of an ore of this type was first observed in Longman (Jiangxi) in 1969. Later it was found in the whole Jiangxi province as well as in Guandong, Guangxi, Hunan and Fuijian. Deposits of this type are now the major source of heavy and medium-heavy rare earths in China.

17.6.4
Worldwide Mine Production and Reserves

From an economic point of view the most important rare earth sources in the world are:

- *bastnaesite deposits* in China and the United States
- *monazite deposits* in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand and the United States
- ion adsorption clays in China
- xenotime, apatite and spent uranium solutions in different countries

The total world reserves are estimated at 100 million tonnes, counted as the content of rare earth oxide REO. Of this quantity China has 43, the former Soviet Union 19, the United States 13 and Australia 5 million tonnes. This large reserve is satisfactory compared to the actual consumption, although this may increase to an extent that is difficult to anticipate. On the other hand, undiscovered resources are thought to be very large. In addition, a high proportion of the rare earth metals used in modern society may appear as a workable scrap. It is estimated that as much as 30% of the large quantity of RE metals in magnets will be recovered and reused.

Total mine production in the year 2000 was 83.5 thousand tonnes REO, of which China accounted for 73, the United States 5 and India 2.7 thousand tonnes [17.14].

17.7
Separation of the RE Elements

The separation of RE metals is one of the most difficult problems within inorganic chemistry. The chemical properties of the elements are so exceptionally similar. When the separation work started with fractional crystallization and precipitation chemists used the small differences in solubility between the RE salts. To some extent the differing basicities of the oxides were also used. As soon as advanced separation techniques, ion exchange and liquid–liquid extraction, were developed the situation changed drastically.

17.7.1
Fractional Crystallization

Fractional crystallization was the original method. It was an arduous task to make the separations in this way while searching for and finding the unknown elements. The fractionations were repeated hundreds or thousands of times to reach the goal of complete separation.

The work often started by wetting the finely ground mineral powder with concentrated sulfuric acid. On heating to dull red heat, sulfates of the RE elements were formed and could be dissolved in ice water (the solubility increases with decreasing temperature). Oxalic acid was added to the aqueous solution and precipitated RE oxalates, which were transformed to oxides by calcination. This oxide mixture was the raw material in the separation work.

One of the oldest methods used the difference in solubility of RE-potassium sulfates. The oxide mixture was dissolved in acid and potassium sulfate was added. Double salts of elements in the cerium group, La, Ce, Pr, Nd and Sm, have a low solubility and were precipitated first. The double sulfates of the elements Eu, Gd and Tb are a little more soluble but precipitated as a medium fraction. Elements of the yttrium group, Y, Dy, Ho, Er, Tm, Yb and Lu, remained in solution.

Different, more specific, separation techniques were developed, each one having its special characteristics. It could be separation of other double salts – nitrates, oxalates – composed of a RE metal ion and another cation present in the solution, for example K^+, Na^+, $NH_4{}^+$ or Mg^{2+}. Double ammonium nitrate may be used for removal of lanthanum and the separation of neodymium from praseodymium. Members within the cerium group may be separated using double manganese nitrates, while elements in the yttrium group are separated using the differences in solubility of their bromates. Auer von Welsbach did much work with RE-ammonium oxalate systems. Charles James in the USA developed an effective technique with RE-magnesium double salts.

Fractional crystallization is, as mentioned, time consuming and demands a great deal of work. Figure 17.15 describes the process in principle.

A separation of cerium group elements is intended in a solution from which cerium is at first removed by oxidation to Ce^{4+} and selective precipitation. Now the aqueous solution L_0 contains RE^{3+} (different lanthanide ions), NH_4^+ and NO_3^-. The separation course will be:

(1) The solution L_0 is evaporated to a volume such that half of its salt content crystallizes on cooling. Crystals K_1 and mother liquor L_1 are separated.

(2a) Crystals K_1 are dissolved in water containing NH_4NO_3 and the solution is evaporated until half of its salt content is crystallized, K_2. The mother liquor L from this crystallization is saved.

(2b) Solution L_1 is evaporated until half of its salt content is crystallized. The mother liquor is now L_2. The crystals K from this crystallization are saved.

(3) The saved mother liquor L and the saved crystals K are brought together (LK in the second row). Water is added until a solution is obtained. It is evaporated in order to get new crystals and new mother liquor.

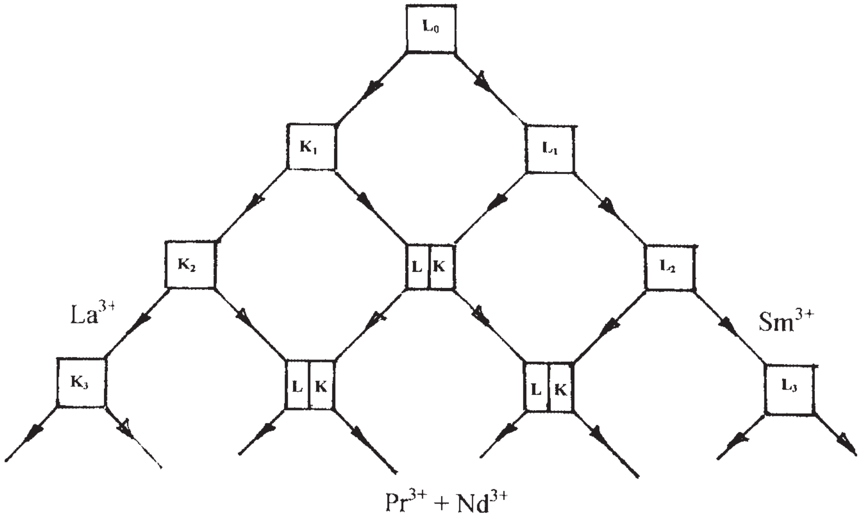

Figure 17.15 Scheme for fractional crystallization of light RE elements.

The process is repeated many times and consistently mother liquors L are taken downwards to the right in the diagram, while crystals K are taken downwards to the left. The solubility varies more at the lanthanum end of the series and there the separation is most effective.

17.7.2
Using the Differences in the Basicities of the Oxides

Oxides of the metals in group 2 in the periodic system, magnesium, calcium, strontium, barium, have a certain solubility in water and are easily dissolved in acids. Their hydroxides are not precipitated if their acid solution is neutralized with ammonia. The corresponding oxides of metals in group 4, titanium, zirconium, hafnium, are insoluble in water and not attacked by weak acids. If strongly acid solutions of these metals are neutralized with ammonia the hydroxides precipitate even before a pH value of 7 is reached. All this implies that the group 2 elements are more basic than the elements in group 4. Some of the RE elements are more like the elements in group 2 – they are more basic – others are similar to the group 4 elements – less basic. There is a possibility of separation, which Mosander discovered in 1838. When he leached cerium oxide with very dilute nitric acid the main component was almost unaffected but the more basic oxide of a hidden element was dissolved. In that way lanthanum was discovered.

A fractional precipitation using differences in basicity is difficult but possible. In a solution containing lanthanum, cerium and other light lanthanides, cerium is oxidized to Ce^{4+} ion. If ammonia or sodium hydroxide is now added, cerium hydroxide starts to precipitate even at a pH value below 4. Among the other elements, those with a more acid character, Nd, Pr, Sm, are enriched in the hydroxides after repeated precipitation. Lanthanum can be found in the last filtrate.

A special variant of the method using differences in basicity is the melting of nitrate mixtures of different RE metals. The nitrates of the least basic elements are decomposed, those of the more basic elements are not. The least basic have now formed salts that are difficult to dissolve in water. The stable nitrates of the more basic elements remain soluble in water. This method was essentially how Nilson discovered scandium. He tried to verify Marignac's discovery of ytterbium. When the nitrate of ytterbium was melted and afterwards leached with water it became clear that the nitrate had been decomposed and now precipitated as a basic salt of ytterbium. In the filtrate, however, an undecomposed nitrate of another metal remained. This metal was christened scandium.

17.7.3
Separation Using Ion Exchange

If a solution containing trivalent lanthanide ions is passed into a cation exchanger containing a resin of sulfonated polystyrene, all the lanthanides are adsorbed in the upper part of the exchanger. On elution with a suitable solution a separation occurs. Around 1950 it was possible to separate kilogram quantities and reach a purity of 99.99% in the different fractions. The separation is improved if certain chelating agents, for instance EDTA, are added to the elution solution. In that way the technique has been still more effective and has been developed into an industrial production method. From 1960 the technique has, however, gradually been replaced by *liquid–liquid extraction,* even if the use of ion exchange has continued for preparing rare earth metals for some electronic applications, when an extreme purity, better than 99.9999%, is required.

17.7.4
Liquid–Liquid Extraction

Two immiscible solvents in contact with each other form two phases. If a dissolved substance is more soluble in one of the solvents than in the other it is distributed between the two. The ratio of the concentrations of the substance in each solvent is the *distribution coefficient*. Liquid–liquid extraction is a separation process that takes advantage of the fact that dissolved substances may have different distribution coefficients in a certain system. A very simple example of a liquid–liquid extraction is given in Figure 17.16.

If a hydrochloric acid solution containing Fe^{3+} and other metal ions, is "shaken" with diethyl ether the trivalent iron spontaneously passes into the ether phase while the other metal ions, such as Al^{3+}, Cr^{3+} Co^{2+} Mn^{2+} or Ni^{2+}, stay in the acid (water) phase.

The technique has been developed to a very high efficiency for separation of RE elements. The immiscible solvents – one aqueous, one organic – flow in opposite di-

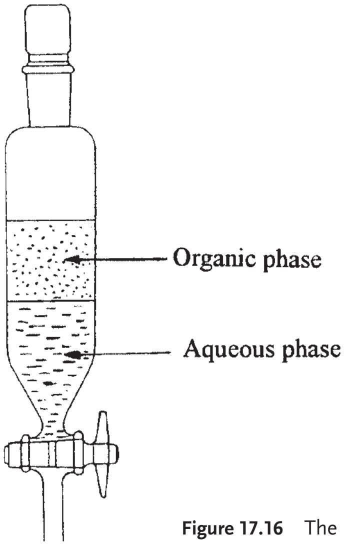

Figure 17.16 The principle of liquid–liquid extraction.

rections. The lighter solvent flows upward while the heavier solvent flows downward. The substance to be separated is in contact with both solvents and dissolves in each stream according to a ratio determined by the distribution coefficient.

The organic phase consists of a solvent, usually kerosene or aromatics. Active extractants with chelating properties are added and are responsible for the transfer of the rare earth elements from the aqueous to the organic phase. An effective extractant is tri-*n*-butyl phosphate (TBP), with which nitrates of the rare earth metals are extracted. Different active extractants with chelating properties, more or less powerful, more or less selective, are used. They can be organophosphoric acids or other P-containing extractants such as tri-*n*-octyl phosphine oxide, as well us long-chained amines.

17.8
Manufacture of Rare Earth Metals

Ores containing monazite, bastnaesite or xenotime are concentrated by ore-dressing processes, heavy medium separation or flotation. After grinding, the concentrates are converted to soluble sulfates or chlorides by digestion with acids or alkalis.

17.8.1
REO Manufacture – One Example

A concentrate of monazite is treated with 50% NaOH solution under pressure at 150°C. Soluble sodium phosphate is formed, while the RE metals and thorium precipitate as hydroxides. The hydroxides are dissolved in nitric acid and thorium hydroxide is selectively precipitated. The nitrate solution, containing a mixture of lanthanum and lanthanides, is now ready for separation. This is carried out using liquid–liquid extraction. In the first treatment the light elements (La, Ce, Pr, Nd) are separated from the heavy ones (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). In the latter fraction yttrium is also present. The two groups are then treated in separate plants in hundreds of process steps involving addition of organic solvents and different extraction agents. Pure fractions of the different RE metals are obtained. From these nitrate solutions the metal is precipitated as carbonate, oxalate or hydroxide. The pure RE oxides are prepared by filtering, washing and calcination.

17.8.2
Pure RE Metals

The rare earth metals are produced by molten salt electrolysis and by metallothermic reduction methods. Some details are given below about the applications of the latter.

17.8.2.1 Metals with High Boiling Point and Low Vapor Pressure

The metal oxide is treated with hydrofluoric acid. The fluoride formed is reduced with calcium. The advantage of using the fluoride instead of the oxide is that liquid calcium fluoride and not solid calcium oxide is formed. This can easily be separated from the pure RE metal. In a subsequent high-temperature process calcium residues are vaporized in vacuum. A very pure RE metal remains. This technique is used for production of the following metals [boiling point (°C) in parentheses]: La (3457), Ce (3427), Pr (3520), Nd (3074), Gd (3273), Tb (3230), Dy (2567), Ho (2700), Er (2868), Lu (3402).

17.8.2.2 Metals with Low Boiling Point and High Vapor Pressure

The final step, vaporization of calcium, does not work for metals with high vapor pressure, as the metal itself would vaporize with the calcium. Instead the oxide is reduced with metallic lanthanum, which has a very low vapor pressure. Lanthanum oxide and a melt of the actual RE metal are formed. The reduction reaction occurs in a tantalum container. The reduced RE metals e.g. samarium, are vaporized and deposit on the walls of the tantalum container. This method is used for [boiling point (°C) in parenthesis]: Sm (1794), Eu (1529), Tm (1950), Yb (1196).

17.9
Rare Earth Metals in Modern Technology – Examples

That the rare earth metals are of little practical value was the general view during the whole of the 19th century. The turn of the century, however, saw the first major application, Auer von Welsbach's incandescent mantle for gas lightning (section 17.4.10.2). Gradually the list of RE applications was increased. At first the RE metals were used mixed, just as they were prepared from monazite sand. One example is *mischmetall*, consisting of about 50% cerium, 25% lanthanum and 25% other rare earth metals. It was used in metallurgy and "Auer metal", made of about 70% mischmetall and 30% iron was also the base for lighter flints. It is still used in cigarette lighters.

Modern technology mainly uses pure RE oxides or metals in many high-tech applications. That they are available is due to the sophisticated separation techniques described above. The reason for their usefulness is their very special electron configuration within the atoms. This creates the basis for special chemical, optical, magnetic and electromagnetic properties.

In the following description of advanced applications so many examples will be given that it may be difficult to keep track. Table 17.19, which indicates which section contains a particular application, may help.

Table 17.19 Applications described in different element sections

Application	Treated in section	Application	Treated in section
Glass polishing Mischmetall	Cerium	Screens and fluorescent lamps	Europium
Catalysis	Cerium	Permanent magnets	Neodymium and Samarium
Optical	Neodymium Praseodymium	Magnetostrictive materials and magnetic storage	Terbium
High temperature	Yttrium	Superconductivity	Yttrium
Ceramic tools	Yttrium	Garnets; YAG, YIG	Yttrium and Neodymium
Magnetic refrigeration	Gadolinium		

17.10
Applications – Some Examples

17.10.1
Scandium

17.10.1.1 In the MIG 29 Aircraft

Scandium is a light metal with a much higher melting point than aluminum (1541°C for Sc compared to 661 for Al) which has interested designers of aircraft. It is, however, very expensive and has hitherto been used only as a minor constituent. In aluminum alloys 0.3% Sc is reported to prevent grain growth during casting or welding and to increase strength due to precipitation of Al_3Sc particles. The Soviet MIG 29 and 31 aircraft used alloys of this type.

17.10.1.2 In Studio Lighting

If scandium iodide with additions of dysprosium and holmium is added to the mercury vapor lamps used in studio lighting, it changes the character of the emitted light to make it more similar to sunlight, which is important for color TV filming. Each lamp only needs the addition of 5 mg scandium.

17.10.1.3 A Monitor for Oil Refining and Termite Tracking

Scandium in nature has one single isotope ^{45}Sc. This is stable. In nuclear reactors a radioactive isotope ^{46}Sc with a half-life of 84 days is produced. This has a strange but established use in monitoring various fractions in industrial processes such as oil refining. In experimental zoology it has also been used for mapping the migratory patterns of termites. Another very special application is the addition of a dilute solution of scandium sulfate to seed, corn and wheat, to improve the germination.

17.10.2
Yttrium

17.10.2.1 In Special Steels and Alloys

In stainless steels for high-temperature applications, RE metals, chiefly yttrium, are used to improve the oxidation resistance. Yttrium is also used in ODS alloys (Oxide Dispersion Strengthened). Yttrium oxide particles with grain size 50–1500 Å are distributed in a matrix of some high-alloy material. The finely dispersed Y_2O_3 particles obstruct the dislocation movement in the alloy and thus improve the creep properties at high temperature. The ODS alloy is manufactured by extrusion or by HIP (Heat Isostatic Pressing).

17.10.2.2 Artificial Diamonds

Single crystals of yttrium aluminum garnet YAG $Y_3A_{15}O_{12}$ are so hard that they scratch glass and they have a very high refractive index. When the crystals are cut as pieces of jewelry, they sparkle like real diamonds. In the jewelry trade it is difficult to distinguish these artificial diamonds from real ones. YAG doped with neodymium is much used in YAG lasers, described in the neodymium section below.

Ferromagnetic yttrium iron garnet YIG is important in the field of microwave techniques. YIG transmits short-wave energy with low energy losses.

A general garnet, a *grossular*, is shown in Figure M27.

17.10.2.3 Toughening Ceramics

Yttrium oxide is also used in modern ceramics. The original white ceramic was made of sintered Al_2O_3. It was very brittle. A dramatic improvement was made by “alloying” aluminum oxide with zirconium oxide ZrO_2. This oxide has a tetragonal crystal structure (T) at the sintering temperature and is monoclinic (M) at room temperature (Figure 17.17). If ZrO_2 is mixed with yttrium oxide before the sintering the tetragonal structure remains metastable at room temperature.

When a crack starts in the ceramic the metastable ZrO_2 grains absorb the crack energy and the energy is used to transform it to the stable monoclinic form. The propagation of the crack is interrupted and the material has been toughened (Figure 17.18).

Zirconium oxide, stabilized with 3–8% Y_2O_3, also has been used in λ-probes for determination of the partial pressure of oxygen in car exhaust fumes that makes it possible to optimize the air–fuel mixture to the engine. A similar solid electrolyte is used as a probe for determining oxygen in molten steel.

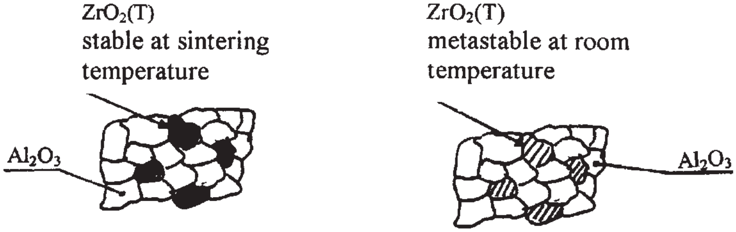

Figure 17.17 Tetragonal ZrO_2, stable on sintering, metastable after sintering.

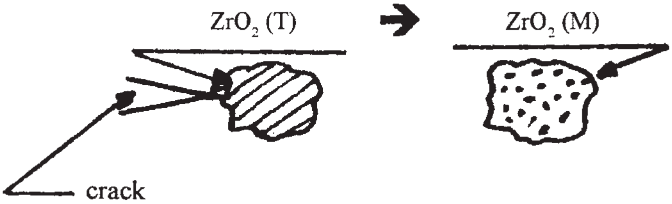

Figure 17.18 A crack transforms metastable tetragonal ZrO_2 to stable monoclinic ZrO_2. The crack loses energy and stops propagating.

17.10.2.4 **Superconducting Ceramics**

When the metal mercury is cooled to a temperature close to absolute zero, it loses all electrical resistance. It is in a state of *superconductivity*. Metals and alloys acting in this way require cooling by liquid helium to become superconductors. Such materials are called conventional superconductors.

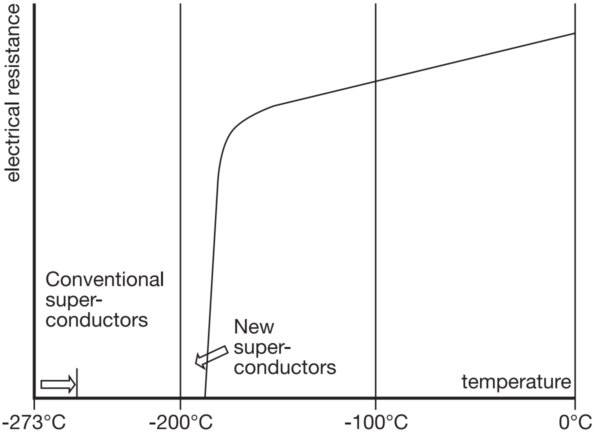

Figure 17.19 Electrical resistance of materials at different temperatures. (After a diagram by Karin Felzin in Forskning & Framsteg (Research & Progress) 8, 1987. With permission.)

In 1986, Alex Müller and Georg Bednortz at IBM in Switzerland reported superconductivity at –240°C in a ceramic material. An explosive development started and the two scientists were awarded the Nobel Prize in the following year. Gradually the composition of the ceramic has been modified, increasing the temperature for superconductivity above the boiling point of nitrogen.

This may lead to changes in our society as revolutionary as were the consequences of the breakthrough in electromagnetism. The element yttrium has attracted much attention, as one of the superconductors is $Ba_2YCu_3O_7$, see Figure 17.19.

17.10.3
Lanthanum

17.10.3.1 Optics and Light

Lanthanum oxide is a component in optical glass and imparts an extra high refractive index to it. It is also added to electrodes for carbon arcs for lighting in film and photographic studios. Lanthanum gives the arc light an emission spectrum very similar to that of sunlight.

Common alkali–calcium silicate and aluminum borosilicate glasses are colorless and transmit visible light although they absorb one part of it. A very special glass containing lanthanum and other metal fluorides has a 10 times better permeability for light than the conventional glass types. For this reason they are used for long distance observations.

17.10.3.2 Cadmium-free Batteries

Thomas Alva Edison invented the alkaline nickel–iron battery at the beginning of the 20th century. Iron is the negative pole, nickel oxide the positive. One cell has a voltage of 1.15 V. Several cells, connected in series, were used in industrial applications and for emergency power. The battery life was restricted to about 10 years.

The nickel–cadmium battery was an improvement, with a lifetime increased to about 25 years. Small Ni–Cd batteries proved to be very useful during the 1980s in connection with the dramatic development of battery-driven equipment, such as video cameras, shavers, portable computers, mobile telephones, and so on. Cadmium is such an environmental problem that great demands were made for ecofriendly alternatives.

When an alkaline battery is charged, the nickel electrode is connected to the positive pole of the rectifier. Oxygen is evolved and nickel oxide formed. At the other pole, iron or cadmium, hydrogen gas is developed. This is a drawback. In the search for an alternative to cadmium for the negative electrode, one motivation was to find an ecofriendly material with great capacity to store the liberated hydrogen with the formation of a metal hydride.

In the 1960s, the unique ability of the rare earth metals to absorb hydrogen was discovered. When metal hydride electrodes were required it was natural to search for them in the RE family. This led to the discovery, at the end of the 1960s, of $LaNi_5$ or more generally intermetallic compounds AB_5. These have the ability to absorb great quantities of hydrogen. A new alkaline battery, Ni–MH, was born. Its positive pole is

Ni, its negative $LaNi_5$ charged with hydrogen. The designation for the negative electrode became MH (metal hydride). Its capacity for electricity exceeded that of the Ni–Cd battery considerably. The new ecofriendly battery type began to replace Ni–Cd and by the start of the 1990s had gained a market share of 30%.

Intensive research work is going on to optimize AB_5. Lanthanum has been replaced by a more or less lanthanum-rich *mischmetall* while part of the nickel has been substituted by other metals. One example is $La_{0.8}Nd_{0.2}Ni_{2,5}Co_{2.4}Si_{0.1}$. Because of the expense tests have been carried out to see whether REM mixtures directly prepared from natural raw materials, e.g. monazite sand, can be used. One composition, which makes a great number of recharges possible, is $(Mm)Ni_{3.5}Al_{0.8}Co_{0.7}$. (Mm) stands for *mischmetall*.

The rapid development of portable electronic equipment makes great demands on batteries. The success of the Ni–MH batteries has been great. Now the lithium battery is developing as a powerful alternative, as described in Chapter 12 Lithium. A comparison is made in Table 17.20.

Table 17.20 Comparison of NiCd, Ni-MH and Li-ion batteries

Type/Property	NiCd	MH	Lithium
Voltage, V	1.2	1.2	3.6
Energy density Wh/liter	150–170	250–294	292–370
Energy density Wh/kg	54–56	68–80	120–150
Cost	Low	Medium	High

Source: L. Y. Zhang in ref. [17.15] p. 235–257.

17.10.3.3 **Stores Hydrogen**

Alloys containing lanthanum may take up to 400 times their own volume of hydrogen gas, and the process is reversible. Therefore these alloys are important in energy systems. The alloy $LaNi_5$ and other similar alloys have been developed to store hydrogen in cars, creating an ecofriendly alternative to the conventional petrol-driven car. In fact, $LaNi_5$ saturated with hydrogen contains more hydrogen atoms per unit volume than does liquid hydrogen.

17.10.3.4 **An Alternative Electron Gun**

In electron microscopes electron beams are used instead of light and the “lens system” is composed of magnets instead of glass or quartz lenses. Originally the electrons were emitted from a glowing tungsten wire and this is still common. A more powerful alternative is *lanthanum boride* LaB_6, which is a conductor of electricity and at high temperature surpasses tungsten as an emitter of electrons.

17.10.3.5 **Biological Trace Element**

Lanthanum compounds are used as biological tracer elements. The lanthanum ion has about the same size as the calcium ion and can replace it in, for instance, nerve cells. The lanthanum ion may then be detected in living material using electron spin resonance spectroscopy.

17.10.4
Cerium

17.10.4.1 Mischmetall

Mischmetall is an alloy with the composition 45–50% Ce, 22–25% La, 18% Nd, 5% Pr, 1% Sm. It was already in use before the start of the 20th century. It was manufactured from monazite sand or bastnaesite. It was shown that cerium has the effect of obstructing grain coarsening in metallurgical applications and mischmetall became the form in which it was added to the melts of steel and other alloys. The technique for manufacturing tough spheroidal graphite iron was discovered when mischmetall was added to a conventional melt of cast iron. On solidification the graphite was not formed as flaked graphite but as spheroidal. Today cerium and mischmetall have been substituted by magnesium for this purpose.

Auer von Welsbach in Austria introduced Mischmetal alloyed with 30% iron during the first decade of the 20th century as a "pyrophoric" alloy. When filed or scratched, the small chips ignite spontaneously and form a flame. This alloy became the perfect lighter. It is gradually being relaced by the piezoelectric cigarette lighter.

17.10.4.2 Cerium Oxide in Glass and Plastic

In 1985, the glass industry accounted for 33% of the total world consumption of lanthanides. The use of lanthanides in glass applications increases. Owing to the still higher increase for other applications – magnets, batteries and hydrogen storage – the percentage of the total used for glass may nevertheless decrease.

The yellowish-white cerium oxide CeO_2 is considered to be the most efficient agent for polishing mirrors, lenses and other precision optics. The oxide is used as a slurry in water. Cerium oxide is also used as a decolorizer, *sapo vitri*, "soap for glass". If a glass melt contains divalent iron Fe^{2+} a bluish-green discoloration is visible. Added CeO_2 oxidizes the iron to Fe^{3+}. Its yellow color is very much fainter and the glass looks clean. In technological applications, for instance in aerospace windows, in ultraviolet sterilizers, in X-ray equipment or in television sets, 1–2% cerium oxide is always added to glass to absorb UV radiation. Cerium is also used to prevent polymers from darkening in sunlight and to suppress discoloration of television glass.

Ytttrium aluminate and yttrium silicate, doped with cerium, are used as luminescent materials for cathode ray tubes in radar systems. Together they cover a broad wavelength region.

17.10.4.3 Catalysts

Exhaust emission control for cars provides an increasing market for cerium. The superficial catalyst layer consists of palladium–rhodium and the carrier is usually an aluminum ceramic. In the 1990s it was found that co-sintering the carrier ceramics with 3.5% cerium oxide CeO_2 decreases the carbon monoxide emission and stabilizes the catalyst function at high temperatures. A further consequence is an improvement in the reduction of NOX to nitrogen gas. The consumption of RE metals is 25–30 g per emission control device. With the manufacture of 25 million cars per year (USA/Japan/Europe) this corresponds to an annual Ce consumption of about 1000 tonnes.

In so-called self-cleaning ovens cerium oxide is incorporated into the walls and catalyzes the oxidation of cooking residues. Cerium also has catalytic functions in the production of some organic chemicals, such as styrene from methylbenzene.

17.10.4.4 Changes Dangerous Red to Safe Red

Cadmium sulfide, cadmium red, has been popular as a red pigment for household wares and toys. The use of toxic cadmium is, however, no longer allowed for these purposes. It may be replaced by cerium sulfide CeS_2, giving a rich red color that is completely non-toxic. A range of colors can be obtained if traces of other lanthanides are added.

17.10.5
Praseodymium

17.10.5.1 Light and Color

The rare earth oxide Pr_2O_3 is among the most refractory substances known. Mischmetall, used in making cigarette lighters, contains about 5% praseodymium metal.

Most of the praseodymium applications utilize its influence on light and its color properties. It is used, along with other rare earths, in the core material for carbon arcs in film studio lights, searchlights and floodlights. Praseodymium produces brilliant colors in glasses and ceramics. Yellow didymium glass, containing praseodymium, absorbs infrared heat radiation and is therefore used in goggles to protec the eyes of welders and glass blowers.

17.10.6
Neodymium

17.10.6.1 Many Different Uses ...

In yttrium aluminum garnet $Y_3A_{l5}O_{12}$, Nd^{3+} ions can replace yttrium in the lattice up to a maximum doping level of 1.5%. Then a YAG laser is obtained [17.11]. A typical laser of this type is a rod some few centimeters long with a mirror at each end, one of which is partly transmitting. When the rod is irradiated with a pulse of light from a normal lamp the Nd^{3+} ions are excited and an intense beam of monochromatic laser radiation emerges from the end of the rod. The wavelength is 1.06 μm (near infrared). The generated laser radiation can be used to cut metals and it is also used in medicine, dermatology, gynecology and urology as well as in plastic surgery.

Neodymium is also a component of the yellow didymium glass described above.

Neodymium oxide is used to color optical glass and ceramics. Many shades, ranging from pure violet through wine-red to warm gray, can be obtained. Light transmitted through neodymium glass shows unusually sharp absorption bands. The glass has been used in astronomical work to produce sharp bands by which spectral lines may be calibrated.

17.10.6.2 ... And One Very Special. The Strongest Magnet

Neodymium's greatest use is in the preparation of an intermetallic compound with iron and boron. This is ferromagnetic and gives the strongest commercial permanent magnets available. The material was developed in military research stations in the United States and the Soviet Union. It was presented in 1983 at a conference in Pittsburgh and within some weeks was being manufactured for civilian purposes. Both Sumitomo and General Motors chose the neodymium compound as base material for high-quality permanent magnets – NIB magnets. They saw possible applications in modern vehicles: fuel pumps, window lifters, door locks and so on.

The magnetic material may be manufactured by two different methods. One involves conventional powder techniques – grinding, pressing and sintering. The other is a rapid solidification process known as *spinning atomization*. A RE–Fe–B alloy is melted and then ejected under pressure from a nozzle onto the surface of a water-cooled rotating metal wheel. The material solidifies rapidly into a thin metal ribbon, approximately 35 µm thick and 1–3 mm wide. The flow rate and the speed of the rotating wheel influence the quench rate (and hence the microstructure) so these process parameters are carefully controlled to achieve the optimum magnetic properties. During experiments with the Nd–Fe–B system the magnetically hard phase $Nd_2Fe_{14}B$ was discovered. An American enterprise, Magnequench International, MQI, has developed this new technique.

The market growth for Nd–Fe–B magnets has been 25–30% per year. From the first laboratory manufacture in 1983, production had increased 10 years later to about 3000 tonnes per year.

17.10.7
Promethium

17.10.7.1 Makes the Hour Hand Visible

For natural reasons, promethium is not available in large quantities. All its isotopes are radioactive (half-life in parenthesis): ^{145}Pm (17.7 years), ^{146}Pm (5.4 years), ^{147}Pm (2.6 years).

The isotope ^{147}Pm is commercially available and has found some use. Its emission of low-energy β-particles is used industrially to measure the thickness of strip steel and paper. To some extent it is also used in miniature batteries with a useful life of about five years. These have been tested for such diverse purposes as pacemakers and guided missiles. A paint containing ^{147}Pm and a material that fluoresces with a bluish-green color after being hit by the β-particles may be used for hour hands and dials in watches. Promethium has replaced radium for reasons of health.

17.10.8
Samarium

17.10.8.1 Samarium–Cobalt Magnets

In the early 1970s it was discovered that the intermetallic compound $SmCo_5$ has markedly ferromagnetic properties and manufacture began. It turned out that the compound Sm_2Co_{17} with small amounts of iron, copper and zirconium has even better magnetic properties. When Nd–Fe–B magnets were introduced and became widely used in the 1980s, the demand for samarium–cobalt magnets was restricted. However, Sm–Co magnets continue to be required and used in small electric motors and for all kinds of fine mechanics. We all use them in quartz watches, walkie-talkies, camera shutters, fax machines and electric motors for hard disks and CD players. They are also components in relays for automatic production equipment. A special advantage of the Sm–Co magnet material is its very high Curie temperature. The magnets keep their ferromagnetism up to 700°C and may be used in microwave applications.

17.10.8.2 Measuring the Age of the Earth

The radioactive samarium isotope ^{147}Sm, found in nature, disintegrates very slowly. Its half-life is $1.06 \cdot 10^{11}$ years. On decay the stable neodymium isotope ^{143}Nd is formed. The reaction is used to determine the age of minerals and rocks, as described in Chapter 4 Geochemistry.

17.10.9
Europium

17.10.9.1 The Red Color on Television Screens

The compounds of many trivalent lanthanide ions fluoresce after stimulation with UV irradiation or electrical discharge. The fluorescence arises from transitions within the f-electron subshell in the ion. This process is especially typical of europium and terbium ions and is used in color television sets. The TV screens are made up of a large number of tiny clusters, each containing three phospor dots, emitting red, green or blue light. The red ones are made of yttrium oxysulfide Y_2O_2S, doped with europium, the green ones of lanthanum oxydisulfide La_2O_2S, doped with terbium. The blue dots have no lanthanide component but are made of zinc sulfide containing silver and aluminum. The television receiver has three separate cathode ray tubes, one for each color. Through different groups of tiny holes in a mask of metal behind the screen, electrons from the red cathode reach the red dots, and similarly for the other two colors. As is well known, cathode rays tubes are being replaced by modern flat panel displays. In these, organic borates of europium, terbium and cerium are used for color generation.

17.10.9.2 Europium in Special Lamps

In energy-saving lamps of the so called trichromatic type, the blue color comes from strontium phosphate, doped with europium, the red from a yttrium–europium mixture and the green from a lanthanum–cerium–terbium mixture. An 18-watt lamp of this type gives as much illumination as a traditional 75-watt lamp and may last for five years.

In the high-pressure mercury lamps for street lighting, yttrium vanadate doped with europium is deposited on the glass. This makes the light brilliant white and more natural.

17.10.10
Gadolinium

17.10.10.1 Ecofriendly Fridge-freezers in the Near Future?

In conventional fridge-freezers some type of CFC, e.g. dichlorodifluoromethane CCl_2F_2 (refrigerant-12), is used. The refrigerator works in four steps: *vaporizing* the CFC or alternative in order to cool the foodstuffs, c*ompressing* the vapor, condensing and *expansion*. It has recently become apparent that gaseous CFCs, which have a very long lifetime, may rise to the stratosphere and contribute to ozone depletion. Because of that the production of CFCs is banned in most countries. Can the conventional refrigeration technique be replaced by another quite different and more ecofriendly procedure?

When a ferromagnetic material is placed in a magnetic field at a temperature just below its Curie temperature, its unpaired electrons arrange their spins parallel with the magnetic field. As regards iron this holds for 3d-electrons, for a lanthanide it is valid for 4f-electrons. This leads to a certain heating of the material. When the magnetic field is switched off the electrons rearrange, which makes the material cooler. This has similarities with the process in a refrigerator. The lanthanides with their unique ferromagnetic properties open up new, bold solutions. But which RE metal?

In the AMR project, *Active Magnetic Refrigerator*, described by K. A. Gschneider Jr and V. K. Pecharsky in ref. [17.15], pp.209–221 it has been found that the temperature range obtained by the AMR technique is around the Curie temperature of the actual metal. Gadolinium has a Curie temperature of +17°C. For cooling from room temperature to 0°C a regenerator consisting of just gadolinium would suffice for a refrigerator to store food but not to freeze it. To cool below 0°C a second material along with gadolinium is needed. A 27% Dy–Gd alloy would make a temperature of –8°C possible, thus allowing the freezing of food. A demonstration and experimental unit is shown in Figure 17.20.

Research at Ames Laboratory has continued and on 7 December 7 2001 Ames Laboratory announced that the Magnetic Refrigerator has been successfully tested [17.16]. Karl Gschneidner Jr. and Kerry Gibson gave the following information:

> Instead of ozone-depleting refrigerants and energy-consuming compressors found in conventional vapor-cycle refrigerators, this new style of refrigerator uses gadolinium metal that heats up when exposed to a magnetic field, then cools down when the magnetic field is removed. The new refrigerator is undergoing further testing. The goal is to achieve larger temperature swings that will allow the technology to provide the cooling power required for spe-

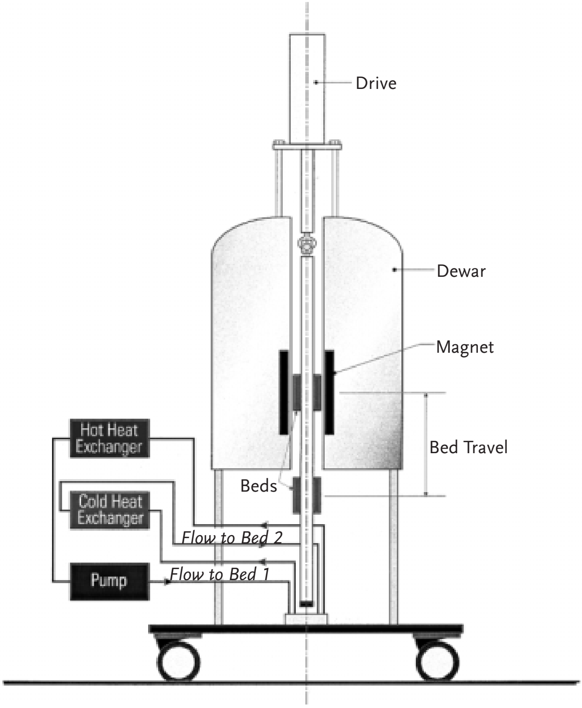

Figure 17.20 Magnetic refrigeration demonstration unit. (Reprinted from *Science and Technology at the Ames Laboratory*, Inquiry, 1997 pp. 4–8 with permission of Ames Laboratory, Iowa State University, USA.)

cific markets, such as home refrigerators, air conditioning, electronics cooling, and fluid chilling.

The magnetic refrigerator employs a rotary design. It consists of a wheel that contains segments of gadolinium powder and a high-powered, rare earth permanent magnet. The wheel is arranged to pass through a gap in the magnet where the magnetic field is concentrated. As it passes through this field, the gadolinium in the wheel exhibits a large magnetocaloric effect – it heats up. After the gadolinium enters the field, water is circulated to draw the heat out of the metal. As the material leaves the magnetic field, the material cools further as a result of the magnetocaloric effect. A second stream of water is then cooled by the gadolinium. This water is then circulated through the refrigerator's cooling coils. The overall result is a compact unit that runs virtually silent and nearly vibration free, without the use of ozone-depleting gases, a dramatic change from the vapor-compression-style refrigeration technology in use today.

17.10.11
Terbium

17.10.11.1 Magnetostriction

Terbium and dysprosium find considerable use for magnetostrictive materials. Magnetostriction is the dimension change caused by magnetization. The first observation of a magnetostrictive effect was in 1842 when James Joule found that a sample of nickel changed in length when it was magnetized. Subsequently cobalt, iron and alloys of these materials were found to show a significant magnetostrictive effect too (Figure 17.21). The length changes were small, less than 0.05 mm/m.

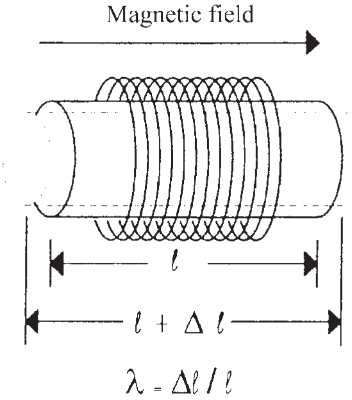

Figure 17.21 Magnetostriction of a magnetic rod [17.17].

One of the first practical applications of magnetostriction was its use in SONAR[5] devices in echolocation during the Second World War. The magnetostriction values of the nickel-based materials used were too low for a wide application of the technique.

In the 1960s the rare earth elements terbium (Tb) and dysprosium (Dy) were found to have very high magnetostrictive strains but they could not be used, as their Curie temperatures are very low, −43 and −188°C respectively. Above the Curie temperature there is no ferromagnetism and no magnetostriction. The observation, however, started an energetic search for materials that would have a large magnetostrictive strain at temperatures above room temperature. The intermetallic compounds $TbFe_2$ and $DyFe_2$ matched the demands, as their Curie temperatures are +431 and +362°C respectively. These materials, however, required very large magnetic fields to generate large strains. By combining the two compounds, the magnetic field required to produce the requisite strains was considerably reduced. The resulting alloy $Tb_{0.27}Dy_{0.73}Fe_{1.95}$, at present the most widely used magnetostrictive material, gives

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[5] Sonar, acronym for SOund Navigation And Ranging, a detection system based on the reflection of underwater sound waves. A typical sonar system emits ultrasonic pulses by using a submerged radiating device; it listens with a sensitive microphone, or hydrophone, for reflected pulses from potential obstacles or submarines.

strains as high as 1.5 mm/m. This is the largest room-temperature strain of any commercially produced magnetostrictive material. Its trade name is *Terfenol-D*, a designation derived from terbium (TER), iron (FE), Naval Ordinance Labs (NOL), and dysprosium (D).

17.10.11.2 Terbium Alloys with Good Memory

During the 1990s, two types of *MiniDiscs* were developed, one a *premastered MD*, similar to a CD in operation and manufacture, the other a *recordable MD*, which can be recorded on repeatedly. The discs are small, diameter 2.5 in (64 mm). A magnetic recording layer of *terbium–iron–cobalt* or *terbium–gadolinium–iron–cobalt* is applied by a PVD technique (Physical Vapor Deposition). A magnetic head captures signals and transfers them for storage in the magnetic alloy layer. The readout of the previously recorded magnetic regions occurs by a laser beam.

Formatting of the disc is carried out by heating with a laser beam to a temperature above the Curie temperature 180°C of the magnetic layer. All information on the disc is removed when the layer has lost its ferromagnetism. At room temperature the disc is again ready for recording information.

17.10.12
Dysprosium

17.10.12.1 Not Many Applications

Dysprosium has not yet found many applications. One important use, however, is in magnetostrictive materials, which have been described in the terbium section above. Another is in the dysprosium oxide–nickel cermet[6], which is used for cooling nuclear reactor rods. This makes use of dysprosium's ability to absorb neutrons.

Dysprosium iodide DyI_3, added to halide discharge lamps, dissociates at the high temperature to dysprosium atoms, which absorb energy and emit it as a very intense, white light.

17.10.13
Holmium

17.10.13.1 Metal in Superconducting Research Magnets

Holmium has almost no commercial applications, although it has unusual magnetic properties, which are used in the pole pieces of superconducting research magnets (Tallahassee, Florida). One variant of the YAG laser material is also holmium doped.

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[6] Cermet is a composite material, co-sintered with a ceramic (an oxide) and a metal powder.

17.10. 14 Erbium

17.10.14.1 Color for Beauty and Protection

Erbium has a limited use. It is, however, possible to exploit the fact that, like many lanthanides, the element has specific light absorption characteristics. Erbium oxide, itself rose pink, colors glass and glazing. This glass absorbs infrared radiation.

17.10.14.2 Telecommunications

In laser technology, erbium-doped fiber lasers provide an advantage in operating near the 1.5-μm wavelength region. Recently, erbium doping of silicon has been tested for special LEDs (light emission diodes). The special feature of erbium is that it has an electron transition in the f-subshell, corresponding to a wavelength of 1.54 μm, a standard wavelength for telecommunications. This is regarded as a very promising development.

17.10.15
Thulium

17.10.15.1 Do We Need Thulium?

The rare metal thulium has almost no practical applications. What it can provide is available –more cheaply – from other lanthanides. It has been suggested, however, that the metal could be incorporated in ceramics, making them magnetic. If so, this material could be used in microwave equipment. The γ-radiation from the radioactive isotope ^{170}Tm has been examined for use in materials testing and as a portable X-ray source for medical use.

17.10.16
Ytterbium

17.10.16.1 A Modern Dental Filling

Ytterbium fluoride is non-toxic and inert, and is not transparent to X-rays. Because of that the compound has been tested as an additive to composite plastic dental fillings. Traces of fluoride ions are continuously set free, giving protection against caries. In addition the ytterbium fluoride gives good X-ray contrast.

17.10.17
Lutetium

17.10.17.1 Catalysts

There are few applications for lutetium. The supply is limited and the price high. If the Lu atom is activated by thermal neutrons its nucleus emits a pure β-radiation. In this form the metal can be used as a catalyst for cracking and polymerization.

17.11
Prices – Not Just a Question of Metal Content in the Earth's Crust

In Table 17.21 the rare earth metals are arranged in order of their mean content in the earth's crust.

The price per kilogram of a rare earth metal naturally depends on the purity and quantity required. Price is also a function of the accessibility of the element, which in turn is a function of its mean content in the earth's crust and also, to a high degree, of how the actual metal occurs. For instance scandium – fifth in abundance among all rare earth metals (see Table 17.21) – occurs in many ores in trace amounts and is produced exclusively as a by-product during the processing of various ores. Thus its accessibility is in no way reflected by its rather high mean content in the crust. As a consequence the price is high. A 1-kg quantity of 99–99.999% scandium metal costs US$2000–12 000.

For yttrium, on the other hand – fourth among rare earths and almost as rare as scandium – large resources are available as monazite, xenotime and ion-adsorption ore. A quantity of 2400 tonnes of yttrium oxide was produced in 2000, of which 2300 tonnes was mined in China. Of course, this concentrated production influences the price. In 5-kg quantities the price for 99.9% yttrium metal with less than 0.15% oxygen is US$100–150 per kilogram.

New large-scale applications reduce the price. Since neodymium became essential for magnets the quantities produced have increased. The Nd metal price is US$10/kg in bulk, and US$125/kg in quantities of 1 kg.

Table 17.21 Rare earth metals – mean contents in the earth's crust

Metal	Ranking order in the earth's crust		Mean content in the earth's crust ppm
	Among the rare earths	Among all elements	
Cerium	1	25	66.5
Neodymium	2	27	41.5
Lanthanum	3	28	39
Yttrium	4	29	33
Scandium	5	31	22
Praseodymium	6	39	9.2
Samarium	7	40	7.1
Gadolinium	8	41	6.2
Dysprosium	9	42	5.2
Erbium	10	43–44	3.5
Ytterbium	11	45	3.2
Europium	12	52–53	2
Holmium	13	56	1.3
Terbium	14	58–59	1.2
Lutetium	15	61	0.8
Thulium	16	62	0.5
Promethium	17	89–92	–

For lutetium – very rare and with few applications – the price is US$3500–5000/kg in kilogram amounts, depending on the purity.

17.12
Biological Roles for Rare Earth Elements

The content of rare earth metal ions in natural water is very low, as the minerals are almost insoluble in water. The elements are non-toxic and not essential for life.

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18
Titanium

18.1 Ti
Facts about Titanium

18.1.1 Ti
The Element

Symbol:	Ti
Atomic number:	22
Atomic weight:	47.88
Ground state electron configuration:	$[Ar]3d^2 4s^2$
Crystal structure:	Hexagonal hcp with $a = 2.95$ Å, $c = 4.69$ Å

18.1.2 Ti
Discovery and Occurrence

Discovery: A black mineral (*ilmenite*) containing an earlier unknown element was discovered in 1791 by the Reverend W. Gregor in Creed, Cornwall, England. In 1795 M. H. Klaproth in Berlin identified the same element in a Hungarian mineral (*rutile*). Klaproth selected the name titanium for the new element. A technical/commercial method for titanium manufacturing was introduced in the 1940s by W. Kroll, Luxembourg.

Most important mineral: Ilmenite $FeTiO_3$ (Figure M29)
Rutile TiO_2 (Figure M28)
Titanite, sphene $CaTiSiO_5$

Ranking in order of abundance in earth crust:	9
Mean content in earth crust:	5650 ppm (g/tonne)
Mean content in oceans:	0.001 ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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18.1.3 Ti

Chemical Characterization

Titanium is a white, lustrous metal with low density and high strength. Its oxide TiO_2, known as titanium white, is used as a brilliant white pigment. Titanium is used – as metal or in alloys – for applications where combinations of corrosion resistance, low weight and high strength are important. Such is the case in jet aircraft, both conventional and supersonic. Titanium is also widely used in missiles and space capsules. The Mercury, Gemini and Apollo capsules were made largely of titanium. In jet engines compressor blades, discs, inlet guide and vanes are typical applications for titanium, alloyed with aluminum and vanadium. The metal is also used in medicine for implants of jaws, teeth and heart pacemaker capsules.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ti^{IV} as in TiO_2 and $TiCl_4$	$Ti(g) \rightarrow Ti^+(g) + e^-$	659	$Ti(g) + e^- \rightarrow Ti^-(g)$
Ti^{III} as in Ti_2O_3 and $TiCl_3$	$Ti^+(g) \rightarrow Ti^{2+}(g) + e^-$	1310	–7.6
Ti^{II} as in TiO and $TiCl_2$	$Ti^{2+}(g) \rightarrow Ti^{3+}(g) + e^-$	2653	
	$Ti^{3+}(g) \rightarrow Ti^{4+}(g) + e^-$	4175	
	$Ti^{4+}(g) \rightarrow Ti^{5+}(g) + e^-$	9581	

Standard reduction potential:	$TiO^{2+}(aq) + 2H^+(aq) + 4e^- \rightarrow Ti(s) + H_2O(l)$	$E^0 = -0.86$ V
	$Ti^{2+}(aq) + 2e^- \rightarrow Ti(s)$	$E^0 = -1.63$ V
Electronegativity (Pauling):	1.54	
Radii of atoms and ions:	Atomic:	140 pm
(WebElements™)	Covalent:	136 pm
	Ti^{2+} (6-coordinate, octahedral):	100 pm
	Ti^{3+} (6-coordinate, octahedral):	81 pm
	Ti^{4+} (4-coordinate, tetrahedral):	56 pm
	Ti^{4+} (6-coordinate, octahedral):	74.5 pm
	Ti^{4+} (8-coordinate):	88 pm

18.1.4 Ti
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
4507 kg m^{-3} 4.51 g cm^{-3}	10.64 cm^3	1941 K 1668 °C	3560 K 3287 °C	522 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
26	22	21	19	21

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$4.5 \cdot 10^{-6}$	$8.6 \cdot 10^{-6}$	$9.9 \cdot 10^{-6}$	$11.1 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
46	390	580	900	1420	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+40.1 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
116 GPa	44 GPa	106 GPa	0.32

18.1.5 Ti
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	19.2 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	425 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	470 kJmol^{-1}
Entropy S^0 at 298 K	30.63 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	14.31	25.02	28.41	32.68	46.80	46.80

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$Ti + O_2 \rightarrow TiO_2$	−889	−845	−766	−678	−594

18.1.6 Ti
Nuclear Properties and X-ray

Isotope range, natural and artificial	39–57

Naturally occuring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**
^{46}Ti	Stable	8.0	+0	–
^{47}Ti	Stable	7.3	−5/2	−0.7885
^{48}Ti	Stable	73.8	+0	–
^{49}Ti	Stable	5.5	−7/2	−1.104
^{50}Ti	Stable	5.4	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{47}Ti	^{49}Ti
Reference compound	$TiCl_4$+C_6D_6	
Frequency MHz (^{1}H = 100 MHz)	5.638	5.639
Receptivity D^P relative to ^{1}H = 1.00	$1.53 \cdot 10^{-4}$	$2.18 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	1.19	0.796
Magnetogyric ratio, radT^{-1}s^{-1}	$-1.511 \cdot 10^7$	$-1.252 \cdot 10^7$
Nuclear quadropole moment, barn	0.29	0.24

Characteristic X-radiation **Z**	 **Element**	 **Kα_2 keV**
21	Sc	4.086
22	Ti	4.505
23	V	4.944

X-ray radiation absorbed by the element **Incoming radiation energy**	 **Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	201
17.37 keV (MoKα_2)	23.7

Neutron absorption	**Thermal neutron capture cross section**	6.1 barns

18.2
Discovery

18.2.1
Mind and Matter

William Gregor was born in Cornwall in 1761 and remained faithful to his home area all his life. For many years he was vicar of Creed, a parish in Cornwall. He was a man of varied interests: landscape painting, music and also a great interest in the geology of his home district. He founded the Royal Geological Society of Cornwall and he acquired such a wide knowledge of mineralogy that Berzelius talked about Gregor as “one of England’s famous mineralogists”.

In the Menachan valley in Gregor’s own parish he found and investigated a black sand and published his results in the German Science Journal Crell’s Annalen in 1791. A summary:

> After repeated treatment of the sand with concentrated sulfuric acid and careful dissolving in diluted sulfuric acid a white residue is obtained that is reddish after annealing. This residue can be dissolved in concentrated sulfuric acid. When the solution is diluted with water it is uncolored. With metallic reducing agents such as zinc, iron or tin it becomes purple colored. In air this color disappears, more rapidly on addition of oxidizing agents. If, on the other hand, the colorless solution is boiled a white precipitate is formed.

The vicar refers to his friend the famous mineralogist Johan Hawkins, who says that he has never seen a mineral like this. It must contain an unknown metal! Gregor proposes that the name of this new element shall be menachanite after the finding-place. Gregor’s description of the dark mineral from the Menachan valley and his correct supposition that it contained a new element was not paid much attention, despite its publication in *Crell’s Annalen*. The discovery was forgotten. Gregor died of tuberculosis in 1817. Today we know that Gregor’s mineral is identical with ilmenite, iron titanium oxide $FeTiO_3$.

18.2.2
Gregor's Menachanite Returns as Klaproth's Titanium

Martin Heinrich Klaproth (Figure 18.1) was a man of mark in chemistry and, moreover, an imposing personality. In 1810, at the age of 67, he became the first holder of the newly established professorship in chemistry at the University of Berlin. He worked there until his death in 1817. He played an important role in the discovery of uranium and titanium.

Figure 18.1 Martin Heinrich Klaproth (1743–1817).

In 1795, four years after Gregor's publication of his investigation of the black sand, Klaproth obtained a sample of a Hungarian mineral, a rutile. He found and isolated a new oxide in it. Klaproth was first to point out that his new oxide was not new. It was actually identical with the oxide that Gregor had earlier isolated from the black mineral in the Menachan valley.

Klaproth gave the metal, whose oxide Gregor and he had independently discovered, the name titanium. He said that there is, of course, no name that can claim to express a new element's characteristic properties. Because of that it is justified to select a name without a special meaning in relation to the element. "As was the case after my discovery of uranium I selected a name from mythology, where the Titans were the first sons of the earth." In Greek mythology the Titans were children of Uranos and the earth goddess Gaia.

The Titans are obviously very scattered. Every chemist who has worked on the analysis of clays has observed that titanium is detectable in almost every sample.

18.2.3
Hunting Titanium Metal

When titanium dioxide TiO_2 had been prepared from ilmenite and rutile it became an important task for chemistry and metallurgy to produce the element in metallic form. The trials involved great difficulties that we, with our present knowledge, fully understand. The background is described in Chapter 3, section 3.4.2.

Klaproth and many contemporary chemists tried in vain to isolate titanium metal, but in 1825 Berzelius succeeded in reducing potassium hexafluorotitanate K_2TiF_6 with metallic potassium. The titanium metal obtained, however, was very impure. The same method was used two decades later by Friedrich Wöhler and Sainte-Claire Deville. They got a powder with a metallic luster and thought at first that their preparation was pure titanium metal, until they found that the reaction product was rich in nitrides. Welders of titanium components today recognize the situation. Even under a protective atmosphere of argon or helium, the slightest traces of nitrogen lead to the formation of yellow titanium nitride.

In 1887, two scientists in Uppsala University introduced a new technique with which they could prepare pure titanium metal. Their method was a forerunner of the Kroll process, the large-scale technique for titanium production today.

> Lars Fredrik Nilson (1840–1899) made extensive investigations into unusual elements and he discovered the rare earth metal scandium. Towards the end of his life he was active in the preparation of rules for using Alfred Nobel's legacy. His work is described in more detail in Chapter 17 Rare Earth Metals.
>
> Sven-Otto Pettersson (1848–1941), professor in Uppsala and Stockholm, was originally a distinguished oceanographer, but he co-operated with Nilson in chemical research regarding unusual elements as titanium.

Nilson and Pettersson prepared titanium chloride $TiCl_4$, and reduced it with sodium metal in a closed steel cylinder. They obtained titanium metal with "only" 5% contamination.

In 1910. Matthew Arnold Hunter [18.1] used the same method but he used very pure titanium chloride, which was reduced with sodium under high pressure in a closed steel container (Figure 18.2). In a typical charge he mixed 500 g $TiCl_4$ and 245 g sodium metal. After heating to dull red heat an explosive reaction started and ended immediately. After the mixture had been cooled and washed with water, small beads of pure metallic titanium were obtained.

In 1925 the two Dutchmen van Arkel and de Boer succeeded in preparing perfectly pure titanium metal with their iodide dissociation process, described in Chapter 19 Zirconium.

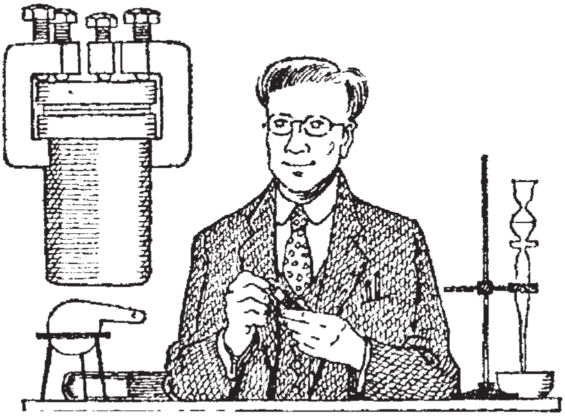


Figure 18.2 Hunter and his steel bomb.

18.3
Titanium Minerals

18.3.1
A Widely Distributed Metal

Titanium is relatively abundant and widely distributed in the earth's crust. In igneous rocks titanium forms the acidic component of basic magmas and the basic component of acidic magmas. In the first case titanates are present, the most important of which are ilmenite $FeTiO_3$ and perovskite $CaTiO_3$. In the second case oxides are formed. Among different minerals with the formula TiO_2, rutile (Figure M28) is the most important. Other variants, with other crystal structures but the same composition TiO_2, are brookite and anatase.

Rutile TiO_2 is a mineral with a metallic or diamond luster and a blood-red to yellowish-brown color. The Latin word rutilus just means golden red. Beautiful specimens can be used as jewelry.

Ilmenite (Figure M29) is a black mineral with a metallic appearance. It can be weakly magnetic. It was originally found in the Ilmen Mountains in the Urals, from where the mineral takes its name. Ilmenite commonly contains 32% titanium and 37% iron but the composition varies considerably, since iron and titanium oxides form a series of solid solutions.

Ilmenite, like rutile, is found in the sand deposits of beaches and rivers but what makes ilmenite particularly important is that it frequently exists crystalline as massive ore deposits, often together with hematite or magnetite.

18.3.2
Production of Mineral Concentrates

Weathering and erosion release the titanium-containing grains in the rocks, and the combined action of rivers, seas and wind concentrate the heavier minerals in placer deposits and ocean beaches. The mining of titanium minerals mainly uses surface methods. The placer deposits in beach sands are collected with dredges. Heavy minerals are then separated from the lighter quartz and clay by gravity spirals or magnetic separators. The concentrate is treated in an ore-dressing site and separated into individual mineral components: rutile, ilmenite, zircon, monazite, etc. The leading production countries are Australia, Norway, Ukraine, the USA and India.

A second very important source of titanium is the titaniferous slag produced by pyrometallurgical processing of ilmenite-containing iron ores, titanomagnetites and titanohematites. This slag can contain up to 95% TiO_2. The biggest producers of this type of titanium material are South Africa and Canada.

Total world production of titanium raw materials in the year 2000 are reported [18.3] in Table 18.1.

Table 18.1 Production of raw materials for titanium in the year 2000

Type	Production, million tonnes	Details
Ilmenite	4.8	Australia 2.2, Norway 0.6, Ukraine 0.6, USA 0.4, India 0.4
Rutile	0.4	Australia 0.2, South Africa 0.1
Titaniferous slag	2.1	South Africa 1.1, Canada 1.0

The demand for TiO_2 is much greater than the annual rutile production from mining, so synthetic TiO_2 is produced in a large scale from ilmenite and titaniferous slag.

18.4
Production of Titanium Oxide – Titanium White

Titanium oxide is a very important inorganic pigment, titanium white. This has led to an increasing demand for raw materials with high TiO_2 contents. About 95% of all titanium is used as titanium dioxide pigment. As already mentioned there is not enough natural rutile to meet the demand and it has therefore gradually been necessary to make up the shortfall with a synthetic alternative. The main method is to produce TiO_2 from titanium slag. The slag is produced in a metallurgical process in which iron is removed from ilmenite or titano-magnetites. In an electric furnace the ore is reduced by coke to metallic iron at 1200–1600°C. A titanium-free pig iron is produced together with a slag rich in TiO_2. Raw materials of this type are produced in Canada and South Africa and to a smaller extent in other countries. An alternative method is the “magnetic” one. Ilmenite is mixed with carbon powder and the mixture is heated to 1200°C. Then the iron oxide is reduced to metal, which is separated from TiO_2 by a magnetic method. Any remaining iron oxide is removed with sulfuric acid.

The final production of TiO_2 for pigments is carried out by two different methods. In the sulfate process (the older method) the raw titanium oxide is treated with concentrated sulfuric acid at about 200°C. Relatively pure titanium hydroxide is precipitated from the sulfate solution by hydrolysis. In a more modern method the raw titanium oxide (the slag) is chlorinated. The $TiCl_4$ formed is separated from other chlorides by distillation. The $TiCl_4$ is burnt at 900–1400°C to form a very pure TiO_2 pigment. In 2000, France, Germany, Japan, the UK and the USA were the leading producing countries of TiO_2 pigment.

18.5
Titanium Metals and Alloys

18.5.1
Chlorine Metallurgy – The Kroll Process

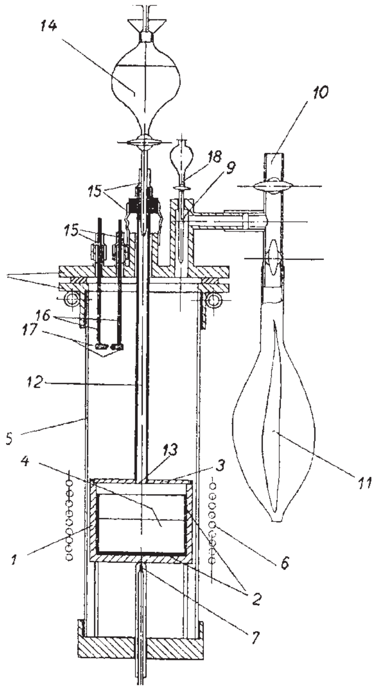
William Kroll (1889–1973) from Luxembourg described an economically and technically feasible way of producing titanium on a largescale [18.2]. This opened the way to the exploitation of titanium. The first step in the Kroll process is the manufacture of titanium chloride. Chlorine gas is passed through a mixture of titanium oxide and carbon in high towers at a temperature of 900°C.

$$TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$$

> At first Kroll used calcium to reduce the $TiCl_4$ to titanium metal but changed to magnesium. The first reaction equipment described in ref. [18.2] is shown in Figure 18.3. The reaction vessel was first exhausted with an oil pump down to a pressure of 0.1 mmHg (0.013 kPa). The vessel then was filled with commercial argon (96% Ar), which was purified by striking an arc between two calcium electrodes mounted inside the vessel. After this calcium scavenging, a few drops of $TiCl_4$ were dripped into the reaction chamber to remove the last traces of moisture. The thick-walled steel crucible, lined with molybdenum sheet and containing magnesium, was heated by a high frequency current to 700°C. The $TiCl_4$ was introduced drop by drop onto the molten magnesium. The following reaction occurred:
>
> $$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$
>
> During the reaction the temperature rose considerably and could be 1100°C by the end of the reaction.

In the modern production process the gaseous titanium chloride is condensed to a liquid that is stored in big tanks. Gaseous $TiCl_4$ is passed at 850°C into molten magnesium.

Electrolysis of magnesium chloride is used to separate chlorine and magnesium, which are recovered and recycled.



1 thick-walled steel crucible.
2 molybdenum sheet.
3 iron sheet cover.
4 magnesium.
5 quartz tube.
6 high frequency induction coil.
7 thermocouple.
8 head of quartz tube with water-cooling.
9 connecting tube to argon supply or vacuum pump.
10 to the oil vacuum pump.
11 rubber balloon for argon.
12 iron tube inlet for titanium tetrachloride.
13 lower open end of tube 12.
14 funnel with TiCl4 supply.
15 flexible tubes.
16 electrodes.
17 calcium rods.
18 small funnel with $TiCl_4$ supply (for gettering).

Figure 18.3 Kroll's first apparatus for producing malleable titanium.

This invention created a new technique, chlorine metallurgy, and the whole industrial world showed a keen interest in it (Figure 18.4), for the production of not only titanium but also other expensive metals and alloys of great technical importance.

The metal obtained from the Kroll process has the character of a crude titanium sponge.

Large-scale producers of purified titanium sponge are Russia (20 000 tonnes in the year 2000) Japan (19 000), Kazakhstan (8000), Ukraine (4000) and China (1900). The production in the USA is not published [18.3] but the production capacity is estimated to 21 600 tonnes/year.

Figure. 18.4 Discussion about chlorine metallurgy on the streets of Paris in October 1956. From left: Olof Drakenberg, MD for the Swedish company Ferrolegeringar, Dr Wilhelm Kroll and Per Enghag, researcher at Ferrolegeringar and teacher at the School of Mining and Metallurgy in Filipstad, Sweden.

18.5.2
Purification and Melting

The crude titanium sponge is contaminated by magnesium metal and chlorides of magnesium and titanium. Vacuum distillation at 900–1000°C removes the impurities and purified titanium sponge is obtained. The step from sponge to molten metal is usually taken by vacuum arc melting. Consumable electrodes are made by mixing and compacting titanium sponge, titanium scrap and alloying components. The electrode is inserted as the negative pole in a vacuum arc furnace and melting takes place when the arc is formed (Figure 18.5). The process occurs at a pressure 1 Pa (0.0075 mmHg or torr) with currents from 15 to 40 kA. The solid titanium is re-melted in a similar manner to improve the homogeneity. The titanium metal or alloy thus obtained can now be used for further processing and production of titanium components.

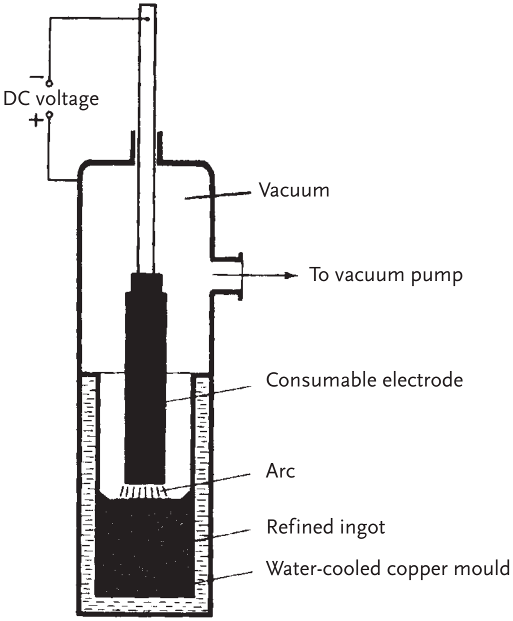


Figure 18.5 The principle of the vacuum arc furnace.

18.5.3
Ferrotitanium

Ferrotitanium alloys are used in the production of titanium alloyed steels. Ferrotitanium with 70% Ti is manufactured in an induction furnace. The raw materials are iron scrap, titanium scrap and titanium sponge. Alternatively an aluminothermic process can be used. In that case the reaction occurs between aluminum powder, ilmenite $FeTiO_3$ and titanium sponge. Ferrotitanium alloys with lower Ti contents are manufactured in this way.

18.6
Modern Uses of Titanium and Titanium Compounds

18.6.1
Titanium White – Titanium Oxide

The TiO_2 pigment gives the best opaque whiteness of all pigments. This use is so widespread that it consumes more than 90% of all the titanium oxide produced. The pigment is used for paints, plastics and fine paper but also to make porcelain glazes opaquely white. Titanium oxide is also part of rutile electrodes for welding.

18.6.2
Corrosion-resistant Metal

Titanium metal has a pronounced tendency for spontaneous passivation[1] and this gives the metal a very good corrosion resistance. The passive film consists of TiO_2 with a thickness of 10–100 Å. The film has a remarkable stability in chloride-containing environments. In chemical plants commercially pure and palladium-containing titanium lead to an increased lifetime, reduced maintenance and reduced iron contamination of products. This has made titanium a very important alternative material in equipment for the production of cellulose.

The very good corrosion resistance in seawater and the fact that titanium metal is non-magnetic has naturally interested designers of submarines.

18.6.3
Compatibility with Human Tissue

The stable passive layer is also helpful in the human body. Its fluids do not "see" a metal in the titanium component but very inert titanium oxide. No disruptive metal ions are dissolved and rejection reactions are eliminated. In medicine, therefore, implants of jaws and teeth, pins for fixing broken bones and heart pacemaker capsules, as well as surgical instruments, are manufactured from titanium or the alloy Ti6Al4V (see below).

18.6.4
A Metal for the Space Age

The most common titanium alloy for conventional machine components, screws and springs, is Ti6Al4V (titanium with 6% Al and 4% V). This alloy can be used at a working temperature of 350°C. 600°C can be reached with the alloy Ti6Al12Sn4Zr2Mo. Owing to titanium's great affinity for oxygen and nitrogen, all welding must be carried out under an inert gas.

The largest consumer of titanium alloys is the aircraft industry. Titanium has a density of 4.5 g/cm^3 and is thus considerably lighter than steel, density 7.85 g/cm^3. It is true that aluminum is still lighter, density 2.7 g/cm^3, but titanium alloys are stronger and can be used at higher temperatures than aluminum alloys. The combination of low weight and high-temperature strength is important for some vital components in airplanes and space capsules. A commercial jet plane contains between 300 and 1100 kg titanium, a supersonic plane may be built of 20–40 tonnes of titanium. In modern jet engines titanium is used for parts that operate up to 600°C. In the compressor, titanium-based alloys are used for blades, discs, inlet guide vanes and cases. The metal is also used for space vehicles. The Apollo capsule was built to a great extent of titanium.

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1) On passivation see Chapter 24 Chromium, section 24.5.1.

18.6.5
Stainless Steels With Titanium – Stainless Even After Welding

Titanium is a strong carbide former and is used as an alloying element in stainless steels, containing some carbon. Titanium binds carbon and decreases the negative effect of carbon on corrosion resistance after welding. In steel manufacture, titanium is added to the melt as ferrotitanium.

18.6.6
Titanium Carbide and Titanium Nitride – Important Hard Materials

Conventional hard metal (cemented carbide), described in Chapter 26 Tungsten, is composed of tungsten carbide with cobalt as a binding element. Modern cemented carbide tools for machining of steel also have considerable contents of titanium carbide TiC. Quite new types of cemented carbide with combinations of titanium carbide and titanium nitride TiN have also been developed.

18.6.7
Coating With Titanium Carbide and Nitride in Chemical Vapor Deposition (CVD) Processes

Titanium chloride $TiCl_4$ is a liquid with a high vapor pressure. It is used for a chemical reaction that has become of great technical importance. If hydrogen and methane CH_4 are passed through $TiCl_4$, a mixture of the carrier gas (H_2) and the reaction gases ($TiCl_4$ and CH_4) is obtained. When this mixture is passed over small tools of cemented carbide, designed for machining steel at 1000°C (10–20 thousand components at a time, see Figure 18.6), the following reaction occurs on the surface of the cemented carbide tool:

$$TiCl_4\ (g) + CH_4\ (g) \rightarrow TiC\ (s) + 4HCl\ (g)$$

The titanium carbide forms a coating with a thickness 5–10 μm that considerably improves the wear resistance of the tool.

If methane is replaced with ammonia or nitrogen a yellow coating of titanium nitride TiN is obtained. With gaseous aluminum chloride $AlCl_3$ and a mixture of H_2 and CO_2, layers of Al_2O_3 are formed.

The high temperature is a drawback of the original CVD technique. It is true that 1000°C is not a high temperature for cemented carbide but if the substrate (base material) is steel or another alloy, its mechanical properties are considerably impaired. The process temperature can be lowered by plasma- or laser-assisted CVD. The temperature can also be kept low (about 400°C) when steel components are coated with titanium nitride using a physical vapor deposition (PVD) technique. Using this technique, drills used in the engineering industry can be covered with golden-yellow, wear-resistant coatings of titanium nitride.

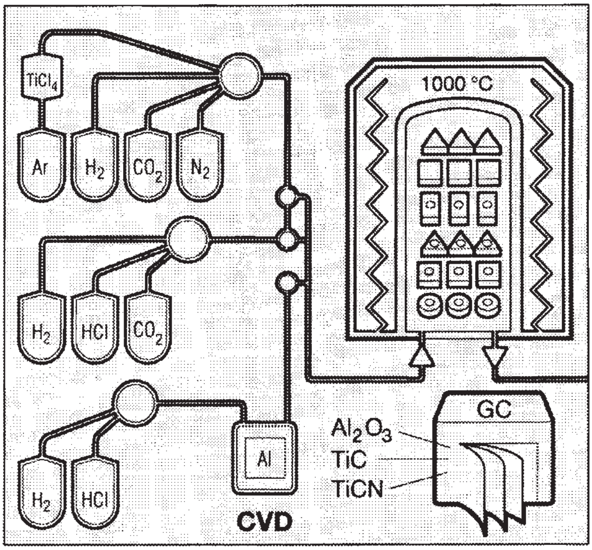

Figure 18.6 Reactor for coating with titanium carbide, titanium nitride and aluminum oxide. (Courtesy of AB Sandvik Coromant, Sweden.)

Special equipment in space vessels that will be exposed to radiation can also be successfully coated with titanium nitride using CVD or PVD technology.

18.7
The Biological Role of Titanium

Titanium is apparently not an essential element for humans. The element shows generally low toxicity. In occupational situations TiO_2 tends to accumulate and can cause lung fibrosis. Some restrictions including respiratory tests and medical X-ray examinations are therefore prescribed for persons heavily exposed to TiO_2 at their workplaces. It is however important to modify production equipment in order to avoid heavy emission.

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18.3 J. Gambogi, Titanium chapter in *Mineral Commodity Summaries 2002*, USGS, Reston, VA, pp.178–179; Titanium chapter in *Minerals Yearbook, 2001*,Vol. I, Metals and Minerals, USGS, Reston, VA, pp. 80.1–80.6. http://minerals.usgs.gov/minerals/pubs/commodity/titanium

19
Zirconium

19.1 Zr
Facts about Zirconium

19.1.1 Zr
The Element

Symbol:	Zr
Atomic number:	40
Atomic weight:	91.22
Ground state electron configuration:	$[Kr]4d^2 5s^2$
Crystal structure:	Hexagonal hcp with $a = 3.23$ Å, $c = 5.15$ Å

19.1.2 Zr
Discovery and Occurrence

Discovery: A new element in the mineral hyacinth was discovered in 1789 by M. H. Klaproth in Berlin. It was named zirconium after the mineral's Persian name *Zargün*. The metal was first isolated in1824 by J. J. Berzelius.

Most important mineral: Zircon $ZrSiO_4$ (Figure M30). Some forms of zircon have excellent gemstone qualities. Baddeleyite ZrO_2. The zirconium in nature contains 0.5–2 % hafnium.

Ranking in order of abundance in earth crust:	18
Mean content in earth crust:	165 ppm (g/tonne)
Mean content in oceans:	$3 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	0.05 ppm
Content in a man's body (weight 70 kg):	3.5 mg

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19.1.3 Zr

Chemical Characterization

Because of its low neutron-absorption cross section and good corrosion resistance zirconium is used in water-moderated nuclear reactors. In tubes for sealing the fuel a hafnium-free zirconium, alloyed with 1.5% tin, is used.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Zr^{IV} as in ZrO_2 and $ZrCl_4$	$Zr(g) \rightarrow Zr^+(g) + e^-$	640	$Zr(g) + e^- \rightarrow Zr^-(g)$
Zr^{III} as in $ZrBr_3$	$Zr^+(g) \rightarrow Zr^{2+}(g) + e^-$	1270	−41.1
Zr^{II} as in $ZrCl_2$	$Zr^{2+}(g) \rightarrow Zr^{3+}(g) + e^-$	2218	
	$Zr^{3+}(g) \rightarrow Zr^{4+}(g) + e^-$	3313	
	$Zr^{4+}(g) \rightarrow Zr^{5+}(g) + e^-$	7752	

Standard reduction potential: $Zr^{4+}(aq) + 4e^- \rightarrow Zr(s)$ $E^0 = -1.55$ V

Electronegativity (Pauling): 1.33

Radii of atoms and ions: (WebElements™)		
	Atomic:	155 pm
	Covalent:	148 pm
	Zr^{4+} (4-coordinate, tetrahedral):	73 pm
	Zr^{4+} (6-coordinate, octahedral):	86 pm
	Zr^{4+} (8-coordinate):	98 pm

19.1.4 Zr

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
6506 kg m^{-3} 6.51 g cm^{-3}	14.02 cm^3	2128 K 1855 °C	4682 K 4409 °C	278 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
26	23	22	21	23

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$5.7 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
73	400	580	880	1250	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+16.8 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
70 GPa	26 GPa	76 GPa	0.35

19.1.5 Zr
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	21 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	580 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	607 $kJmol^{-1}$
Entropy S^0 at 298 K	38.99 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	18.7	25.36	28.9	33.6	32.5	33.5

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Zr + O_2 \rightarrow ZrO_2$	–1043	–1005	–905	–815	–725

19.1.6 Zr
Nuclear Properties and X-ray

Isotope range, natural and artificial 81–105

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{90}Zr	Stable	51.45	+0	–	–	–	–
^{91}Zr	Stable	11.22	+5/2	–1.303	–	–	–
^{92}Zr	Stable	17.15	+0	–	–	–	–
^{94}Zr	Stable	17.38	+0	–	–	–	–
^{96}Zr	Active	2.80	+0	–	$3.8 \cdot 10^{19}$ y	$\beta^-\beta^-$	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{91}Zr
Reference compound	$ZrCl_2(C_5H_5)_2/CH_2Cl_2$
Frequency MHz (^1H = 100 MHz)	9.296
Receptivity D^P relative to ^1H = 1.00	$1.07 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	6.09
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-2.497 \cdot 10^7$
Nuclear quadropole moment, barn	–0.206

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
39	Y	14.882
40	Zr	15.692
41	Nb	16.521

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	134
17.37 keV (MoKα_2)	16.5

Neutron absorption	**Thermal neutron capture cross section**	0.185 barns

19.2
Discovery

19.2.1
Hyacinth in the Revelations

Minerals containing the metal zirconium were known a long time ago. In the Book of Revelation, at the end of the New Testament in the Bible, it is written that the precious stone *hyacinth* is one of the stones in the wall round the New Jerusalem. And hyacinth is the mineral zircon, zirconium silicate, highly regarded in ancient and in modern times for its beauty. Pure zircon is colorless with a beautiful luster because of its high refractive index. The mineral always contains radioactive substances, uranium and thorium, and the radiation causes an inner structural change. This phenomenon results in absorption of some wavelengths of light and the production of a colored mineral. A change of this type is most pronounced in green zircons. The most usual zircon color is yellow to brown.

At the end of the 18th century investigation using chemical and mineralogical methods started to find out what zircon really is. Martin Heinrich Klaproth began to work with the problem in 1789. In his own comments he states that zircon in the long run has been regarded as *sapphire*, *ruby*, *topaz* and as *hyacinth*. Klaproth further said that A. G. Werner (1750–1817), professor of geology in Freiberg, was the first to classify zircon as a specific mineral. He placed zircon close to diamond in the mineralogical system. Chemical analyses made before Klaproth, for instance by Torbern Bergman in Uppsala, had not revealed any new element in the mineral. When Klaproth analyzed a hyacinth from Ceylon he discovered that it contained the oxide of an unknown element. After the mineral’s Persian name *Zargün (gold-colored)* he gave the name *zirconium earth* to the oxide of the new metal. Klaproth’s hyacinth analysis gave the composition 70% ZrO_2 and 25% SiO_2. The year 1789 is also regarded as the year of discovery for zirconium.

19.2.2
A First Sight of Zirconium Metal

The metal zirconium is very strongly bound to oxygen in the oxide ZrO_2. Reduction with carbon has no prospect of success. However, in 1824, 35 years after Klaproth's discovery, Berzelius was able to prepare potassium fluorozirconate K_2ZrF_6 and reduce it with potassium metal. The product was a black metal powder. Berzelius reported that it was impossible to compact the powder to a metal of conventional appearance so the product was obviously impure. In the following years many unsuccessful attempts were made to isolate pure ductile zirconium metal.

19.3
Zirconium Minerals

19.3.1
General

The metal zirconium is not as rare as might be expected. It is eighteenth in abundance in the earth's crust and more common than copper and zinc together. The most important mineral is *zircon*, zirconium silicate $ZrSiO_4$. *Baddeleyite*, zirconium oxide ZrO_2 (Table 19.1) is also important. There are, however, no zircon mines. Zircon is recovered as a by-product from the extraction of titanium from ores containing the minerals rutile and ilmenite.

Table 19.1 Properties of important zirconium minerals

Mineral	Formula	Crystal form	Density g/cm^3	Hardness[a)]	Color
Zircon Figure M30	$ZrSiO_4$	Tetragonal bipyramidal	4.67	7.5	Yellow, brown, brownish-red. Diamond luster
Baddeleyite	ZrO_2	Monoclinic, prismatic	5.7–6.0	6.5	Brown to black

a) In 1822 the mineralogist Friedrich Moh introduced a practical method of determining mineral hardness by scratching. It has become universally known as Moh's scale. An unknown mineral is compared to ten standard minerals on the scale (Moh's hardness value in parenthesis): Talc (1), Gypsum (2), Calcite (3), Fluorite (4), Apatite (5), Orthoclase (6), Quartz (7), Topaz (8), Corundum, ruby and sapphire (9), Diamond (10).

19.3.2
The Mineral Zircon – Zirconium Silicate

Zircon occurs in silica-rich igneous rocks, particularly granite and pegmatite, and also in metamorphic and sedimentary rocks but rarely in workable concentrations. In spite of that, zircon is the dominant commercial zirconium mineral. Weathering and erosion liberate the zircon grains, and the action of water in rivers and seas concentrates the heavier minerals in placer deposits, deltas and ocean beaches. Zircon is therefore recovered from sands in beach deposits. Australia and South Africa are major zircon exporters. From the beach sands the heavy minerals are concentrated by gravity separation from quartz, light minerals and clay. The concentrate is treated in an ore-dressing site and separated into individual mineral components: rutile, ilmenite, zircon, monazite, etc.

760 000 tonnes of zirconium mineral were produced during the year 2000. The unpublished US production figure is excluded from this total. Australia produced 353 000 tonnes, South Africa 270 000 tonnes and Ukraine 75 000 tonnes [19.3].

After different manufacturing processes only a small part (5%) of this quantity is used for production of zirconium metal and alloys. The main quantity is used as zirconium silicate (the mineral zircon), as zirconia (zirconium oxide) in conventional and advanced ceramic applications and for production of zirconium chemicals.

19.3.3
Baddeleyite – Zirconium Oxide

The mineral baddeleyite was discovered on Ceylon (Sri Lanka) in 1892. It is named after its discoverer, the mineralogist Joseph Baddeley. The main deposits of baddeleyite are today in Brazil, South Africa, Sri Lanka and Russia.

Baddeleyite is zirconium dioxide and thus, from a technical point of view, a better raw material than zircon, but its high price and limited availability have made it less attractive than zircon sand.

19.4
Modern Uses of Zircon and Zirconium Oxide

The oxide can be manufactured from the mineral zircon by caustic fusion at 650°C.

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$$

The cooled mass is treated with water, which dissolves the silicate while hydrated zirconia is precipitated by hydrolysis. After filtering it can be transformed to zirconium oxide by heating.

19.4.1
General Ceramic Applications ...

The mineral *zircon* $ZrSiO_4$ is used for moulds in foundries. Its high thermal conductivity improves the cooling rate compared to other mould materials. *Zirconium oxide* is used in firebricks. It has very good temperature resistance and is, after sintering, also used for crucibles and other components for work at high temperatures. When zirconia is heated, a phase transformation occurs at a temperature of about 1200°C.

The corresponding volume change makes the use of pure zirconia impossible for many applications.

19.4.2
… and Some Very Special Ones

Zircon has a rather high content of the radioactive elements uranium and thorium and is used in the radioactive age determination of the earth's crust, see Chapter 4, Geochemistry.

Zirconium oxide is used for making sanitary ware white and opaque. The oxide has also been used in place of TiO_2 as the pigment for white camouflage paints for use in snow environments. ZrO_2 simulates snow more closely in the infrared and microwave spectrum.

Over 300 tonnes of single-crystal cubic ZrO_2 are grown each year to provide the jewelry trade with low-cost gems.

19.4.3
Transformation-toughened Zirconia

ZrO_2 has a monoclinic crystal structure (M) at room temperature but is tetragonal (T) at sintering temperature. The transformation temperature is about 1200°C. If zirconium oxide is mixed with stabilizers such as yttrium oxide Y_2O_3 (about 6%) before sintering, the tetragonal structure remains (metastable) to room temperature.

When a crack starts in this partly stabilized zirconia (PSZ) (Figure 19.1), the tetragonal grains are restructured to monoclinic. The energy of the crack is then absorbed and crack propagation stops. The fundamental reason to this positive effect is an increase of the grain volume of 5% at the transformation T→M. These *transformation toughened* ceramics are characterized by extremely fine-grained structure and increased strength and toughness. Compare also Figures 17.17 and 17.18. The Y_2O_3-stabilized zirconia is, however, best suited for temperatures below 500°C. For higher temperatures MgO-stabilized zirconia is more suitable. Stabilized zirconia is used for cutting tools, ceramic motor components, tunnel liners for the aerospace industry, and also experimentally also piston heads, valve seats and – in quite another field – dental fillings in teeth.

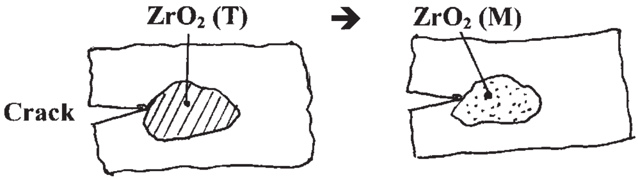

Figure 19.1 Diagram to show how the transformation T→M stops crack propagation.

If a higher content of stabilizer is added (13–14% Y_2O_3) a "fully stabilized" zirconia is obtained. This is an ion-conducting material and has been used in oxygen sensors and in fuel cells.

19.4.4
White Ceramics Containing Zirconia

An important application for zirconium oxide is as an "alloying element" in aluminum oxide ceramics. Sintered aluminum oxide is brittle. It has been found that the toughness can be considerably improved by mixing aluminum oxide with 4–15% zirconium oxide and sintering the two together. Then a "white ceramic", tough enough for many applications, e.g. tools, is obtained.

19.4.5
Zirconium in Ultrasonic Transducers

The effect known as *piezoelectricity* was discovered in quartz crystals by the two brothers Jacques and Pierre Curie in 1880, then 24 and 21 years of age. The phenomenon implies that a crystal acquires an electric charge when compressed and on the contrary an applied electrical charge causes a length change. The word *piezo* is Greek for "push". The effect involves a very useful cooperation between electrical and mechanical oscillations. If an electrical oscillation is applied to such a piezoelectric ceramic it will respond with mechanical vibration and can be a source for ultrasonic sound. A standard material for this piezoelectricity is lead zirconate titanate PZT. It is used in piezoelectric ceramics for applications as gas furnace igniters, in microphone and phonograph crystals, and for ultrasound imaging in materials testing and in medicine. Alternative materials are barium titanate and lead titanate.

Ultrasound is sound with such a high frequency that the human ear cannot detect it. It means a frequency of above 15 000 Hz (15 kHz). To generate sound with this high frequency an AC current with the same frequency must be used.

As soon as the piezoelectric crystal has emitted a pulse it is switched-over to a receiver When the sound returns as an echo the oscillations of the echo are changed to electrical impulses that are recorded on the oscilloscope screen. In the equipment the time is calculated for the passage of the sound forwards and backwards. As the speed of the sound in the actual material is known the time can be recalculated to distance. This is described in Figure 16.2 (p. 370).

19.5
Zirconium Metal and Alloys

19.5.1
The Start of Industrial Production

In 1914 D. Lely and L. Z. Hamburger reported [19.1] that they, for the first time, had succeeded in preparing ductile zirconium metal. They reduced resublimed zirconium chloride with very pure sodium in a high-pressure vessel.

During World War I there was a rumor that the Germans had manufactured a zirconium-alloyed steel with superior properties for war equipment. This started a powerful research activity into zirconium in England, France and the USA. No results that would have verified the rumor were obtained.

In 1925 van Arkel and de Boer [19.2] published their first report about their famous method of producing metals in pure form by thermal decomposition of the metal iodide. In the zirconium case, impure zirconium metal is placed in an evacuated container and treated at 300°C with iodine vapor to form ZrI_4. This tetraiodide is diffused to an electrically heated filament of tungsten or zirconium wire. At 1300–1400°C the zirconium iodide is dissociated to iodine gas and very ductile zirconium metal. From 1925 to 1945 the iodide process was the method used for obtaining pure, ductile zirconium metal.

Right up to the time after World War II the use of zirconium metal was insignificant. The metal was expensive and inessential. Since the availability increased through the Kroll process the metal has found uses in the chemical industry for building process equipment in applications that need high corrosion resistance.

19.5.2
Modern Zirconium Metal Manufacture

Zirconium production with the Kroll process is carried out by the following steps [19.4]:

- Chlorination of zircon sand in a fluidized bed at 1100°C in the presence of carbon. Chlorine is both a reactant and a fluidizing gas.
- $ZrSiO_4 + 4C + 4Cl_2 \rightarrow ZrCl_4 + SiCl_4 + 4CO$
- The gas mixture after the reactor is cooled to 200°C in a condenser and zirconium and hafnium chlorides are collected together as a powder.
- If the metal is intended for nuclear power purposes the hafnium chloride is removed.
- Ductile metal is produced by reduction of pure zirconium chloride with molten magnesium under an inert gas, argon or helium (The Kroll process).

The world production capacity is set out in Table 19.2.

Table 19.2 Annual world production capacity for zirconium metal [19.4]

Country	Production capacity tonnes
USA	4000
Ukraine[a)]	2700
France	1800
India	270
Total	8800

a) Calcium-reduced zirconium, refined by zone-melting in Russia

The utilization of this capacity varies from year to year and is particularly dependent on the development of commercial nuclear power.

19.5.3
Zirconium for Nuclear Power

The current predominant use of metallic zirconium is for commercial and military nuclear power. The rapid development of nuclear power changed the situation for zirconium and resulted in a big increase in demand. The background to this is that in tubes for containing the fuel in the uranium reactors a material is needed that absorbs thermal neutrons only to a very small extent and at the same time has corrosion resistance sufficiently high to withstand the very corrosive environment in the reactor. Zirconium is such a metal.

There were, however, two large problems. One was that no commercial manufacturing method was available at the time when the exploitation of atomic energy started. The American Atomic Energy Commission initially used the iodide method. Impure zirconium metal was refined until its properties matched those required for material for fuel-rod containment tubes. It was expensive, but the development of the Kroll process solved that problem.

The other big problem was the hafnium content of natural zirconium. In the actual tubes the hafnium content must be lower than 100 ppm, because hafnium absorbs neutrons 550 times more strongly than zirconium. Zircon sand, the most important ore, has a hafnium content of 1.5–2.5% (relative to zirconium). Thus it was necessary to find a separation method with which hafnium-free zirconium could be manufactured. The solution of this problem was *liquid–liquid extraction*. From an impure zirconium solution in hydrochloric acid, iron is first removed by solvent extraction. Then ammonium thiocyanate is added to the chloride solution containing Zr + Hf. Hafnium is extracted into an organic phase of methyl isobutyl ketone. The pure zirconium solution in the water phase is worked up for zirconium. Hafnium is recovered from the ketone solution by scrubbing with dilute sulfuric acid.

The separation technique described and the Kroll process created the possibility of manufacturing hafnium-free zirconium on an industrial scale for atomic energy purposes. To optimize the mechanical and corrosion properties, the metal is alloyed with 1.5% tin and a low but precisely specified oxygen content (0.1%). This material, *Zircaloy*, is used for containing the fuel in uranium reactors all over the world.

19.5.4
Zirconium – Special Uses

Small quantities of zirconium are also used for special applications. In *photo flash equipment* the very high flame temperature, 4660°C, can be used. Another use is as a *scavenger material* in the vacuum technique. The scavenger function implies that zirconium, when present in a heated evacuated container, removes any traces of oxygen present.

19.6
Biological Role

Zirconium is apparently not an essential element for humans. The element shows generally low toxicity.

References

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20
Hafnium

20.1 Hf
Facts about Hafnium

20.1.1 Hf
The Element

Symbol:	Hf
Atomic number:	72
Atomic weight:	178.49
Ground state electron configuration:	$[Xe]4f^{14}5d^{2}6s^{2}$
Crystal structure:	Hexagonal hcp with $a = 3.20$ Å, $c = 5.05$ Å

20.1.2 Hf
Discovery and Occurrence

Discovery: In 1923 the Dutch physicist D. Coster and the Hungarian chemist C. G. von Hevesy at Niels Bohr's laboratory in Copenhagen discovered the element 72, sought for a long time. The element got its name after *Hafnia*, Latin for Copenhagen

Most important mineral: Hafnium is present in all zirconium minerals. It is obtained as by-product of zirconium production and prepared because it is necessary to remove hafnium from the zirconium used in the nuclear industry.

Ranking in order of abundance in earth crust:	46–47
Mean content in earth crust:	3.0 ppm (g/tonne)
Mean content in oceans:	$7 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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20.1.3 Hf
Chemical Characterization

Hafnium is a metal that closely resembles zirconium. Because the element has a good absorption cross-section for thermal neutrons, almost 600 times that of zirconium, it may be used for nuclear reactor control rods. Hafnium carbide and hafnium nitride are very hard and wear resistant.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Hf^{IV} as in HfO_2 and HfF_4	$Hf(g) \rightarrow Hf^{+}(g) + e^{-}$	659	$Hf(g) + e^{-} \rightarrow Hf^{-}(g)$
Hf^{III} as in $HfCl_3$	$Hf^{+}(g) \rightarrow Hf^{2+}(g) + e^{-}$	1440	–
	$Hf^{2+}(g) \rightarrow Hf^{3+}(g) + e^{-}$	2250	
	$Hf^{3+}(g) \rightarrow Hf^{4+}(g) + e^{-}$	3216	

Standard reduction potential:	$Hf^{4+}(aq) + 4e^{-} \rightarrow Hf(s) \quad E^0 = -1.70$ V	
Electronegativity (Pauling):	1.3	
Radii of atoms and ions:	Atomic:	155 pm
(WebElements™)	Covalent:	150 pm
	Hf^{4+} (4-coordinate, tetrahedral):	72 pm
	Hf^{4+} (6-coordinate, octahedral):	85 pm
	Hf^{4+} (8-coordinate):	97 pm

20.1.4 Hf

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
13 310 kg m^{-3} 13.31 g/cm^{-3}	13.41 cm^3	2506 K 2233 °C	4876 K 4603 °C	144 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
25	23	22	21	21

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
–	$6.0 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
–	296	426	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K $+5.3 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
–	–	–	–

20.1.5 Hf
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	25.5 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	661 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	619 $kJmol^{-1}$
Entropy S^0 at 298 K	43.56 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	–	25.73	27.0	29.0	34.1	33.5

Standard free energy ΔG^0 of oxide formation kJ/mole O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Hf + O_2 \rightarrow HfO_2$	–1053	–1013	–919	–828	–740

20.1.6
Nuclear Properties and X-ray

Isotope range, natural and artificial 154–185

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{176}Hf	Stable	5.21	+0	–	–	–	–
^{177}Hf	Stable	18.60	–7/2	0.7936	–	–	–
^{178}Hf	Stable	27.30	+0	–	–	–	–
^{179}Hf	Stable	13.63	+9/2	–0.6409	–	–	–
^{180}Hf	Stable	35.10	+0	–	–	–	–
^{174}Hf	Active	0.16	+0	–	$2 \cdot 10^{15}$ y	α	2.495 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{177}Hf	^{179}Hf
Reference compound	–	
Frequency MHz (^1H = 100 MHz)	4.04	2.54
Receptivity D^P relative to ^1H = 1.00	$2.61 \cdot 10^{-4}$	$7.46 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	1.49	0.426
Magnetogyric ratio, $radT^{-1}s^{-1}$	$1.086 \cdot 10^7$	$-0.682 \cdot 10^7$
Nuclear quadropole moment, barn	3.36	3.79

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
71	Lu	52.965
72	Hf	54.611
73	Ta	56.277

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (Cu$K\alpha_2$)	156
17.37 keV (Mo$K\alpha_2$)	87.9

Neutron absorption	**Thermal neutron capture cross section**	105 barns

20.2
Discovery

The metal hafnium, hidden in the precious stones zircon and hyacinth, known from antiquity, could not be discovered until the chemistry of zirconium was made clear.

In the titanium group of the periodic table the elements ^{22}Ti and ^{40}Zr were known at the end of the 19th century. It was time to look for element 72 and its discovery was announced in 1911. Professor Georges Urbain at the Sorbonne University in Paris had devoted a couple of years to patient research into rare earth metals. Together with Auer von Welsbach from Austria and Charles James from the USA, he is the discoverer of lutetium. During spectroscopic analysis of some residues from his rare earth metal investigations Urbain found some lines that he thought originated from element 72. He gave the presumed new element the name *celtium*. The year was, as mentioned, 1911.

Three years later a new scientific method for identifying elements with specific atomic numbers was discovered in England. At the age of 27 Henry Gwyn Jeffreys Moseley found a relationship between an element's atomic number and its X-ray frequency. Moseley's law, as the relationship is called, opened new possibilities for identifying elements (the method is described in Chapter 10 Blowpipe and Spectroscope). The young Moseley's achievement was thus epoch-making in the history of science. In 1915, the year after his discovery, he was killed in the war at the Dardanelles.

As soon as Georges Urbain had heard of Moseley's new law, he took his sample of celtium and visited Moseley. In an unpublished report to the British Association's meeting in Sidney in 1914 Moseley wrote that the "X-ray spectrum shows that celtium is a mixture of earlier known rare earth metals" [20.1]. Thus element 72 was still undiscovered. The situation regarding known and unknown elements at the beginning of the 1920s is described in Figure 20.1.

As zirconium of greater and greater purity became available, chemists found that there was something unclear about the element. Determinations of atomic weight in samples from different sources showed variations. The American scientists E. F. Smith and F. A. Genth said that "zirconium is not simple" and they expressed the suspicion that "there is some other element hidden in the metal".

Niels Bohr in Copenhagen stated from a theoretical viewpoint that Urbain's celtium could not be element 72. As the missing metal belongs to group 4 it should

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	**43**	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	**72**	73 Ta	74 W	**75**	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	**85**	86 Rn
7	**87**	88 Ra	89 Ac	104	105	106	107	108	109									

6	58 Ce	59 Pr	60 Nd	**61**	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

7	90 Th	91 Pa	92 U

Figure 20.1 Unfilled places, Nos. 43, 61, 72, 75, 85 and 87 in the periodic table at the beginning of the 1920s.

not be found among the rare earth metals in group 3 and it should be quite different from lutetium. Instead it was much more likely to occur along with zirconium.

At Niels Bohr's institute, the Hungarian George Charles de Hevesy and the Dutchman Dirk Coster were assigned to investigate a zircon mineral from Norway. Coster was a physicist with great experience of spectroscopic investigations. Using Moseley's method he was able in 1923 to identify element 72 in the Norwegian mineral and later in many other zirconium ores. The chemist de Hevesy could soon describe different methods for separating the new element from zirconium. The discovery was made in Copenhagen, in Latin *Hafnia*, which was the reason for naming the new element *hafnium*.

20.3
Minerals

The ionic radii for zirconium and hafnium are almost identical (0.86 and 0.85 Å) and because of that hafnium is associated with zirconium in minerals. The hafnium content is in general ca. 2% (relative to zirconium). A notable exception is a deposit in Nigeria where a zircon with 6% hafnium is found. Also a Norwegian scandium mineral *thortveitite* and a mineral from Mozambique contain more Hf than Zr.

20.4
Manufacture of Hafnium

In cooperation with a Danish colleague *Thal Janzen,* George de Hevesy separated hafnium from zirconium by fractional crystallization of fluorides. In 1925 they also isolated the element itself. The modern method for separation with liquid–liquid extraction is described in Chapter 19 Zirconium.

20.5
Uses of Hafnium

A very special situation arose from the discovery that it was necessary to separate zirconium and hafnium if zircaloy was to be used in uranium reactors. Hafnium became available but was there any need for this new metal? Some applications have in fact been found.

Because of its resistance to high temperatures, it is used with zirconium as a structural material in nuclear power plants. In nuclear reactors control rods are used to absorb thermal neutrons, making it possible to regulate the fission process. Material in such rods must have a high absorption cross-section for thermal neutrons; it must also have good hot-water corrosion resistance and good mechanical properties. Hafnium is such a material. Hafnium and Hf–Zr alloys have also been suggested for use in spent nuclear fuel storage racks.

If the turbine vanes and combustion zones of jet aircraft engines can withstand higher working temperatures the engine efficiency is improved. Such an effect is obtained if 1–2% Hf is added to the nickel-based superalloys.

An interesting property of hafnium is that the metal (like zirconium) can dissolve much hydrogen in its lattice. It is possible to reach a content corresponding to the formula HfH_2.

20.6
Biological Role

Hafnium is apparently not an essential element for humans. The element shows generally low toxicity.

References

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21
Vanadium

21.1 V
Facts about Vanadium

21.1.1 V
The Element

Symbol: V
Atomic number: 23
Atomic weight: 50.94
Ground state electron configuration: [Ar]$3d^3 4s^2$
Crystal structure: Cubic bcc with $a = 3.03$ Å

21.1.2 V
Discovery and Occurrence

Discovery: In 1801, A. M. Del Rio in Mexico discovered a new metal in a brown lead ore. He gave the new element the name *erythronium*. When confirmation was sought in Europe the metal was said to be chromium and the discovery was not accepted. In 1830, N. G. Sefström in Sweden discovered vanadium in iron, manufactured from an ore in Smålands-Taberg. F. Wöhler in Germany showed that erythronium and vanadium are in fact identical. Sir Henry Roscoe prepared pure vanadium metal in 1867. His method was reduction of vanadium chloride with hydrogen.

Most important mineral: Vanadium is found in many minerals. Two examples:
Vanadinite $Pb_5(VO_4)_3Cl$ (Figure M31)
Patronite VS_4.
Vanadium is obtained as by-product of steel manufacture and during the treatment of certain crude oils, especially those from Venezuela and Mexico.

Ranking in order of abundance in earth crust: 20
Mean content in earth crust: 120 ppm (g/tonne)
Mean content in oceans: 0.0025 ppm (g/tonne)
Residence time in oceans: $100 \cdot 10^3$ years
Mean content in an adult human body: 0.03 ppm
Content in a man’s body (weight 70 kg): 2 mg

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21.1.3 V

Chemical Characterization

Vanadium is a metal, used in many alloys. Ferrovanadium and ferrochromium are added to steel in order to produce chrome-vanadium steels, used for springs and transmission gears. Vanadium metal and aluminum metal are used for the important titanium alloy Ti_6Al_4V (6% Al, 4% V). The major use of vanadium, besides metallurgy, is as a catalyst in the chemical industry. Vanadium pentoxide has replaced platinum as a catalyst for the manufacture of sulfuric acid.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
V^V as in V_2O_5, HVO_3, VO_2^+, and VF_5	$V(g) \rightarrow V^+(g) + e^-$	651	$V(g) + e^- \rightarrow V^-(g)$
V^{IV} as in VO_2, VO^{2+}, and VCl_4	$V^+(g) \rightarrow V^{2+}(g) + e^-$	1414	−50.6
V^{III} as in V_2O_3 and VF_3	$V^{2+}(g) \rightarrow V^{3+}(g) + e^-$	2830	
V^{II} as in $V(OH)_2$ and VBr_2	$V^{3+}(g) \rightarrow V^{4+}(g) + e^-$	4507	
	$V^{4+}(g) \rightarrow V^{5+}(g) + e^-$	6299	
	$V^{5+}(g) \rightarrow V^{6+}(g) + e^-$	12 363	

Standard reduction potential:	$VO_2^+(aq) + 4H^+(aq) + 3e^- \rightarrow V^{2+}(aq) + 2H_2O(l)$	$E^0 = +0.361$ V
	$VO_2^+(aq) + 4H^+(aq) + 5e^- \rightarrow V(s) + 2H_2O(l)$	$E^0 = -0.236$ V
Electronegativity (Pauling):	1.63	
Radii of atoms and ions:	Atomic:	135 pm
(WebElements™)	Covalent:	125 pm
	V^{2+} (6-coordinate, octahedral):	93 pm
	V^{3+} (6-coordinate, octahedral):	78 pm
	V^{4+} (6-coordinate, octahedral):	72 pm
	V^{4+} (8-coordinate):	86 pm
	V^{5+} (4-coordinate, tetrahedral):	49.5 pm
	V^{5+} (6-coordinate, octahedral):	68 pm

21.1.4
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
6110 kg m^{-3} 6.11 g cm^{-3}	8.34 cm^3	2183 K 1910 °C	3680 K 3407 °C	489 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
32	31	31	33	38

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$5.1 \cdot 10^{-6}$	$8.4 \cdot 10^{-6}$	$9.9 \cdot 10^{-6}$	$10.9 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	873 K	1473 K
26	182	253	380	540	–

Mass magnetic susceptibility χ_{mass} at 293 K $+62.8 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
128 GPa	47 GPa	154 GPa	0.36

21.1.5 V
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	22.8 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	455 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	514 $kJmol^{-1}$
Entropy S^0 at 298 K	28.91 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	13.5	24.89	27.5	30.1	40.9	46.2

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3V + O_2 \rightarrow 2/3V_2O_3$	–760	–741	–662	–584	–
$4/5V + O_2 \rightarrow 2/5V_2O_5$	–575	–551	–471	–	–

21.1.6 V
Nuclear Properties and X-ray

Isotope range, natural and artificial 43–60

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{51}V	Stable	99.75	–7/2	5.157	–	–	–
^{50}V	Active	0.25	+6	3.347	$1.4 \cdot 10^{17}$ y	EC or β^+ β^-	2.208 MeV 1.037 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{50}V	^{51}V
Reference compound	$VOCl_3$+C_6D_6	
Frequency MHz (^1H = 100 MHz)	9.970	26.303
Receptivity D^P relative to ^1H = 1.00	$1.39 \cdot 10^{-4}$	0.383
Receptivity D^C relative to ^{13}C = 1.00	0.796	2190
Magnetogyric ratio, $radT^{-1}s^{-1}$	$2.671 \cdot 10^7$	$7.046 \cdot 10^7$
Nuclear quadropole moment, barn	0.21	–0.052

Characteristic X-radiation Z	 Element	 Kα_2 keV
22	Ti	4.505
23	V	4.944
24	Cr	5.405

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	220
17.37 keV (MoKα_2)	26.4

Neutron absorption	Thermal neutron capture cross section	5.06 barns

21.2
Discovery

21.2.1
To the New World

Andrés Manuel del Rio, born in Madrid in 1764, was a clever young man. He was permitted to study early at the university in Alcalad de Henares. At the age of fifteen he obtained a degree in Latin, Greek and Theology. He clearly had varied interests. It is said that he took part in an experimental physics competition and had such a great success that he received a royal award so that he could start studies at the newly founded Mining and Metallurgical Academy at Almadén, the location of the large Spanish deposits of cinnabar and of mercury manufacture. This education led him to further studies in France, Germany, Hungary and England. In the Bergakademie Freiberg A. G. Werner's teaching made a deep impression on him that helped to mould his own life as a teacher and scientist within the geological field. As a fellow-student in Freiberg he had Baron Alexander von Humboldt, who developed into a traveling ambassador for science and technology, supplying news and information between the Old World and the New. In France, during the revolution, Del Rio came to know Lavoisier and studied with him although it very nearly cost him his life, as it did his teacher. Del Rio, however, was able to escape the reign of terror disguised as a water carrier.

The desire of the Spanish Crown to support geological education and research arose from the Spanish possessions in South America and Mexico. Mexico in particular was rich in valuable minerals.

In Mexico City a mining college, *Real Seminario de Mineria,* had been built up during the period 1788–1792. This work, described in Chapter 26 Tungsten, was led by Don Fausto de Elhuyar. In 1793 this *Seminario* appointed Del Rio as professor in mineralogy and in the following year he arrived in Mexico and took up his duties. He immediately started to organize the mineralogical collections and after a year he published a new book *Elementos de Orictognesia*. This textbook was well regarded by von Humboldt, who wrote that it was the best mineralogy book in the Spanish language. Del Rio also soon made important contributions to the technology of mining.

When Mexico liberated itself from the Spanish Crown in 1821 Del Rio decided to stay in the new country, and he continued his duties there for the benefit of the country's industry, based as it was on geology, mining and metallurgy. He was active practically to his death in 1849. He died at the age of 85 after having served his new home country for 55 years.

21.2.2
A New Metal in Zimapán's Brown Lead Mineral?

Many minerals from different parts of the country were investigated at the mining college in Mexico City. One of these minerals has given Del Rio a place in the history of element discoveries. In the Cardonal mine in the district of Zimapán, located in the state of Hidalgo in central Mexico, a mineral known as *Plomo pardo de Zimapán* occurred. It was a lead mineral but what more was in it?

After chemical investigation Del Rio found, in addition to lead, up to 15% of a new metal. At least he thought it was new. It had similarities with chromium in that different colors could be obtained in solutions with different oxidation states. The year was 1801 and Vauquelin had discovered chromium in 1797. Del Rio gave the name pan-chromium to his new metal but changed it to *erythronium*.

When von Humboldt visited Mexico in 1803 he got samples of the brown lead mineral. He divided it into several portions and sent the samples to different laboratories in Europe with Del Rio's results in accompanying letters.

Del Rio did not claim his priority strongly enough. Instead he began to doubt. Was his metal really new? Or was it chromium? His hesitation increased when he read Fourcroy's description of chromium in *Systèmes de connaissances chimiques,* published in 1800. Del Rio himself wrote also in an annotation to his translation into Spanish of Karsten's mineralogical tables: "I think that the brown lead mineral from Zimapán consists of yellow chromium oxide and a surplus of lead oxide." Further reasons for doubting the existence of erythronium came in 1805. H. V. Collet-Descotils, a friend of Vauquelin, wrote in an analytical report that the supposed new metal was chromium and nothing else.

But Collet-Descotils was wrong. The presumed new metal was not chromium. It *was* new! One of the samples of the brown lead mineral that von Humboldt had sent to Europe had found its way to Friedrich Wöhler. He found that the Zimapán mineral contained a new element and that Del Rio in fact had been right in his first analytical results. Various circumstances had, however, delayed Wöhler´s investigation and the result was not published until 1831. In the previous year, Nils Gabriel Sefström in Sweden had discovered the same element in an ore from Smålands-Taberg and given it the name *vanadium*.

Now we know that Del Rio's brown lead from Zimapán was the mineral *vanadinite,* $Pb_5[Cl(VO_4)_3]$ (Figure M31).

21.2.3
A Doctor Becomes a Metallurgist

Nils Gabriel Sefström (Figure 21.1) was born in 1787 in the province of Helsingland in central Sweden. After senior high school he assisted his father, the clergyman, in his office. At the age of 22 he began to study medicine in Stockholm. In chemistry he had Berzelius as his teacher, and a friendship was formed between the two (Berzelius was only eight years older than his student Nils Gabriel). This strongly encouraged their coming cooperation, not least in connection with the discovery of vanadium. Nils Gabriel presented his doctor's thesis in 1813 and worked for some years as an assistant physician at the *Hospital of the Royal Order of the Seraphim*. Parallel with this service he was also teacher of chemistry and natural history at the Royal Military Academy.

Figure 21.1 Nils Gabriel Sefström (1787–1845). Drawing by S. Diez.

At the beginning of the 19th century, scientists and doctors were not nearly as specialized as is the case nowadays. However, even for his time, Nils Gabriel Sefström seems to have had an unusual breadth of knowledge and interests. He was a doctor of medicine, an eminent chemist – a result of Berzelius' education – but also a competent geologist and mineralogist. He was noted for his talents and working capacity. At the age of 30 appointments came quickly. In 1818 he was appointed professor and in 1820 he was nominated as manager for the new mining and metallurgical school in Falun, which opened in 1822. He remained in this position until 1838. In 1839 he was appointed additional member of the Royal Board of Mining and leader of its chemical laboratory and mineral cabinet. He died in Stockholm in 1845 at the age of 58.

From the day he started his work at the school in Falun his interest in medicine declined and he was completely absorbed in research and education closely connected to mining and metallurgy.

21.2.4
Iron With Cold Brittleness

A great authority on iron metallurgy in Sweden (and Europe) was Sven Rinman (Chapter 8, Iron, section 8.7.2). In his *Mining and Metallurgical Dictionary (Bergwerkslexikon)* he had described a method to determine whether a specific iron was likely to be brittle at about 200°C. This *cold brittleness* is caused by a high content of phosphorus in the iron. Sefström himself described the method in the *Transactions of The Royal Swedish Academy of Sciences* in 1830:

> Some years ago the inspector [bergmästare] Rinman described a method with which it is easy to detect the disposition for cold brittleness in iron. The method is founded on the fact that iron of that sort, after etching with hydrochloric acid, gives a black powder.

The black powder consists of almost insoluble phosphides. This simple method seems to have very little to do with the discovery of vanadium. Sefström's use of the method and his ability for critical analysis, however, was of decisive significance.

21.2.5
Del Rio's Lost Element Appears in Sweden

In his new metallurgical activity on one occasion Sefström needed an iron free from cold brittleness. He selected a material, a bar iron, produced following earlier recommendations from Rinman. Thus it should not have been necessary to make Rinman's test, but the careful and thorough Sefström nevertheless made it. To his astonishment he found a black residue after the treatment with hydrochloric acid – an indication of cold brittleness! Was something special about this iron? Sefström found one answer. The iron had not been manufactured from some of the well-known and very pure iron ores from the central mining district. Instead, an ore from Smålands-Taberg in southern Sweden (Figure 21.2) had been used. But even that was expected to be very low in phosphorus. Why then the black powder? Sefström had 0.2 g of the powder and he analyzed it. This was in 1830. He found no phosphorus but half of the powder was silica. Further were there small amounts of lime, iron oxide and alumina. In addition Sefström found a new element in the black powder, an element with similarities to chromium and uranium. Sefström had discovered a new element and he gave it the name *vanadium* after the goddess Vanadis in Nordic mythology.

Greater quantities were needed for further investigation. The new element's likeness to chromium made Sefström believe that vanadium should be oxidized more easily than iron and thus be enriched in the slag during the carbon elimination process for cast iron. And exactly so! From the slag large quantities of the new metal could be obtained.

> Cast iron produced in a blast furnace has a high carbon content and is brittle and not forgeable. At this time, the first part of the 19th century, the carbon elimination process was of the Walloon forging type during which oxidation

From Thomas Thomson's "Travels in Sweden During the Autumn of 1812"

Figure 21.2 A picture from Smålands-Taberg in Sweden 1812. (From Mary Weeks *Discovery of the Elements*).

> removes carbon as CO. Alloying elements with greater affinity to oxygen than iron, e.g. vanadium, are enriched in the molten slag.
>
> The process occurred on a hearth of firebricks in a frame cast from iron. Preheated cast iron was placed on a bed of charcoal and slag from the previous melting and covered with a new layer of charcoal. Strong heating with an air blast caused the cast iron to melt. Drops of molten iron fell through the hearth and were strongly oxidized in front of the air blast openings. On the furnace bottom half-melted iron with a very low carbon content was formed. (Cast iron melts at ca. 1150°C, pure iron at 1538°C). The half-melted mass was placed under a hammer driven by a water wheel and forged to long rods, bar iron.

In 1830 Sefström wrote about the investigation of the slag in *Transactions of the Royal Swedish Academy of Sciences*:

> The slag is first ground as fine as possible. Grains of metallic iron are oxidized with nitric acid. ... Three parts of slag is then mixed with two parts of saltpeter and 1 part of soda. The mixture is heated in crucible of cast iron during 4 hours at a temperature as high as possible without melting of the crucible. The mass is then pulverized, covered with water and boiled, preferably in a silver vessel.

Ammonium vanadate, a white crystalline powder, is precipitated from the alkaline water solution, and now in quantities large enough for further investigations of the goddess Vanadis metal.

21.2.6

A Scientific Triangle Drama

Ever since his time of study in Stockholm Sefström had had good contact with his teacher Berzelius. Thus it was quite natural that he informed him of the important discovery. As early as May 1830, obviously with the small quantity he extracted from rod iron, experiments started in Berzelius' laboratory: "... When the new body was reduced with hydrogen to a lower oxidation state it gave bluish-green solutions with acids. It was also soluble in alkalis."

The third person in the triangle drama about vanadium was Friedrich Wöhler, well-known for his synthesis of urea. Wöhler became very famous when, in 1828, he opened the hermetically sealed borderline between inorganic and organic chemistry through his synthesis of urea. This synthesis was the first preparation ever of an organic substance in the laboratory. It overthrew the earlier concept that chemists could indeed prepare inorganic acids, alkalis and salts but never organic substances. These could only be formed in living matter, people, animals and vegetables.

Our knowledge of the different twists in the final phase of the discovery of vanadium is founded on the correspondence between Berzelius and Wöhler just before and after the year 1830. The correspondence confirms that Sefström's vanadium discovery was made public before Wöhler could confirm that Del Rio's erythronium was a new element and identical with Sefström´s vanadium.

In January 1829 Wöhler (Figure 21.3) wrote from Berlin to Berzelius in Stockholm:

> I do not remember if I have informed you that, before my illness, I began to analyze the mineral thulite (at first with hydrofluoric acid) and also to ana-

Figure 21.3 Friedrich Wöhler (1800–1882) [21.1].

> lyze the brown lead ore from Zimapán. handed over to me by Humboldt. Some substance in it modifies its high content of chromium so that chromic acid and caustic potash is colorless instead of yellow. God knows what this mineral contains! I cannot blame Del Rio that he thought he had found a new element in the mineral. Much to my disgust I had to interrupt these experiments (due to my hydrofluoric acid poisoning).

As far as can be judged, Wöhler's poisoning made it possible for Sefström to be first with the discovery of vanadium.

In a letter to Wöhler, Berzelius recorded that, just before Christmas 1830, Sefström came to Stockholm with a considerable quantity of ammonium vanadate for common work on the new metal. Berzelius wrote that vanadium is "a rogue" evidently due to its many colors in different oxidation states. The two scientists' working days were long and Christmas was not allowed to be an obstacle. Many properties of vanadium were observed recorded in the period of Sefström's Christmas holidays from his school.

In the letter to Wöhler, Berzelius distinctly stated that Sefström has the priority for the discovery of vanadium. He also notes that he had sent Poggendorff a short paper about vanadium, written by Sefström. A sample of ammonium vanadate was also enclosed in the letter.

Wöhler, now recovered and healthy, examined both Del Rio's brown lead and Sefström's ammonium vanadate and rapidly established that Sefström's vanadium and the element in the Zimapán mineral were identical. In January 1831 he wrote to Justus Liebig:

> ... Just now the Swedish metal is my main interest. ... I was a donkey who did not, already two years ago, discover it in the brown lead ore from Zimapán. I was occupied with analysis of it when the news about Sefström´s discovery reached me (from Berzelius). ... It is moreover the same metal that del Rio found in the Mexican brown lead ore and called erythronium.

Wöhler also sent a sample isolated from the brown lead mineral and asked Berzelius to confirm the identity between erythronium and vanadium. He also expressed his disappointment of having missed the discovery of vanadium. In an answer dated 22nd January 1831 Berzelius firstly wrote that Sefström himself had analyzed the sample and confirmed the identity between erythronium and vanadium. Secondly Berzelius told a jocular anecdote, often quoted:

> In the far North lived the goddess Vanadis, beautiful and charming. One day there was a knock on her door. She remained sitting comfortably and thought: This visitor may knock again – but that didn't happen. The goddess was anxious to see the visitor, who had been so reticent about coming in. She ran to the window and looked. Ah... she said to herself. It is Wöhler! Well, he got his desserts. He could have been more eager. He didn't even look up to the window. ... Some days later there was another knock at the door. And the knocking came again and again. Finally the goddess opened the door and Sefström entered. After this meeting vanadium was born.

The anecdote may be an example of Berzelius desire to create a joyful and inspiring atmosphere and to avoid envy between students and colleagues. Wöhler had certainly not forgotten how he, as a young student, had paid his first visit to Berzelius, how he nervously rang the bell to his flat in Stockholm and how Berzelius himself met him and, in excellent German, inquired about Wöhler's journey. Even on that first day they visited the Karolinska Institutet where Berzelius lectured on chemistry for medical students. In his *Jugend-Erinnerungen eines Chemikers* [*A chemist's memories from his youth*], published in 1875, Wöhler says that he was astonished and pleased by Berzelius' kindness, his calm and his eminent ability to carry out experiments.

In his January letter in 1831 Berzelius also consoled Wöhler by expressing his admiration for the scientific exploit to be the first person to synthesize an organic substance: "More genius is needed to synthesize urea than to discover ten new elements."

The history of the discovery of vanadium reaches a pleasant conclusion when Wöhler in his answer of February 1831 gives thanks for the anecdote, which had given him great pleasure.

> It first annoyed me that I had not paid a visit to the fair goddess. Yet, if I had succeeded in charming her with my lead mineral I should even so have had only half of the honor for the discovery. Del Rio was so much earlier than I with the discovery. Sefström, however, has the honor undivided. He succeeded by using quite another method.

Wöhler continued his work with vanadium, among other things searching for the element in other brown and green lead ores. He also proposed the name vanadinite for $Pb_5[Cl(VO_4)_3]$, the mineral in these ores (see Figure M31).

21.2.7
Vanadium Metal in History

Throughout the whole period of discovery, the first three decades of the 19th century, vanadium minerals had been found and vanadium compounds been prepared. The metal itself, however, had not been isolated. Berzelius showed early that it was impossible to prepare vanadium metal by reduction of the oxide with carbon. This gave vanadium carbide. Nor did reduction with metallic potassium give the pure metal.

Many decisive steps in the history of vanadium were taken in the 1860s by an Englishman, Sir Henry Enfield Roscoe. He was well known for his respected chemistry textbooks, translated into many languages. However, he investigated different vanadium compounds. He ascertained that vanadium's highest oxidation number is 5. This later became the reason for placing the element in group 5 of the periodic table. In 1867, Roscoe produced a silver-white powder by hydrogen reduction of vanadium chloride VCl_2. It was probably the first nearly pure vanadium metal prepared. In honor of Roscoe, a vanadium mineral has been given the name roscoelite

In 1927, Marden and Rich at the Westinghouse Lamp Company prepared metal with 99.8% vanadium by reduction of the oxide V_2O_5 with calcium at 900–950°C. In this pure form the metal is ductile.

21.3
Vanadium in Nature

21.3.1
Vanadium Minerals

Patronite is a black mineral consisting of an impure vanadium sulfide, whose exact composition is not known. It is, however, often given the formula VS_4. It was the mineral in the famous deposit Minas Ragra in Peru, once the largest known vanadium deposit but now empty. Another mineral is roscoelite, a vanadium analogue of muscovite, and thus a vanadium-bearing mica. This is found in a number of rich gold-bearing veins. Vanadinite, $Pb_5[Cl(VO_4)_3]$, well known from the history of the element's discovery, is still important. It is a red, yellow or brown mineral, which often encrusts other minerals in lead mines.

21.3.2
Vanadium in Different Sources

Vanadium is widespread in the earth's crust, twice as abundant as copper and ten times more than lead. Titanium minerals such as ilmenite often have a V-content of 0.1–0.3%. Vanadium is usually obtained as by-product from the extraction of iron from V-containing iron ores, uranium from V-containing carnotite and phosphorus from V-containing phosphate rocks.

The phosphate rocks of Idaho and Montana contain 0.1–0.5% vanadium pentoxide. The vanadium content is extracted as oxide during the manufacture of phosphoric acid and phosphate fertilizers. Certain dust ores in Arkansas also contain vanadium in sufficient amount for the extraction of vanadium pentoxide.

Vanadium is present in some oils, especially those from Venezuela and Mexico. The content can be as high as 1.5 g vanadium per kg oil. Residues after combustion of such oils therefore become a vanadium raw material. In the soot the V-content can be up to 6%, in the fly ash 13% and in boiler residues up to 20%.

21.3.3
Vanadium in Titaniferous Rock

In magnetic iron ore, magnetite, the V-content can be 1–2%. This is the case in South Africa. The Bushveld-complex in Transvaal is a very large magmatic magnetite formation. In the eastern and western parts of this complex, there are heavy deposits of titaniferous rock with a vanadium content of up to 2%. That is one of the biggest vanadium reserves of the world. China is, however, reported to have the greatest reserves. The USGS estimates that the world vanadium reserve base is sufficient to meet vanadium demand for many hundreds of years.

21.4
Mine Production

The production of vanadium in mines is reported in Table 21.1.

Table 21.1 Mine production of vanadium in 2002 [21.2]

Country	Mine production Tonnes, vanadium content	Percentage of total
China	39 000	58.2
South Africa	18 000	26.9
Russia	9 000	13.4
Other countries	1 000	1.5
Total	67 000	100

21.5
Manufacture of Vanadium and Vanadium Products

The most important products in trade are vanadium pentoxide V_2O_5 and ferrovanadium. This can be illustrated by the information about US imports in the year 2000 (Table 21.2).

Table 21.2 Vanadium pentoxide and ferrovanadium are important trade products

Product	US-import 2000. Tonnes, contained vanadium	Note
Vanadium pentoxide	900	From South Africa 98 %
Ferrovanadium	2500	From South Africa 29 %, Canada 24 %, China 20 %, Czech Republic 11 %, others 16 %

Vanadium pentoxide is the raw material for production of vanadium metal, and ferrovanadium is an alloy that is added to a steel melt to give the steel a specified vanadium content. In addition ash, ore, and slag containing 1900 tonnes of vanadium were imported to the USA in 2000.

21.5.1
Vanadium Pentoxide From Iron Ores

V-containing iron ores are, as mentioned, important vanadium raw materials. The metal can be extracted in two ways.

21.5.1.1 Roasting of Ore Concentrate With Soda

After ore dressing a vanadium-rich concentrate is mixed with soda. Roasting (heating with free access of air) gives sodium vanadate, which is leached out with water. With sulfuric acid a vanadium hydroxide is precipitated that can be redissolved in soda to a pure solution of sodium vanadate. Addition of ammonium chloride precipitates white crystalline ammonium vanadate NH_4VO_3. This can be calcined to give orange vanadium pentoxide, suitable for production of pure vanadium and of ferrovanadium.

21.5.1.2 Roasting of Steel Manufacturing Slag with Soda

Pig iron (raw iron) is manufactured in a blast furnace. The vanadium content stays in the raw iron. During subsequent steel manufacture, oxygen is blown over or through the melt to oxidize and remove the carbon. At the same time vanadium is oxidized and the oxide goes to the slag. This slag can be used as raw material for the soda roasting process to extract vanadium.

> In 1924 a young student in metallurgy had to undertake a practical project for his examination. The task was to study slag formation in the Bessemer and Thomas processes for steel making (Chapter 8 Iron) and the work was done in Swedish steelworks [21.3]. When he analyzed the slag and summed up FeO, CaO, SiO_2 and so on, he did not get 100%. To his surprise the slag contained vanadium. He was then able to develop and patent a process for manufacturing vanadium pentoxide. By a first, short, blowing of air through the raw iron a small quantity of slag, high in vanadium oxide and silica, was formed. When this was removed, blowing could continue to complete the steel production. The vanadium slag was roasted with soda and leached in water. From the solution ammonium vanadate was precipitated. After drying and melting, flakes of vanadium pentoxide were obtained.

The process has in our day attracted interest for more thorough-going scientific research [21.4] in connection with modern metallurgical processes using oxygen instead of air as the oxidizing agent.

21.5.2
Manufacture of Vanadium Metal

Vanadium metal is produced by calcium reduction of V_2O_5 in a pressure vessel. High-purity ductile vanadium can also be obtained by reduction of vanadium trichloride with magnesium.

21.5.3
Manufacture of Ferrovanadium

Two types of ferrovanadium are available, one with 60–80% V, one with 45–50% V. The former is mainly produced in an aluminothermic process. V_2O_5, aluminum metal and iron, also metallic, are mixed and the following reaction is started

$$3V_2O_5 + 10Al \rightarrow 6V + 5Al_2O_3$$

The iron melts and high-alloyed ferrovanadium is obtained.

The low-alloyed type is produced from slag or other vanadium-containing raw materials (such as oil residues) with a silicothermic method in an arc furnace.

21.6
Uses of Vanadium

Vanadium is mainly used in materials technology. 90% of vanadium consumption is as an alloying element for steel. It is the element's tendency to form hard, stable carbides and nitrides that is utilized. Low concentrations, about 0.05%, make the steels fine-grained and tough[1]. Chromium–vanadium steels with 0.2–0.3% V are used for springs and transmission gears in engine parts. Higher concentrations, 2–3% as in high speed steels, give improved wear resistance.

Vanadium is also used in the titanium alloy Ti6Al4V (with 4% V). This alloy accounts for 50% of all titanium-based alloys.

The major use of vanadium, besides metallurgy, is as a catalyst in the chemical industry. Vanadium pentoxide has replaced platinum as a catalyst for manufacturing sulfuric acid.

In 2001 vanadium products, corresponding to about 58 000 tonnes of vanadium were produced. China accounted for half of this quantity, South Africa for 30%.

21.7
Biological Role

The decomposition of vanadium-containing rocks under the influence of water and wind makes the metal available in soils. This is important as vanadium is an essential element for many species, including human beings. The exact biological function is unclear. Probably the ability to change between different oxidation states is important. Vanadium-containing bacteria take part in the transfer of atmospheric nitrogen to chemically bound nitrogen.

[1] Indian wutz steel was delivered to Damascus and forged by experienced masters. Their swords were famous for strength and toughness. Modern research has revealed that traces of vanadium, from the original ore, were responsible for the formation of a fine-grained structure and toughness.

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22
Niobium

22.1 Nb
Facts about Niobium

22.1.1 Nb
The Element

Symbol:	Nb
Atomic number:	41
Atomic weight:	92.91
Ground state electron configuration:	$[Kr]4d^4 5s^1$
Crystal structure:	Cubic bcc with a = 3.30 Å

22.1.2 Nb
Discovery and Occurrence

Discovery: C. Hatchett in England discovered the oxide of niobium in an American mineral in 1801. He called the element *columbium* and the mineral *columbite*. H. Rose in Germany rediscovered the element in 1844 and called it niobium. IUPAC, the International Union of Pure and Applied Chemistry, decided in 1950 that the name should be niobium (Nb) and not columbium (Cb). C. W. Blomstrand, professor at the University of Lund in southern Sweden was probably the first to see the metal. In 1864 he heated niobium chloride in an atmosphere of hydrogen and got steel-gray niobium with a metallic luster.

Most important mineral: *Columbite* is a continuous mineral series with niobium and tantalum. *Niobite* $(Fe,Mn)(Nb,Ta)_2O_6$ with 78% Nb_2O_5 is "end mineral" on the Nb-side. (Figure M32). Compare tantalite in the tantalum chapter.

Ranking in order of abundance in earth crust:	32–33
Mean content in earth crust:	20 ppm (g/tonne)
Mean content in oceans:	$1 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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22.1.3 Nb
Chemical Characterization

Niobium is a steel-gray, lustrous metal that resists the action of most acids. It is used as an alloying element in some stainless steels. Owing to its strong inclination to form carbides it prevents intercrystalline corrosion after welding. In hot-rolled structural steel niobium is used as a micro-alloying element in contents of about 0.05%. The effect is a fine-grained microstructure and a tough steel even after subjection to a high rolling and welding temperature. Niobium is also used in superalloys based on nickel and cobalt, intended for jet engine components.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Nb^{V} as in Nb_2O_5, NbF_5 and $NbOCl_3$	$Nb(g) \rightarrow Nb^{+}(g) + e^{-}$	652	$Nb(g) + e^{-} \rightarrow Nb^{-}(g)$
Nb^{IV} as in NbO_2 and NbF_4	$Nb^{+}(g) \rightarrow Nb^{2+}(g) + e^{-}$	1380	−86.1
Nb^{III} as in $NbCl_3$ and $Nb(CN)_8^{5-}$	$Nb^{2+}(g) \rightarrow Nb^{3+}(g) + e^{-}$	2416	
Nb^{II} as in NbO	$Nb^{3+}(g) \rightarrow Nb^{4+}(g) + e^{-}$	3700	
	$Nb^{4+}(g) \rightarrow Nb^{5+}(g) + e^{-}$	4877	
	$Nb^{5+}(g) \rightarrow Nb^{6+}(g) + e^{-}$	9847	

Standard reduction potential:	$Nb_2O_5(s) + 10H^{+}(aq) + 10e^{-} \rightarrow 2\,Nb(s) + 5H_2O(l)$	$E^0 = -0.644$ V
	$Nb^{3+}(aq) + 3e^{-} \rightarrow Nb(s)$	$E^0 = -1.10$ V
Electronegativity (Pauling):	1.6	
Radii of atoms and ions:	Atomic:	145 pm
(WebElements™)	Covalent:	137 pm
	Nb^{3+} (6-coordinate, octahedral):	86 pm
	Nb^{4+} (6-coordinate, octahedral):	82 pm
	Nb^{4+} (8-coordinate):	93 pm
	Nb^{5+} (4-coordinate, tetrahedral):	62 pm
	Nb^{5+} (6-coordinate, octahedral):	78 pm
	Nb^{5+} (8-coordinate):	88 pm

22.1.4 Nb
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
8570 kg m^{-3} 8.57 g cm^{-3}	10.84 cm^3	2750 K 2477 °C	5017 K 4744 °C	265 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
53	53	55	58	64

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$5.2 \cdot 10^{-6}$	$7.3 \cdot 10^{-6}$	$7.8 \cdot 10^{-6}$	$8.2 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
30	152	192	271	430	590

Mass magnetic susceptibility χ_{mass} at 293 K	$+27.6 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
105 GPa	38 GPa	203 GPa	0.35

22.1.5 Nb
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	26.9 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	690 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	726 kJmol^{-1}
Entropy S^0 at 298 K	36.40 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	17.4	24.60	26.3	28.0	33.4	38.6

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/5\ Nb + O_2 \rightarrow 2/5 Nb_2O_5$	–705	–675	–587	–495	–

22.1.6 Nb
Nuclear Properties and X-ray

Isotope range, natural and artificial	83–110

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{93}Nb	Stable	100	+9/2	6.1705

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{93}Nb
Reference compound	$KNbCl_6$/MeCN
Frequency MHz (^{1}H = 100 MHz)	24.476
Receptivity D^P relative to ^{1}H = 1.00	0.488
Receptivity D^C relative to ^{13}C = 1.00	2790
Magnetogyric ratio, radT^{-1}s^{-1}	$6.567 \cdot 10^7$
Nuclear quadropole moment, barn	–0.32

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
40	Zr	15.692
41	Nb	16.521
42	Mo	17.374

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	145
17.37 keV (MoKα_2)	17.9

Neutron absorption	**Thermal neutron capture cross section**	1.15 barns

22.2
Discovery

22.2.1
Native Peoples Hunting Minerals

Governor John Winthrop was the first holder of this office in Massachusetts, New England, in North America. Although he had emigrated to America and the British colony of Massachusetts in 1630 he took part in the foundation of the Royal Society in London in 1660. In his position in America he was anxious to find valuable minerals that “must be available in this wilderness”. He reported, as a support for his presumption, that the indigenous people often collected beautiful minerals in connection with their hunting and brought them to the governor’s office. “But it is always small superficial specimens, collected without system”. The governor regretted that he did not have enough time to devote himself to an activity that was so important for the country. His grandson, also John Winthrop, had followed in his grandfather’s footsteps in having an interest in the study of nature.

Sir Hans Sloane (1660–1753) in London was an active man of science, president of the Royal Society and editor of the distinguished journal *Philosophical Transactions*. He was also an interested collector. Books, pictures, coins and minerals from his collection were placed at the disposal of the British Museum. Sir Hans had close contact with John Winthrop Jr in Connecticut, who in 1734 was elected as a member of the Royal Society. John donated more than six hundred specimens of minerals from New England, which were incorporated in the mineralogical collection of the British Museum. This turned out to be of great importance in the history of element discoveries. At the beginning of the 19th century the element niobium, or columbium as it was called, was discovered in the mineral collection from New England.

22.2.2
A Discovery in the Museum

Charles Hatchett (1765–1847) grew up in an affluent family in London. His father was a famous manufacturer of state coaches. When he was six, Charles and his family moved into a new home, the beautiful Bell Ville House. During his adolescence he had a good education and especially studied chemistry. He was also, with a view to the future, taught a lot about economics and management. Charles was only an active chemist for one decade at the turn of the century, that is when he was 30–40 years old. After that he gradually had to take over the responsibility for the family business. During his chemical period he cooperated with both Henry Cavendish and Humphry Davy. In his first publication, in the *Philosophical Transaction* dated 1796, he described an investigation of lead molybdate and the properties of molybdic acid. There he refers to *the celebrated Scheele* and his work with molybdæna.

The minerals in the British Museum, including among others the specimens from New England donated by John Winthrop some decades earlier, needed identification and listing. Charles Hatchett was engaged for the task. The beginning of the 19th century was a time when chemists also had knowledge of mineralogy. The American collection was mainly made up of iron ore minerals. One specimen, however, attracted Charles' special interest – a black, heavy stone that gave a golden streak when scratched against porcelain. It contained iron and was similar to the chromium mineral chromite. But there was no chromium in it. In 1801, Hatchett found that two-thirds of the mineral was a metal oxide with reactions different from any known oxide.

He then concluded that he had discovered a new element. In consultation with distinguished chemists in England he gave the new element the name *columbium,* with reference to its American origin. As a consequence the mineral was given the name *columbite.*

22.2.3
One Element or Two?

The year after Hatchett's discovery in London, Anders Gustaf Ekeberg in Uppsala found the element *tantalum* in minerals from Ytterby in the Stockholm archipelago and at Kimito, near Åbo in Finland (see Chapter 23 Tantalum). Soon disputes arose about whether Hatchett's columbium and Ekeberg's tantalum really were two different elements or if they were two names for one and the same metal. Neither Hatchett nor Ekeberg could take much part in this discussion. The former had no time to devote to chemistry, as his family insisted on his working for the business. The latter suffered from poor health and died in 1813. Other clever chemists analyzed and argued and came to an agreement.

A very prominent English chemist at this time was *William Hyde Wollaston*, discoverer of the elements palladium and rhodium. Berzelius met Wollaston and expressed his admiration for his knowledge and personal integrity: "I have got more out of an hour's conversation with him than from the reading of heavy printed writings". In his travel diary Berzelius writes that there is a phrase that "whoever argues against Wollaston is wrong". Nevertheless it was what Berzelius had to do in the battle about columbium and tantalum.

In 1809 Wollaston analyzed both columbite and tantalite. From his investigation he concluded that columbium and tantalum were identical and his opinion was accepted by many chemists right up to the 1840s. If this was the truth the consequence would be that the metal columbium/tantalum had been discovered by Hatchett in 1801 before Ekeberg's discovery in 1802. Hatchett thus should have the priority. In support of Ekeberg, his former teacher Berzelius argued that *if* the elements were identical the name ought to be tantalum and not columbium. A geographical name like columbium was not good, especially as "we are not in fact quite sure about the origin of the examined mineral". Berzelius' opinion seems to have been shared by many chemists. Within four decades the metal was named tantalum.

But the conflict remained latent, a conflict that in middle of the 1840s received an unexpected solution. Continued research made clear that there are in fact two separate metals, columbium and tantalum.

The new metal, or the two new metals columbium/tantalum, were present in minerals alternatively called columbite and tantalite. In the period 1840–45 a distinguished German analytical chemist, *Heinrich Rose*[1], made careful studies on columbites and tantalites from different deposits. He was able to show that in a Bavarian columbite from Bodenmais there were at least two different metallic elements with great chemical similarity. At one stage of the investigation, in fact, he thought that there were three different elements present, one heavy that he called tantalum and two lighter. One of these he called *niobium,* after *Niobe,* a daughter of *Tantalus* in Greek mythology, while the other was named *"pelopium"* after *Pelops,* Niobe's brother. Rose, however, changed his mind. Pelopeum was a mistake. There was only one light element. The reason for the mistake was that niobium forms two chlorides, one yellow $NbCl_5$ and one white $NbOCl_3$. Rose thus claimed to have discovered *one* new element, niobium. Ekeberg from Uppsala remained, 30 years after his death, the sole discoverer of tantalum.

Jean Charles Galissard de Marignac (1817–1894) was professor of chemistry at the University of Geneva. He made very accurate determinations of atomic masses and was complimented for this by Berzelius, who wrote to him: "The patience you show when you repeat every determination several times, the acumen with which you vary your methods and the fact that you use only such methods as can give reliable results, ensure you full confidence from all chemists."

The scrupulous Marignac conclusively proved that niobium and tantalum are different elements. He made the separation using the fact that potassium heptafluorotantalate K_2TaF_7 is much less soluble in dilute hydrofluoric acid than is pentafluorooxoniobate, K_2NbOF_5. After careful separation Marignac could determine the atomic weights of the two metals.

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[1] Members of the German family Rose have played an important role within chemistry and mineralogy. A "family chronicle" is given in Chapter 46 Arsenic, Antimony and Bismuth. Heinrich Rose (1795–1864) studied with Berzelius in Stockholm 1820–1821. In 1823 he became professor of chemistry at the University of Berlin and considerably developed analytical chemistry.

22.2.4
A New Name Question

One name question had thus got an answer but *another* had arisen. About tantalum no further discussion was needed. But the lighter element – should it be called columbium following Hatchett or niobium following Heinrich Rose? And furthermore: were columbium and niobium identical or two different elements? An American chemist, J. Lawrence Smith, was contemporary with Rose and had studied with Justus Liebig in the 1840s. He was thus familiar with European chemical literature and probably with Rose's work on niobium and tantalum. He was professor of chemistry at the university in Louisville 1854–1866 and in 1877 was the second president of the American Chemical Society. In 1877, Smith stated in the *American Journal of Science* that in 1844 Rose had been of the opinion that he had discovered a new element niobium while Hatchett's columbium was identical with tantalum. However, according to Smith, Rose's further work revealed that niobium was actually identical with columbium. That solved the chemical identification problems. The difficult name question – columbium or niobium – remained to be answered.

Marignac accepted Rose's name niobium. It was also generally accepted on the European continent. In the USA the element's name was columbium; in England both names were used. At the Amsterdam conference in 1949 of the International Union of Pure and Applied Chemistry it was decided that the name niobium (Nb) should be valid for all the world and that columbium (Cb) should not be used. This is also contained in an official nomenclature report in *J. Am. Chem. Soc.*, 1960, 82, 5525.

22.2.5
The Element Niobium

Hatchett never isolated the metal columbium from its oxide. Nor could Rose prepare niobium in metallic form. This is not surprising. No matter what name it was given, the element was very tightly bound to oxygen. *C. W. Blomstrand*, professor at the University of Lund in southern Sweden was probably the first to see the metal. In 1864 he heated niobium chloride in an atmosphere of hydrogen and got steel-gray niobium with a metallic luster.

In 1906 Werner von Bolton at Siemens & Halske in Germany manufactured niobium by the aluminothermic method and purified it by repeated re-melting in a vacuum furnace.

22.2.6
The Niobium and Vanadium Discoveries – Great Similarities

The history of element discoveries shows notable similarities for niobium and vanadium as shown in Table 22.1.

Table 22.1 Similarities in the history of vanadium and niobium discoveries

Element	Vanadium	Niobium
First discovery		
Year	1801	1801
Discoverer	Del Rio	Hatchett
First name of the element	Erythronium	Columbium
Hesitation about the element		
Was it	Chromium?	Tantalum?
Rediscovery		
Year	1830	1840–45
Discoverer	Sefström	Rose
New name for the element	Vanadium	Niobium
Chemistry of the element clarified		
By	Roscoe	Marignac/Blomstrand
When	1860s	1860s
The element in pure metallic form		
Reduction of	V chloride	Nb chloride
Reduction with	Hydrogen	Hydrogen
When	1867	1864
By	Roscoe	Blomstrand

22.3
Niobium and Tantalum Minerals

Niobium and tantalum are present in the earth's crust as oxides in minerals that form a continuous series between the two extreme minerals *niobite* $(Fe,Mn)(Nb,Ta)_2O_6$ with 78% Nb_2O_5 and *tantalite* $(Fe,Mn)(Ta,Nb)_2O_6$ with 84% Ta_2O_5. A common name for all minerals within the series is *columbite* (Figure M32).

Table 22.2 shows some properties and compositions for the two end minerals. In minerals in the series some other metals can be present in varying contents: calcium, rare earth metals, titanium, uranium, thorium. Radioactive elements present have an influence on the minerals, changing their originally lustrous, black surface to a dull brownish-black color. In this process the hardness decreases considerably.

For niobium production very big quantities of pyrochlore are extracted in Brazil and Canada. The world production of mineral concentrates (pyrochlore) was 25 600 tonnes in 2001 (counted as niobium) of which 22 000 tonnes (86%) were produced in Brazil and 3180 tonnes (12%) in Canada [22.1].

Table 22.2 Niobium and tantalum minerals[a]

Mineral	Chemical formula	Crystalline form	Density g/cm³	Nb_2O_5 %	Ta_2O_5 %
Pyrochlore	$(Ca,Na)_2(Nb,Ta)_2O_6(O,OH,F)$	Cubic	4.3	63.6	–
Figure M33			↓	↓	↓
Microlite	$(Ca,Na)_2(Ta,Nb)_2O_6(O,OH,F)$	Cubic	6.4	3.6	77.0
Niobite	$(Fe,Mn)(Nb,Ta)_2O_6$	Ortho-	5.3	78.0	–
Figure M32		rhombic,	↓	↓	↓
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	dipyramidal	8.1	2.0	83.6
Figure M32					
Tapiolite	$(Fe,Mn)(Ta,Nb)_2O_6$	Ditetragonal,	7.3–	1.4–	86.0–
		dipyramidal	8.0	11.2	73.9
Euxenite	$(Y,Ce,U,Pb,Ca)(Nb,Ta,Ti)_2(O,OH)_6$	Orthorombic,	5.0	41.4	3.8
			↓	↓	↓
Tanteuxenite	$(Y,Ce,U,Pb,Ca)(Ta,Nb,Ti)_2(O,OH)_6$	dipyramidal	5.9	3.8	47.3
Samarskite	$(Y, U,Ca)\ (Nb,Ta,Fe^{III})_2(O,OH)_6$	Orthorombic,	5.0	46.4	1.8
		dipyramidal	↓	↓	↓
Yttrotantalite	$(Y, U,Ca)(Ta,Nb,Fe^{III})_2(O,OH)_6$		5.7	20.4	39.6
Fergusonite	$(Y,Er,Ce,Fe)(Nb,Ta,Ti)O_4$	Tetragonal,	5.6–	34.8–	27.0–
		dipyramidal	5.8	47.1	2.0

[a] According to Dana's System of Mineralogy, 7. Ed., Vol. 1, 7th ed. Table arranged by S. V. Sölver, Mining and Metallurgical School, Filipstad, Sweden.

22.4
Industrial Niobium Manufacture

22.4.1
Separation of Niobium and Tantalum

Marignac's fractional crystallization is slow. Solvent-extraction methods are faster and much more effective. Concentrates containing niobium and tantalum are dissolved in a mixture of hydrofluoric and sulfuric acids. Extraction with isobutyl ketone takes both metals to the organic phase. Niobium and tantalum can be extracted selectively from the ketone phase, niobium with sulfuric acid, tantalum with ammonium fluoride solution [22.2].

22.4.2
Manufacture of Niobium Metal and Ferroniobium

Surprisingly, niobium can be obtained using carbon reduction [22.3]. In a first reaction between niobium oxide and carbon, niobium carbide NbC is formed. This is ground together with a carefully calculated amount of Nb_2O_5. The mixture is compacted to a cylinder, which is heated in a vacuum to ca. 2000°C. Then the following reaction occurs:

$$5NbC + Nb_2O_5 \rightarrow 7Nb + 5CO$$

Other industrial methods are reduction of $NbCl_5$ or K_2NbF_7 with sodium.

Ferroniobium is manufactured using the aluminothermic method described for ferrovanadium. The alloy is used as a furnace addition to give steel a specified niobium content. Brazil is the world's biggest producer of ferroniobium. An aluminothermic charge can be composed of 18 tonnes pyrochlore, 4 tonnes hematite, 6 tonnes aluminum powder and 0.5–0.75 tonnes each of lime and fluorspar. From the reaction an 11-tonnes ingot with 65–70% Nb is obtained.

22.5
Uses of Niobium

Niobium is used as an alloying element in two types of steel.

In some stainless steels niobium (or titanium) is added to prevent inter-crystalline corrosion after welding. The carbon in the steel is bound as niobium carbide.

In hot-rolled structural steel intended for welding, niobium is used as a micro-alloying element in contents about 0.05%. The effect is a fine-grained microstructure even after the high rolling and welding temperature. In spite of the low niobium content this is, in tonnage, the biggest application of niobium and corresponds to about 75% of the total niobium consumption.

Niobium is also very much used in superalloys based on nickel and cobalt, intended for jet engine components, rocket subassemblies, and combustion equipment. The important alloy Inconel 718 contains (%) 53 Ni, 19 Cr, 5 Nb and 1 Ti.

In the year 2001 the total world consumption of niobium was 27 500 tonnes.

22.6
Niobium in Life

The mineral columbite is extremely insoluble in water and the concentration of dissolved niobium is very low. The element has no biological role.

References

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23
Tantalum

23.1 Ta
Facts about Tantalum

23.1.1 Ta
The Element

Symbol:	Ta
Atomic number:	73
Atomic weight:	180.95
Ground state electron configuration:	$[Xe]4f^{14}5d^36s^2$
Crystal structure:	Cubic bcc with a = 3.30 Å

23.1.2 Ta
Discovery and Occurrence

Discovery: Anders Gustaf Ekeberg in Uppsala discovered the oxide of an unknown metal in a mineral from Ytterby near Stockholm in 1802. He gave the new element the name tantalum after Tantalus in Greek mythology. The first ductile tantalum, manufactured by W. von Bolton in Germany 1903, was used for the metal filament in electric light bulbs.

Most important mineral: *Columbite* is a continuous mineral series with niobium and tantalum. *Tantalite* $(Fe,Mn)(Ta,Nb)_2O_6$ with 84% Ta_2O_5 is the "end mineral" on the Ta-side (Figure M32). Compare niobite in Chapter 22 Niobium.

Ranking in order of abundance in earth crust:	52–53
Mean content in earth crust:	2 ppm (g/tonne)
Mean content in oceans:	$2 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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23.1.3 Ta
Chemical Characterization

Tantalum is a grayish metal that is almost immune to chemical attack at temperatures below 150°C. It is in fact dissolved only by hydrofluoric acid and free sulfur trioxide. Although it is very hard it can be drawn into fine wire. Owing to its corrosion resistance tantalum has largely replaced platinum in standard weights and in some laboratory ware. The largest use of tantalum is for capacitors in electronic circuits.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ta^{V} as in Ta_2O_5, $TaCl_5$ and $TaOF_3$	$Ta(g) \rightarrow Ta^+(g) + e^-$	761	$Ta(g) + e^- \rightarrow Ta^-(g)$
Ta^{IV} as in TaO_2 and TaI_4	$Ta^+(g) \rightarrow Ta^{2+}(g) + e^-$	1500	–31
Ta^{III} as in $TaBr_3$ and TaF_3			

Standard reduction potential: $Ta^{5+}(aq) + 5e^- \rightarrow Ta(s)$ $E^0 = -0.81$ V

Electronegativity (Pauling): 1.5

Radii of atoms and ions: (WebElements™)		
	Atomic:	145 pm
	Covalent:	138 pm
	Ta^{3+} (6-coordinate, octahedral):	86 pm
	Ta^{4+} (6-coordinate, octahedral):	82 pm
	Ta^{5+} (6-coordinate, octahedral):	78 pm
	Ta^{5+} (8-coordinate):	88 pm

23.1.4 Ta

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
16 650 kg m^{-3} 16.65 g cm^{-3}	10.87 cm^3	3290 K 3017 °C	5731 K 5458 °C	140 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
58	57	58	58.5	60

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$4.8 \cdot 10^{-6}$	$6.3 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$	$7.2 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
25	123	167	255	430	615

Mass magnetic susceptibility χ_{mass} at 293 K	$+10.7 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
186 GPa	69 GPa	203 GPa	0.34

23.1.5 Ta
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	31 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	750 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	782 $kJmol^{-1}$
Entropy S^0 at 298 K	41.51 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	19.7	25,36	26.8	27.9	31.2	34.2

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/5\ Ta + O_2 \rightarrow 2/5 Ta_2O_5$	–765	–725	–645	–565	–485

23.1.6 Ta
Nuclear Properties and X-ray

Isotope range, natural and artificial 156–186

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{181}Ta	Stable	99.99	+7/2	2.371	–	–	–
^{180}Ta	Active	0.01	+1	–	8.15 h	EC or β^+ β^-	0.854 MeV 0.708 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{181}Ta
Reference compound	$KTaCl_6/MeCN$
Frequency MHz (^1H = 100 MHz)	11.990
Receptivity D^P relative to ^1H = 1.00	0.0374
Receptivity D^C relative to ^{13}C = 1.00	214
Magnetogyric ratio, $radT^{-1}s^{-1}$	$3.244 \cdot 10^7$
Nuclear quadropole moment, barn	3.17

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
72	Hf	54.611
73	Ta	56.277
74	W	57.982

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	162
17.37 keV ($MoK\alpha_2$)	91.4

Neutron absorption	**Thermal neutron capture cross section**	20.5 barns

23.2
Discovery

23.2.1
Ekeberg – Weak, Strong and Versatile

Anders Gustaf Ekeberg (1767–1813) was a chemist, active at the University of Uppsala.

He was born in Stockholm, became a student at the university in 1784 and graduated Master of Science in 1788. Vorpommern, now in northern Germany, was at this time a Swedish possession and so was Greifswald with its university. This institution became very important for the development of connections between Germany and Sweden. Ekeberg studied at this university 1789–90 and had professor C. E. von Weigel as teacher. This man had translated Lavoisier's works into German and probably influenced Ekeberg to be a convinced anti-phlogistonist. This became important when Ekeberg returned to Uppsala as associate professor and teacher of chemistry during the 1790s.

In a brochure of 1795 with the title *An attempt at a Swedish Nomenclature in Chemistry adapted to the latest Discoveries* an outline is given of a chemistry without phlogiston, a chemistry based on Lavoiser's modern principles and experiments regarding the nature of combustion. The brochure was published anonymously as Ekeberg tried to avoid personal controversies with the head of his institution, the temperamental professor Johan Afzelius, who stuck to phlogiston and had no faith in the many new ideas [23.1].

It was a very special task for Ekeberg to teach chemistry to Berzelius, twelve years younger than himself. In his autobiographical notes Berzelius indicates how much he esteemed his former teacher and how much he appreciated him as a scientist. He also refers to this in the context of his participation in the priority discussions after the discoveries of niobium and tantalum.

Ekeberg suffered from poor health and his vigour declined towards the end of his short life. A serious cold in childhood had reduced his hearing and it became still weaker over the years. An explosion during an experiment with an oxygen–hydrogen gas mixture destroyed the sight on one eye. This happened in 1801, the year before his discovery of tantalum. In spite of his general weakness his contributions to science were outstanding. He is remembered for three important achievements to chemistry, namely

- the discovery of the element tantalum
- actively working to free Swedish chemistry from the phlogiston theory
- teaching chemistry to Jöns Jacob Berzelius.

Ekeberg was a man of great talent, in the humanities as well as in science. Many patriotic odes and speeches are still extant from his youth. He was also very well acquainted with the history and mythology of classical antiquity. This was a significant motive in his choice of *tantalum* as the name of the element he discovered.

23.2.2
Tantalus – Son of Zeus

As chemist in Uppsala and also as assistant in the Laboratorium Chymicum in Stockholm Ekeberg developed into a very capable mineral analyst. In 1797 he investigated a sample from Ytterby feldspar quarry outside Stockholm, finding and confirming Gadolin's discovery of gadolinite, three years earlier (Chapter 17 Rare Earth Metals). But Ekeberg also discovered another mineral with a new, unknown element. He isolated its oxide and found it to be almost insoluble in acid. This gave the discoverer the idea for a name for the new element.

> To the new member among the metals I give the name Tantalum, partly to follow the custom of adopting names from mythology, and partly to allude to the fact that the oxide of this metal is incapable of feeding itself even in the middle of a surplus of acid.

King Tantalus of Lydia, son of Zeus, was condemned to eternal pangs of hunger and thirst in Hades for having insulted the gods. He was placed in a lake, the water of which reached up to his lips. As soon as he started to drink the water sank. Over him hung branches with delightful fruits, but they moved aside when he tried to eat. This ancient Greek myth has given us the expression "suffer the torments of Tantalus", which means that we cannot reach things that are temptingly near. This myth is thus the background to the name for element 73.

23.2.3
Tantalum or Columbium?

As described in Chapter 22 Niobium, Hatchett found a new element in 1801 that he called columbium. The disputes about whether columbium and tantalum were two names for one and the same element or if they really were two different metals have likewise been described there.

It is not known how Ekeberg reacted to the situation when the tantalum/niobium discoveries attracted international interest within chemistry. Perhaps he suffered the torments of Tantalus, when his priority in the discovery of tantalum was questioned and the recognition was withdrawn. The element name tantalum was indeed accepted, and in spite of his frail health he had experienced a wonderful time in 1802 when he discovered the new element. But that the metal had been discovered in England the year before was the general opinion in 1813 when Ekeberg passed away. However, as Chapter 22 makes clear, investigations and results in the 1840s showed that the tantalum found in 1802 was a unique element. Since then, no one has questioned Ekeberg's priority.

23.2.4
The Element Tantalum

In 1825 Berzelius reduced K_2TaF_7 with potassium and got an impure metal. Rose prepared a purer metal powder in 1866 by reduction with sodium. Commercial production today is based on these old reactions.

The first ductile tantalum was manufactured by W. von Bolton at Siemens & Halske in Germany in 1903 and was used for metal wire in electric light bulbs. Many millions of tantalum wire lamps were produced until the metal tungsten replaced it. Tungsten is less volatile at the high working temperature and is thus more suitable.

23.3
Tantalum and Niobium Minerals

Niobium and tantalum are present in the earth's crust as oxides in minerals that form a continuous series between the two extreme minerals *niobite* $(Fe,Mn)(Nb,Ta)_2O_6$ with 78% Nb_2O_5 and *tantalite* $(Fe,Mn)(Ta,Nb)_2O_6$ with 84% Ta_2O_5. A common name for all minerals within the series is *columbite* (Figure M32).

Table 22.2 (p. 558) shows the compositions and some properties of the minerals. Minerals in the series may contain varying amounts of some other metals: calcium, rare earth metals, titanium, uranium or thorium. Any radioactive elements present have an influence on the minerals, changing their originally lustrous black surface to a dull brownish-black color. In this process the hardness decreases considerably.

The biggest producers of tantalite concentrates are located in Australia, Brazil, Rwanda, Canada, Congo and Ethiopia (Table 23.1).

Tantalum is even present in some tin ores. During tin extraction, tantalum goes to the slag, which thus becomes an important, though decreasing, source of the metal.

Table 23.1 World production in 2001 of tantalum mineral concentrates (contained tantalum)

Country	Production tonnes	Percentage of total	Note
Australia	660	50.9	Columbite–tantalite
Brazil	340	26.2	Tantalite
Rwanda	95	7.3	–
Canada	77	5.9	Tantalite
Congo (DRC)	60	4.6	Columbite–tantalite
Ethiopia	47	3.6	Tantalite
Other countries	19	1.5	
Total (round)	1300	100	

Figures taken from ref. [23.2]

23.4
Industrial Tantalum Manufacture

Methods for separating tantalum and niobium are described in refs. [23.3–5] and in Chapter 22 Niobium.

Tantalum can be manufactured by carbon reduction in the same way as described for niobium: first a reaction between Ta_2O_5 and carbon to form Ta carbide and then, at a higher temperature:

$$5TaC + Ta_2O_5 \rightarrow 7Ta + 5CO$$

Another industrial method is reduction of K_2TaF_7 by sodium. The two reactants are loaded into a steel bomb. After an external heating the exothermic reaction proceeds vigorously. After cooling, the bomb contents are treated with water and methanol to remove excess sodium and salts.

Tantalum is also manufactured by electrolysis of melts with the percentage composition: 60 KCl, 25 KF, 10 K_2TaF_7, and 5 Ta_2O_5. The electrolysis is carried out in iron crucibles, which are also the cathode. This method made the metal commercially available in the USA in 1922.

The tantalum powder produced by the described methods must, for most purposes, be converted into a massive form. This is carried out by *arc melting* using a consumable electrode as described in Chapter 18 Titanium (see Figure 18.5, p. 505). Another method is *electron beam melting* in which the compacted powder is heated by electron bombardment in a high vacuum furnace.

23.5
Uses of Tantalum

World consumption of tantalum was about 2000 tonnes in 2001. Tantalum, like niobium, is used in superalloys based on nickel and cobalt, intended for aircraft engines and other high-temperature applications. Tantalum carbide TaC is, to a limited extent, used as a hard component in cemented carbide. The oxide is used to make special glass with a high refractive index for camera lenses

Two tantalum properties have, however, given the metal its special importance in modern industry.

23.5.1
Excellent Corrosion Resistance

A passive layer on the metal gives tantalum excellent corrosion resistance and makes the metal suitable for use in chemical industry for applications where the chemical attack is very strong. Tantalum is in fact as resistant as platinum to many corrosive agents and has replaced platinum in laboratory ware and weights in analytical balances. In the chemical industry it is used as liners for reactors and for manufacturing corrosion- and heat-resistant equipment.

23.5.2
The Modern Capacitor

The major use, however, more than 60% of the total consumption, of tantalum is very special. The metal is very widely used for electronic components, mainly capacitors. The dielectric necessary for a capacitor is simply the passive layer. Applications for this type of capacitor are mobile telephones and other communication systems and instruments for controlling ships, aircraft, missiles and weapons systems. Tantalum is also used for rectifiers in low-voltage systems such as railway-signal systems.

23.6
Tantalum in Life

The mineral tantalite is extremely insoluble in water and the dissolved concentration of tantalum is very low. The element has no biological role. The resistance of metallic tantalum to attacks from different agents also makes it compatible with body tissues. Because of that the metal can, like titanium, be used for implants and in other medical applications.

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24
Chromium

24.1 Cr
Facts about Chromium

24.1.1 Cr
The Element

Symbol:	Cr
Atomic number:	24
Atomic weight:	52.00
Ground state electron configuration:	[Ar]$3d^54s^1$
Crystal structure:	Cubic bcc with $a = 2.88$ Å

24.1.2 Cr
Discovery and Occurrence

Discovery: The mineral "Siberian red lead", crocoite, a lead chromate, was discovered by Lehmann in the 1760s in the Beresof Mine, Ural Mountains. In 1770 the mineral was again found there and characterized by Pallas. The red lead was investigated and a new metal, chromium, was isolated in 1797 by Nicolas-Louis Vauquelin in Paris. The technically important mineral chromite was discovered in 1798 in the Ural Mountains.

Most important mineral: Chromite $FeCr_2O_4$ (Figure M35)

Ranking in order of abundance in earth crust:	21
Mean content in earth crust:	102 ppm (g/tonne)
Mean content in oceans:	$3 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	1000 years
Mean content in an adult human body:	0.03 ppm
Content in a man's body (weight 70 kg):	2 mg

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24.1.3 Cr

Chemical Characterization

Chromium is a steel-gray, lustrous, hard metal. It is an essential trace element and has a role in glucose metabolism. Compounds of hexavalent chromium are toxic. Chromium is a very important alloying element for steel. More than 12% Cr makes steel stainless.

Oxidation states:

Cr^{III} as in Cr_2O_3, $CrCl_3$, and $Cr_2(SO_4)_3$
Cr^{VI} as in CrO_3, K_2CrO_4, and $Na_2Cr_2O_7$
Cr^{II} as in $CrCl_2$
Even Cr^{IV} and Cr^{V} exist

Ionization energy (kJ mol^{-1}):

$Cr(g) \rightarrow Cr^+(g) + e^-$	653
$Cr^+(g) \rightarrow Cr^{2+}(g) + e^-$	1591
$Cr^{2+}(g) \rightarrow Cr^{3+}(g) + e^-$	2987
$Cr^{3+}(g) \rightarrow Cr^{4+}(g) + e^-$	4743
$Cr^{4+}(g) \rightarrow Cr^{5+}(g) + e^-$	6702
$Cr^{5+}(g) \rightarrow Cr^{6+}(g) + e^-$	8745

Electron affinity (kJ mol^{-1}):

$Cr(g) + e^- \rightarrow Cr^-(g)$
-64.3

Standard reduction potential:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^0 = +1.33$ V
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $E^0 = -0.74$ V

Electronegativity (Pauling): 1.66

Radii of atoms and ions:
(WebElements™)

Atomic:	140 pm
Covalent:	127 pm
Cr^{2+} (6-coordinate, octahedral):	87 pm
Cr^{3+} (6-coordinate, octahedral):	75.5 pm
Cr^{4+} (4-coordinate, tetrahedral):	55 pm
Cr^{4+} (6-coordinate, octahedral):	69 pm
Cr^{5+} (4-coordinate, tetrahedral):	48.5 pm
Cr^{5+} (6-coordinate, octahedral):	63 pm
Cr^{5+} (8-coordinate):	71 pm
Cr^{6+} (4-coordinate, tetrahedral):	40 pm
Cr^{6+} (6-coordinate, octahedral):	58 pm

24.1.4 Cr

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
7190 kg m^{-3} 7.19 g cm^{-3}	7.23 cm^3	2180 K 1907 °C	2944 K 2671 °C	449 J K^{-1} kg^{-1}

Thermal conductivity Wm^{-1}K^{-1}

173 K	**273 K**	**373 K**	**573 K**	**973 K**
120	96.5	92	82	66

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$2.3 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$	$8.8 \cdot 10^{-6}$	$11.8 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
5	127	161	252	472	800

Mass magnetic susceptibility χ_{mass} at 293 K	$+44.5 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
279 GPa	115 GPa	162 GPa	0.21

24.1.5 Cr
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	15 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	340 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	397 $kJmol^{-1}$
Entropy S^0 at 298 K	23.77 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	10.0	23.35	27.7	31.9	41.2	39.3

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$4/3\ Cr + O_2 \rightarrow 2/3 Cr_2O_3$	−704	−665	−580	−495	−400

24.1.6 Cr
Nuclear Properties and X-ray

Isotope range, natural and artificial	43–63

Naturally occuring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half life**	**Decay mode**	**Decay energy Q**
^{52}Cr	Stable	83.78	+0	–	–	–	–
^{53}Cr	Stable	9.50	−3/2	−0.4745	–	–	–
^{54}Cr	Stable	2.37	+0	–	–	–	–
^{50}Cr	Active	4.35	+0	–	1.8 · 1017 y	EC or β^+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{53}Cr
Reference compound	K_2CrO_4/D_2O
Frequency MHz (^1H = 100 MHz)	5.652
Receptivity D^P relative to ^1H = 1.00	$0.863 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	0.493
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-1.515 \cdot 10^7$
Nuclear quadropole moment, barn	−0.15

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
23	V	4.944
24	Cr	5.405
25	Mn	5.888

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	249
17.37 keV ($MoK\alpha_2$)	30.3

Neutron absorption	**Thermal neutron capture cross section**	3.1 barns

24.2
Discovery

24.2.1
Europe Meets Asia

During the reign of Catherine II of Russia 1762–96 (Figure 24.1) a vigorous foreign policy was pursued, resulting in substantial expansion of the Russian empire. Catharina also took many initiatives to support science and technology. It was important for her to use scientists to map Russia's own natural resources. Great attention was paid to the Urals Mountains. On their eastern slopes, on the Siberian border where Asia meets Europe, ore deposits had already been discovered in 1702. The Beresof gold mines were well known. The town Yekaterinburg was founded in 1721. With the building of the trans-Siberian railway the town became a center for mining and for the metallurgical and chemical industries. The town also became famous in political history when tsar Nicolas II with his family was murdered there in July 1918. In 1924 the Soviet authorities changed the town's name to Sverdlovsk. Nowadays the name Yekaterinburg has been restored.

Figure 24.1 Empress Catherine II of Russia (1729–1796).

24.2.2
Siberian Red Lead

Johann Gottlieb Lehmann was mining director in Prussia and a teacher in Berlin. In 1761 he was employed as professor of chemistry in St Petersburg. He was appointed by Catherine herself to travel through the empire and describe mineralogical discoveries that could be of interest for technical and economic development. The area round Yekaterinburg was subject to great activity as also were areas further east.

At this time the famous chemist and poet M. V. Lomonosov, a member of the Russian Academy of Science, worked in St Petersburg (see further Chapter 9 Hydrogen). Lomonosov reported that Lehmann discovered and analyzed the mineral that became known as *the red lead of Siberia*, nowadays known as *crocoite* $PbCrO_4$ (Figure M34). In 1766 Lehmann observed and reported the beautiful green color of the solution of the red mineral in hydrochloric acid. He also found that the mineral contained lead but no new element. Lehmann's investigations could not be continued as he died suddenly, perhaps in an explosion in his laboratory.

Catherine had grown up in Germany, the daughter of the governor in Stettin, and she had very good relations with her former native country. The same year that Lehmann died she engaged a new Berliner, *Peter Simon Pallas*. He had studied in different European seats of learning and was well educated in science and medicine. During the period 1768–74 he made extensive expeditions in Siberia and the Ural Mountains. He described Beresof near Yekaterinburg and how gold, copper, silver and lead were mined there. Pallas also described the remarkable red Siberian lead, heavy and semitransparent. The color varied. Large crystals were red like cinnabar. Small irregular pyramids had similarities with rubies. Grinding gave a yellow powder useful for painting.

The achievements of Lehmann and Pallas made the red Siberian mineral known and accessible to better equipped laboratories in Europe.

24.2.3
From the Outskirts of the French Revolution to the Center of Chemistry

Nicolas-Louis Vauquelin (Figure 24.2) discovered the new metal chromium. He was born in 1763 in a farming family in the small village St André d'Hébertot in northwestern France. At the age of fourteen he became a dishwasher and laboratory assistant in a pharmacy in Rouen. Later he moved to Paris and continued his work in pharmacy. He was engaged by the famous scientist and chemist Antoine-François de Fourcroy, active in the new French antiphlogiston chemistry in the circle round Lavoisier. This was a stroke of luck for young Nicolas-Louis but also for chemical science.

Fourçroy himself had grown up under poor circumstances and was thrown upon his own resources of talent and diligence to fulfil his advanced studies. He was successful and was at 30 elected a member of the Academie des Science. He became an enthusiastic teacher of chemistry and he found in Vauquelin an equally enthusiastic pupil and assistant. In addition, Fourcroy's two unmarried sisters saw it as their mis-

Figure 24.2 Nicolas-Louis Vauquelin (1763–1829).

sion to give Nicolas-Louis a home and support so that he could study physics, chemistry and philosophy in Paris.

This was in the time of the French revolution. A story tells us that young Vauquelin met a Swiss guardsman, who had succeeded in escaping from the massacre in the Tuileries but was now being attacked by the mob in the street. Vauquelin took part in the fight and saved the soldier's life. His contribution against the revolution did not have the disastrous consequences for him as for Lavoisier, the pioneer of a new era in chemistry, who had to pay with his life for supposed anti-revolutionary actions. Vauquelin did have to leave Paris in 1793, but the new authorities were obviously aware of his pharmacy experiences and placed him as a pharmacist in a military hospital. Soon he was able to return to Paris and begin to teach chemistry at the institution that soon became the École Polytechnique. Later he was professor at the École des Mines. Nicolas-Louis had reached a goal. He had access to a good laboratory and he had the best contacts in the center of modern chemistry. His own fundamental work in chemistry could start.

24.2.4
The Discovery of the New Metal Chromium

In 1797 Vauquelin got a sample of Siberian red lead for investigation. He began with a recapitulation of its history: He pointed out that all specimens of the substance in different mineral collections in Europe came from one single place, the Beresof gold mine.

The transparency and crystalline structure raised questions among mineralogists and chemists about its nature. Its lead content was well known. But what was the reason for the red color?

> Vauquelin boiled the powdered mineral in potassium carbonate solution. A yellow solution was formed and a white precipitate of lead carbonate. He investigated the yellow solution carefully and made the following observations:

- Beautiful red precipitate after adding a mercury salt
- Yellow precipitate after adding a lead salt solution
- The yellow color of the solution changes to red after addition of tin(II) chloride (stannous chloride)

Vauquelin was now convinced that he had a new metal in his beakers. Trying to isolate the unknown element he evaporated to dryness a solution from which he had removed lead.

He ignited the rest and obtained the oxide of the unknown metal. He heated the powdered oxide and charcoal strongly for half an hour in a furnace. After slow cooling, he observed a network of metallic needles in the crucible.

In fact the reaction between chromium oxide and carbon at atmospheric pressure does not give chromium metal but chromium carbide, as chromium is a strong carbide former.

Perhaps Vauquelin obtained a mixture of chromium metal and chromium carbide. Anyhow he should get the full credit for the discovery of chromium as he:

- found an earlier unknown element in Siberian red lead
- established that the mineral is a compound of lead and an "acid" of the unknown metal
- isolated the "acid" of this new metal
- prepared the oxide and its reaction product with carbon

What name should be given to the new element? Vauquelin's friend and teacher M. Fourcroy was still active as professor of chemistry in Paris. René-Just Haüy, mineralogist and founder of the fundamental laws in crystallography, also belonged to the group of research scientists. Fourcroy and Haüy proposed the name *chromium* after the Greek word *chromos* for color. The reason was of course that the new metal formed so many colored compounds. Vauquelin accepted this suggestion.

An Englishman, E. D. Clarke, visited the Laboratorium Chymicum in Stockholm and its director P. J. Hjelm in 1799. What he wrote in his travelling report is remarkable: "He (Hjelm) showed me a very great chemical curiosity; namely a mass of chromium in the metallic state nearly as large as the top of a man's thumb".

Had Hjelm, only two years after the discovery of chromium, obtained a sample from Vauquelin? Or had the Laboratorium Chymicum repeated the Paris experiment on a larger scale in its powerful furnace equipment?

24.2.5
Chromos in Cleopatra's Emeralds and in Red Rubies

During the period of discovery, chemists were surprised at chromium's different colors. When Lehmann dissolved the red lead chromate mineral from Yekaterinburg he observed and reported the green color of its hydrochloric acid solution. We say today that it is the trivalent chromium ion that is green. When Vauquelin boiled the powdered mineral with potassium carbonate and filtered he saw the yellow color of the filtrate. He had hexavalent chromium in his beaker.

Lehmann was not the first to observe the green color of chromium. As early as 2000 BC, emeralds were extracted from mines by the Red Sea, later called Cleopatra's mines. Emerald is an aluminum beryllium silicate, a *beryl*. It has its beautiful green color just from chromium. Emerald is the noblest gem in the beryl group, nobler than the yellow *precious beryl* and the blue *aquamarine*. There are many large emeralds that compete with diamonds and rubies in value and celebrity. Today the biggest and most beautiful emeralds are found in Columbia.

A red mineral color caused by chromium was also seen long before the days of Lehmann, Pallas and Vauquelin. The mineral corundum is aluminum oxide in a clear, transparent form. The beautiful red *ruby* is corundum "contaminated" with chromium. Color in minerals is caused either by ion complex formations or by pigmentation. Therefore one metal can give different colors to a colorless mineral. If the corundum contains iron or titanium instead of chromium the precious blue stone *sapphire* is obtained.

24.2.6
Hard on the Heels of the Discovery of Chromium

The new metal chromium was discovered in 1797. Before the end of the century two discoveries of lead-free chromium minerals were made. These minerals are known today as chromite, $FeCr_2O_4$, that is $FeO \cdot Cr_2O_3$. Chromite is in reality a chrome spinel with the general formula $([Mg, Fe^{2+}][Cr,Al,Fe^{3+}])_2O_4$. In good chromium ore, of course, Fe predominates in the first square bracket and Cr in the second.

In 1798, Tobias Lowitz in St Petersburg and M. H. Klaproth in Berlin found chromium in a mineral originating in the Ural Mountains. They got the samples from Count Musin-Pushkin in St Petersburg

In 1799, Tassiert, a German chemist active in France, discovered chromium in an iron mineral from the Var region of southeastern France. This interested Fourcroy, who anticipated that iron–chromium ores might be source materials for a diversified manufacture of chromium chemicals. Due to the richness of color of the metal's compounds the minerals could be used for painting and for manufacturing colored glass and china.

Tobias Lowitz really was following close upon Vauquelin's heels regarding chromium discovery. But, although he was one of the pioneers, he was only number two and has therefore remained rather unknown in the history of the discovery of the elements. Tobias was the son of a professor of mathematics in St Petersburg, who had moved from Göttingen in Germany. The son was sent to Göttingen to study chemistry. Shortly after his return to Russia he continued with chemical activities. It is possible that he was saddened to see France take "the gold medal" in the competition over chromium. About that we know nothing with certainty. Perhaps he felt great satisfaction that he was the first to find chromium in the iron–chromium mineral that was given the name *chromite*. He could not have imagined, however, that this mineral would be the dominant raw material in the worldwide metallurgical industry in the 20th century. Doubtless it was a source of satisfaction that he was elected as Lomonosov's successor in the Russian Academy of Science.

The metal chromium demanded a heavy sacrifice from Tobias Lowitz. As he continued to work on chromium chemistry an explosion occurred in his laboratory and he lost his left hand.

After a long period of suffering he died in St Petersburg in 1804.

24.3
Chromium Deposits

24.3.1
Large-scale Chromite Discoveries

In 1827 Isaac Tyson discovered chromite ore deposits on the border between Maryland and Pennsylvania in the USA. This made the USA the leading supplier for many years. Twenty years later high-grade chromite ore was found near Bursa in Turkey. After some years Turkey became the main source of supply. This continued until the mining of chromium ore began in India and South Africa around 1910.

24.3.2
Deposits and Production of Chromite in Our Time

Chromite, $FeCr_2O_4$ (Figure M35) is the only chromium mineral that is economically important in our time.

In the pure mineral the Cr_2O_3 content is calculated at 68%. The production of chromite ores and concentrates was about 15 million tonnes in the year 2000 (see Table 24.1 and Figure 24.3).

Table 24.1 Production of chromite ores and concentrates (with an average of 42% Cr_2O_3) in the year 2000

Territory	Production Million tonnes	Percentage of total	Note
W. Europe	1.19	8.0	Finland 0.63; Turkey 0.56
E. Europe	2.78	18.7	Kazakhstan 2.62
Africa	7.81	52.5	South Africa 7.01; Zimbabwe 0.65
Americas	0.62	4.2	Brazil 0.59
Asia and Australia	2.24	15.1	India 1.95
Middle East	0.23	1.5	Iran 0.15
Total (rounded)	15	100	

Source: ref. [24.1].

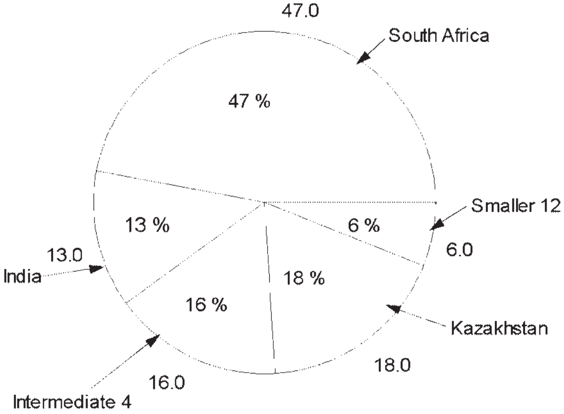

Figure 24.3 Distribution of chromite production among 19 countries. Intermediate 4: The countries Zimbabwe, Finland, Brazil and Turkey. Smaller 12: The countries Iran, Pakistan, Madagascar, Russia, Australia, China, Albania, United Arab Emirates, Cuba, Sudan, Oman and the Philippines. (Source: ref. [24.1].)

24.4
Manufacture of Chromium Products

24.4.1
An Overview

Chromite ore is the raw material for the manufacture of a very diversified group of alloys, refractory and chemicals. This is indicated in Figure 24.4[1)].

24.4.2
Chromium Chemicals

High-temperature calcination of chromite ore and soda ash leads to oxidation of chromium to sodium chromate, which is leached out by water. After acidifying, sodium dichromate, the basic material for chromium chemicals, is formed. Chromium trioxide CrO_3, chromic acid, prepared from sodium dichromate, is used for preparing the baths for chromium plating. Hexavalent chromium chemicals are also still used to some extent in pigments, for corrosion protection and for timber treatment. Chromic acid is also used for video/audio tapes although iron-based tapes have taken over more than 90% of this market.

As color pigments, chromium compounds have had varied use. Chrome green is Cr_2O_3, chrome yellow is $PbCrO_4$, and thus has the same composition as the mineral

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[1)] Dressing (concentration) of chromite ore gives dressed ore, an ore concentrate. For dressed ore see Chapter 1 Introduction, Table 1.1.

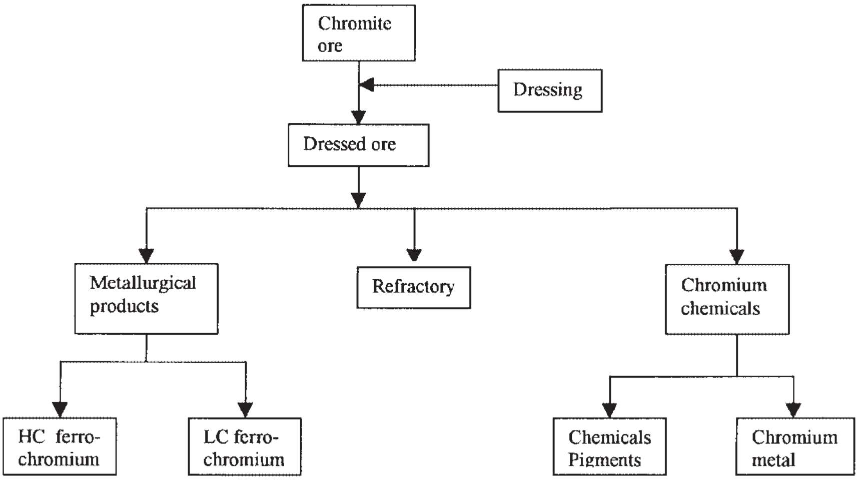

Figure 24.4 From ore to different chromium products.

Siberian red lead. Chrome red is Pb_2CrO_5, lead oxide chromate. In our day the use of color pigments containing lead and hexavalent chromium is of course restricted for environmental reasons.

Different trivalent chromium products, chromium oxide, chromium hydroxide and chromium sulfate, are made by reduction of dichromate. Chromium sulfate is used in leather tanning. Skins are mainly derived from animals that are butchered for the food industry. To protect the skin from putrefaction it is transformed to leather by the tanning process. The tanning agent is fixed to the reactive groups of collagen, the protein in the skin. That stops the spontaneous decomposition of collagen.

24.4.3
Refractory

Manufacturing of *fire brick refractory* for metallurgical furnaces began in the 1880s. The use of chromite as a refractory is based on its low thermal expansion, its high melting temperature and its good structural stability. Refractory products such as chrome brick, chrome-magnesite brick and plastic cement are manufactured from ores high in chromium and aluminum and low in iron and silicon. An excess of magnesium oxide is added to form magnesium silicate during firing.

24.4.4
Chromium Metal

A century after Vauquelin, in 1894, Hans Goldschmidt in Essen developed the *aluminothermic* method. With this technique, metals that are strongly bound to oxygen can be produced in pure form. The reaction between chromium oxide and aluminum

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

is very exothermic and continues spontaneously after it has been started by supplying extra energy. This can be done using a small amount of a very strong oxidizing agent such as CrO_3 and a corresponding amount of Al.

A similar method is *reduction of chromium oxide with silicon*. This reaction, however, is not exothermic enough to run spontaneously, so the process has to be carried out in an electric furnace.

Metallic chromium is also produced by an *electrolytic method*. Ferrochromium is crushed and dissolved at a temperature near the boiling point in a mixture of sulfuric acid and used anolyte. In a crystallizer the iron is separated as iron ammonium sulfate at a temperature of 5°C. The temperature in the electrolytic cells is 53°C. In the process sulfuric acid and hexavalent chromium are formed in the anolyte. Because of that it must be prevented from mixing with the catholyte. Otherwise the divalent chromium there will be oxidized and the chromium precipitation disturbed. The cathode material is 316-type molybdenum-alloyed stainless steel, the anode material silver-alloyed lead or titanium covered with iridium. For environmental reasons dichromate plants are closed and the aluminothermic part of the chromium metal production increases. About 1990 it was 60 % and in the beginning of the 2000s 90 %.

About half of all available chromium metal is used for the production of superalloys, that is nickel alloys with 15–20% chromium content, used for aero engines and other advanced purposes. The rest is mainly used for corrosion-resistant alloys other than stainless steels, for aluminum alloys and for hardfacing of alloys. The total world consumption of chromium metal was about 22 000 tonnes in the year 2002. That the USA consumed 40% of this can be expected because of its dominance in the world's aerospace industry. Europe is the second largest region, with about 33% of the total consumption. The major countries are the UK, Germany and France [24.2].

24.4.5
Ferrochromium – The Raw Material for Stainless Steels

Ferrochromium is an alloy of iron and chromium. More than 80% of all chromite ore is consumed in manufacturing this alloy. It is mainly used as the chromium source for the manufacture of stainless steels and other chromium steels. HC ferrochromium with high carbon content (5–6%) is manufactured in electric furnaces with coke as the reducing agent. The process has a high energy consumption, 4000 kWh per tonne of chromium metal. Plants for ferrochromium production have therefore been located in areas with low energy prices. This was one reason why Sweden, without its own chromium deposits, was a pioneer country in this field and in the production of stainless steels.

HC ferrochromium could earlier not be used directly for manufacturing stainless steels with low carbon content. With sophisticated metallurgical techniques a ferrochromium "*affiné*" with carbon < 0.2% was then manufactured. Owing to new methods in stainless-steel making, HC ferrochromium today can be used even for low-carbon stainless steels. Yet two types of ferrochromium are still produced. One with high carbon content, >4%, one with low, C < 4%.

Nowadays the biggest manufacturers of ferrochromium are South Africa, Kazakhstan and India (see Table 24.2).

Table 24.2 Production of high-carbon grade ferrochromium[a] in the year 2000

Territory	Production Thousand tonnes	Note
W. Europe	638	Finland 261; Norway 154; Sweden 136
E. Europe	664	Kazakhstan 537
Africa	2683	South Africa 2417; Zimbabwe 266
America	154	Brazil 154; US not reported
Asia & Middle East	695	India 377; China 184; Japan 123
Total world	4834	

Source: ref. [24.1].

[a] The production of other types of ferrochromium, <4%C, was 402 thousand tonnes in the year 2000.

24.5
Why Are Stainless Steels Stainless?

Chromium steel became available in 1870 when Julius Braun established the Chrome Steel Works in Brooklyn for manufacturing structural and tool steels (not stainless). Chromium became of great importance from the metallurgical point of view around 1910, when the alloy ferrochromium was introduced and the production of stainless steels started.

Chromium is a metal that is spontaneously passivated. That means that a thin, dense and transparent oxide layer with good adherence is formed on its surface in contact with air. This is the reason why chromium-plated components preserve their brightness even in markedly corrosive environments. Chromium steels share this property when the chromium content is more than 12% (see Figure 24.5). Because of that, stainless steels are steels with a content of more than 12% chromium.

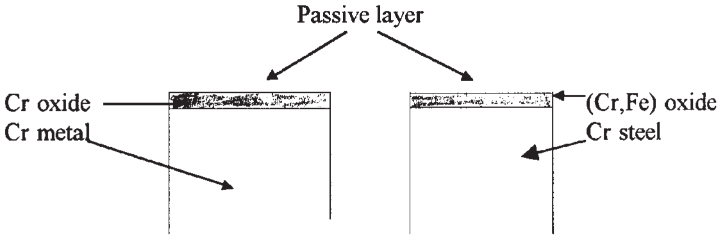

Figure 24.5 Diagram of passive layers on chromium metal and on chromium steel.

About 1910 three discoveries, independent of each other, were made:

- H. Brearly in Sheffield tried to develop a new hardwearing material for rifled barrels in large guns. A steel with 9–16% chromium and up to 0.7% carbon fulfilled the requirements and was patented. As so often happens, a military use gave rise to a civilian one. The steel became an outstanding knife material in cutlery and was well known as *stainless cutlery*. Brearly's steel is the origin for the *martensitic stainless steels* often with 14% chromium and 0.5% carbon, used for different sharp-edged tools e.g. surgical knifes and razor blades.
- At the same time B. Strauss in Essen, Germany, was working to measure the high temperatures in metallurgical furnaces and needed a heat-resistant tube material for the thermoelements. For this, the *austenitic stainless steels*, rich in both chromium and nickel, were developed. This group of stainless steels is today predominant for both wet corrosive conditions and for high-temperature purposes.
- F. M. Beckett in Niagara Falls in the USA tried at the same time to find a steel, with a scaling temperature as high as 1200°C that could be used for crucibles and plates in heat-treatment furnaces. He found that a steel with a chromium content of more than 20% was suitable. This discovery was the origin of the *ferritic stainless steels*.

As an alloying element chromium has a ferrite-forming effect. One consequence of this is that the structure of these steels is similar to that of unalloyed iron. Corrosion and scaling resistance are, however, much better because of the passive layer. Even at 12–13% Cr they withstand attacks of water and of oxidizing acids like nitric acid, but the steel has no resistance to the non-oxidizing acids, sulfuric and hydrochloric acids.

If the nickel content is high enough, there are striking changes in the structure and properties of stainless steels. A steel with 18% Cr and 8% Ni is austenitic, and this greatly influences its properties. The corrosion resistance is improved while the machinability is diminished. These austenitic stainless steels, often also alloyed with molybdenum for better resistance to pitting corrosion, nowadays form the biggest part of the stainless-steel family. They are used in many different applications, varying from the sink unit in kitchens to advanced equipment in aggressive environments in the chemical industry.

In 2000 the world production of stainless steels was 20 million tonnes. Of this quantity 73% was austenitic. Stainless steels are important for growing economies. The remarkable changes of stainless steel production in China testifies this: in 1998 0.88, in 2000 1.73 and in 2002 2.92 million tons.

24.6
Chromium Plating and Chromating

It is important to be aware of the difference between the two techniques c*hromium plating* and *chromating*. The former creates a chromium metal layer on the substrate, while the latter gives a conversion coating as a foundation for lacquering or painting.

24.6.1
Chromium Plating

It is difficult to get a bright chromium layer. During the first decade of the 20th century, professor W. D. Bancroft at Cornell University in the USA conducted systematic and successful research into chromium plating. E. Liebrich's German patent of 1924 and C. G. Fink's US patent of 1925 are considered to be milestones. They clarified the essential importance of a high content of hexavalent chromium in the bath and a carefully adjusted percentage of sulfuric acid (1% of chromic acid).

A typical conventional chromium-plating bath contains 250 g/l CrO_3 and 2.5 g/l H_2SO_4.

Figure 24.6 shows how the plating speed varies with the current density for such a bath.

There are two principal types of electrolytic chromium plating.

- *Decorative plating* of a very thin layer, 0.3 μm[2], on nickel layers, e.g. on bicycle handlebars. The corrosion protection is created by a rather thick nickel layer, 10–20 μm,

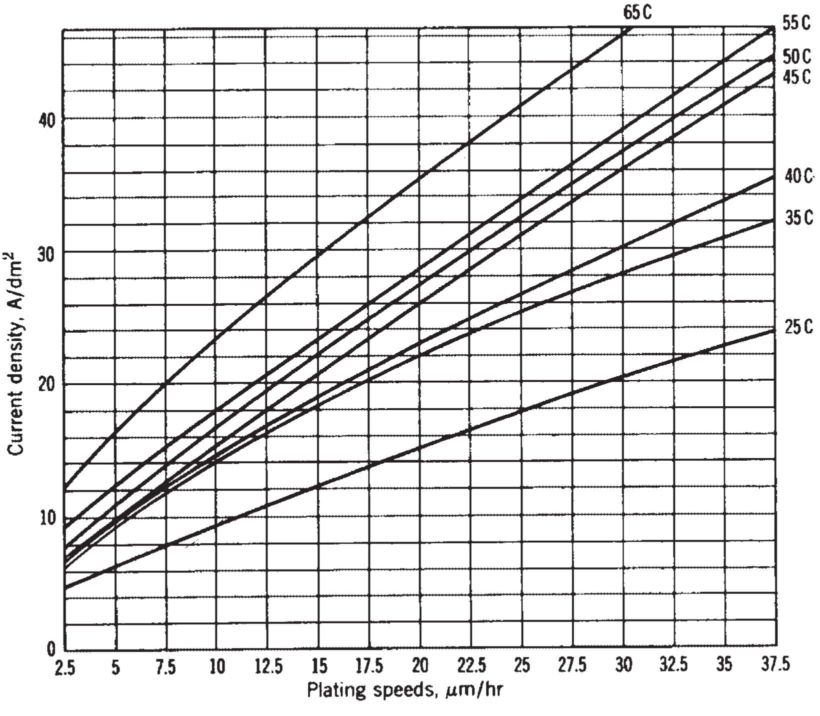

Figure 24. 6 The speed of chromium plating at different current densities and temperatures [24.3].

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[2] 1 μm = 1 micron = 0.001 mm = 10^{-6} m.
The American denomination 1 mil = 1 milliinch = 25 μm.

but the thin chromium layer serves as a non-tarnishing surface finish that retains its brightness.

- *Functional plating (hard chromium plating)*[3] with heavy coatings, 10–50 μm. These layers are applied to a steel surface as a rule without intermediate coatings. Hard chromium plating takes advantage of the special properties of chromium metal: low coefficient of friction and resistance to wear, heat and corrosion. The very important development of hydraulic systems in modern technology would scarcely have been possible without the availability of hard chromium plating.

24.6.2
Chromating

Chromating is a process in which different components, usually zinc-plated steels or light metals such as aluminum or magnesium, are dipped in a solution containing hexavalent chromium. Thin layers of zinc, aluminum or magnesium chromate are formed on the surface of the substrate. The method is used for different reasons:

- to provide a foundation for paint or lacquer
- to protect zinc against “white rust”
- to provide a variety of decorative effects. Varying the composition of the chromating bath can give the layer different colors.

24.7
Chromium – A Poison or an Essential Element for Life?

24.7.1
Dangerous or Not Dangerous?

Chromium has a bad reputation for toxicity. And chromium is toxic and carcinogenic if present as hexavalent chromium in chromate and dichromate ions, CrO_4^{2-} and $Cr_2O_7^{2-}$. There are numerous studies documenting this effect, so when hexavalent chromium is used or formed in technical processes much attention must be paid to the environment. The concentration of chromic acid in the working area is regulated and only very low values, max 0.02 mg hexavalent chromium per kg air, are accepted. Great efforts are made nowadays to replace, for example, the present baths for chromium plating and chromating, containing hexavalent chromium, with baths containing trivalent chromium.

Technical products such as stainless steels, in which chromium is present as an alloying element, lead to very low risks as chromium has such a low solubility. The dissolved Cr^{3+} concentration in all natural waters is also very low as the ion forms stable complexes with humus.

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[3] Chromium on a “hard chromium” plated component is not harder than a decorative layer, but because of its layer thickness it can withstand harder wear.

The US EPA has an Emission Measurement Center EPS [24.4]. From the EPS it is possible to obtain supporting software for test method technology.

24.7.2
An Essential Element for Life!

Many studies report beneficial effects of trivalent chromium. The element is described by WHO [24.5] as essential owing to its ability to strengthen the activity of insulin and its influence on carbohydrate and lipid metabolism. Biological systems commonly contain chromium as Cr^{3+} in small concentrations [24.6]. It is thought, but disputed, that chromium is essential for life and involved in human glucose metabolism [24.7]. Chromium intake has been shown to be positive for humans and decreases the symptoms of diabetes in people with glucose intolerance [24.8]. An adequate intake of chromium for an adult is 50–200 μg/day and the content of chromium in tissues is 100–1000 μg/kg dry weight.

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25
Molybdenum

25.1 Mo
Facts about Molybdenum

25.1.1 Mo
The Element

Symbol:	Mo
Atomic number:	42
Atomic weight:	95.94
Ground state electron configuration:	$[Kr]4d^5 5s^1$
Crystal structure:	Cubic bcc with $a = 3.15$ Å

25.1.2 Mo
Discovery and Occurrence

Discovery: In 1778, C. W. Scheele reported results from his investigation of the mineral *molybdœna* (MoS_2) and the properties of a *new earth* (MoO_3) that he had prepared. In 1781 Peter Jakob Hjelm in Stockholm reduced the oxide MoO_3 to a metal (with high carbon content) and gave the new element the name molybdenum. The discovery year for the element was 1781.

Most important mineral: Molybdenite MoS_2 (Figures M36 and M37)

Ranking in order of abundance in earth crust:	58–59
Mean content in earth crust:	1.2 ppm (g/tonne)
Mean content in oceans:	0.01 ppm (g/tonne)
Residence time in oceans:	$100 \cdot 10^3$ years
Mean content in an adult human body:	0.1 ppm
Content in a man's body (weight 70 kg):	7 mg

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25.1.3 Mo
Chemical Characterization

Molybdenum is a metal with chemical properties similar to those of chromium but, unlike chromium, it is soluble in dilute nitric acid. The metal is used chiefly for alloying of steel. Wire made from the pure element is used to carry the glowing tungsten filament in incandescent lamps. MoS_2 is a black powder that crystallizes like graphite and is, because of that, an essential component *in solid lubricants*, which can be used at much higher temperatures than conventional lubricants.

Molybdenum is essential for the biological utilization of nitrogen from the environmental nitrogen cycle.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Mo^{VI} as in MoO_3, MoO_4^{2-}, and MoO_2Cl_2	$Mo(g) \rightarrow Mo^+(g) + e^-$	684	$Mo(g) + e^- \rightarrow Mo^-(g)$
Mo^{V} as in $MoCl_5$, Mo_2S_5, and $[Mo(CN)_8]^{3-}$	$Mo^+(g) \rightarrow Mo^{2+}(g) + e^-$	1560	−71.9
Mo^{IV} as in MoO_2, MoS_2, and $MoBr_4$	$Mo^{2+}(g) \rightarrow Mo^{3+}(g) + e^-$	2618	
Mo^{III} as in MoF_3	$Mo^{3+}(g) \rightarrow Mo^{4+}(g) + e^-$	4480	
Mo^{II} as in $[Mo(CN)_7]^{5-}$ and Mo_6Cl_{12}	$Mo^{4+}(g) \rightarrow Mo^{5+}(g) + e^-$	5257	
	$Mo^{5+}(g) \rightarrow Mo^{6+}(g) + e^-$	6641	
	$Mo^{6+}(g) \rightarrow Mo^{7+}(g) + e^-$	12125	

Standard reduction potential: $MoO_4^{2-}(aq) + 4H_2O(l) + 6e^- \rightarrow Mo(s) + 8OH^-(aq)$ [alkaline solution]
$E^0 = -0.913$ V

Electronegativity (Pauling): 2.16

Radii of atoms and ions: (WebElements™)		
	Atomic:	145 pm
	Covalent:	145 pm
	Mo^{3+} (6-coordinate, octahedral):	83 pm
	Mo^{4+} (6-coordinate, octahedral):	79 pm
	Mo^{5+} (4-coordinate, tetrahedral):	60 pm
	Mo^{5+} (6-coordinate, octahedral):	75 pm
	Mo^{6+} (4-coordinate, tetrahedral):	55 pm
	Mo^{6+} (6-coordinate, octahedral):	73 pm

25.1.4 Mo
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
10 220 kg m^{-3} 10.22 g cm^{-3}	9.39 cm^3	2896 K 2623 °C	5830 K 5557 °C	251 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
145	139	135	127	113

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$4.8 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
7	50	76	127	233	372

Mass magnetic susceptibility χ_{mass} at 293 K	$+12 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
329 GPa	130 GPa	234 GPa	0.27

25.1.5 Mo
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	(30) kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	590 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	658 kJmol^{-1}
Entropy S^0 at 298 K	28.66 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	13.5	24.06	26.5	28.4	36.7	43.9

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$Mo + O_2 \rightarrow MoO_2$	–535	–502	–415	–322	–
$2/3Mo + O_2 \rightarrow 2/3MoO_3$	–445	–411	–330	–	–

25.1.6 Mo
Nuclear Properties and X-ray

Isotope range, natural and artificial 86–110

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{92}Mo	Stable	14.84	+0	–	–	–	–
^{94}Mo	Stable	9.25	+0	–	–	–	–
^{95}Mo	Stable	15.92	+5/2	–0.9133	–	–	–
^{96}Mo	Stable	16.68	+0	–	–	–	–
^{97}Mo	Stable	9.55	+5/2	–0.9335	–	–	–
^{98}Mo	Stable	24.13	+0	–	–	–	–
^{100}Mo	Active	9.63	+0	–	$1.0 \cdot 10^{19}$ y	$\beta^-\beta^-$	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{95}Mo	^{97}Mo
Reference compound	Na_2MoO_4/D_2O	
Frequency MHz (^{1}H = 100 MHz)	6.517	6.654
Receptivity D^P relative to ^{1}H = 1.00	$5.21 \cdot 10^{-4}$	$3.33 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	2.98	1.90
Magnetogyric ratio, radT^{-1}s^{-1}	$-1.751 \cdot 10^7$	$-1.788 \cdot 10^7$
Nuclear quadropole moment, barn	0.022	0.255

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
41	Nb	16.521
42	Mo	17.374
43	Tc	18.251

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	155
17.37 keV (MoKα_2)	19.1

Neutron absorption	**Thermal neutron capture cross section**	2.6 barns

25.2
Discovery

25.2.1
Molybdœna – A Lead Ore Without Lead

The word *molybdœna* is derived from the old Greek word *molybdos,* with the meaning *lead* and once stood for lead glance, lead ores and lead objects. Lead glance is a mineral with blackening. properties. Gradually other blackening substances, e.g. graphite, got the designation *molybdœna*. We are in our day familiar with pencils that are "lead pencils" although they contain graphite and not lead. The mineral *molybdœna* had its name long before the element molybdenum was known. The reason for that is of course its blackening character. In Cronstedt's Mineralogy the mineral was called (in Latin) *molybdœna membranacea nitens* (leaf-shaped and shining). In German the mineral was called *Wasser-Bley,* expressing a supposed lead content. Johan Heinrich Pott showed about 1740 that Wasser-Bley was not a lead mineral. It can be said that this was the first step on the way to the discovery of molybdenum. He, however, thought that Wasser-Bley and graphite were identical.

23.2.2
A Trainee Shows the Way

Bengt Qvist, an apprentice in the Swedish Board of Mines, reported in 1754 about an investigation of *molybdœna*. The report, *Observations about Blyerts (Blacklead)* gave some important findings about the mineral molybdenum sulfide:

- the specimen is taken from Bispbergs Klack (in the Swedish province Dalecarlia) where it is present as veins in quartz or feldspar
- it is a light mineral, loose and shining, built of coarse leaves or lammelœ, forming a pyramidal figure
- the mineral is easy to carve with a knife and the leaves can easily be divided into pieces
- its weight is 4.709 times the weight of water
- at a moderate heat the mineral loses sulfur and forms a yellow "chalk" (an oxide)
- even the chalk is volatile at an increased temperature.

These early findings of young Bengt Qvist have been verified surprisingly well. Today the density of molybdenum sulfide is determined as 4.7–4.8 g/cm^3. The mineral gives off SO_2 on gentle heating and even the oxide itself is volatile at 750°C.

Experiments with reduction of the chalk with mixtures of carbon, coal dust and tallow at the highest possible temperature, "bellows heat" for 7–8 minutes, failed. He was unable to find a new metal, but he wrote that he had a feeling that the mineral really contained some special metallic "essence".

25.2.3
A New Earth Is Identified

During the year 1777–78 Carl Wilhelm Scheele obtained samples of *molybdœna* from different sources, among them professor Torbern Bergman in Uppsala and assessor J. G. Gahn in Falun. It was expected that Scheele in his pharmacy in the small Swedish town Köping would find an answer to the century-old question: *Is there an unknown metallic "essence" in molybdœna*. Many had tried to find the answer, all had failed. Scheele had shown an outstanding experimental cleverness in his work with phosphorus, hydrofluoric acid, manganese and chlorine, as well as with air and its components. Bergman and Gahn had good reason to expect positive results again from Scheele, although the experimental equipment in the Köping pharmacy was very simple. By May 1778 Scheele could report to his colleagues about his experiments with the "so-called lead ore". He emphasized that

> I do not mean the ordinary lead ore that is available in the pharmacies. The stuff I investigated is quite different from that. It is instead the mineral that Axel Fredrik Cronstedt called *molybdœna membranacea nitens* in his Mineralogy and with which Mr Qvist and others probably made their experiments.

The results were published in the Transactions of the Royal Swedish Academy of Sciences [25.1].

When we try to follow this description we find that Scheele proceeded systematically and with impressive care.

25.2.3.1 Molybdœna Contains Sulfur

The mineral was mixed with arsenic acid (oxidation agent) and heated in a retort. When water had disappeared the temperature was increased. A heavy vapor was formed that was collected in a receptacle as a liquid. It was sulfuric acid.

25.2.3.2 Molybdœna Contains a New Earth – *Terra Molybdœnæ*

When the mineral was treated with boiling dilute nitric acid, nitrous gases were evolved. After evaporation to dryness the residue on the bottom of the beaker was gray. After five repetitions of the process – treatment with nitric acid and evaporation – a white residue was obtained. This white substance could be sublimed and collected on iron sheets as white or yellowish scales. The white earth could also be prepared by melting molybdœna with saltpeter. Scheele made an important statement from these results: "I have thus seen an earth that up to now has probably been unknown.

As the substance has the character of an acid I will call it acidum molybdœnœ." Scheele had an active correspondence with professor Torbern Bergman. That this authority accepted Scheele's conclusion provided valuable support.

In modern chemical terminology, Scheele's new earth is molybdenum(VI) oxide MoO_3. In his continuing work he himself usually used the designation molybdœna for the mineral and *terra molybdœnœ* for the earth, the oxide. The metal molybdenum was still unknown.

25.2.3.3 **The New Earth Attracts Phlogiston**

Scheele subjected *terra molybdœnœ* to blowpipe analysis and observed that when the oxide was placed in a cavity on a piece of charcoal and heated it vaporized and formed a white coating beside the cavity. When he treated this white coating with the blue, reducing part of the flame the sublimate changed its color from white to blue. With the oxidizing tip of the flame he got the white color back. He could also show that a colorless solution of *terra molybdœnœ* in acid became blue when metallic zinc or iron were added. Again, in modern chemical terms, Scheele showed that the still unseen metal has different oxidation states. In the reducing blowpipe flame the metal is reduced (*it attracts phlogiston*). Likewise reduction occurs with zinc metal in a hydrochloric acid solution.

25.2.3.4 **Molybdœna Can Be Synthesized From the New Earth and Sulfur**

One part of *terra molybdœnœ* (white oxide) was mixed with three parts of sulfur. The content in the retort was heated until the excess of sulfur was driven away. The final product was a shining, blackening powder with all the properties characteristic of natural molybdœna.

25.2.3.5 **Much Success – But Not Reduction to Metal!**

Scheele tried very hard to reduce the earth at high temperature with carbon-rich fluxes but failed. He says resignedly: "I did not notice the least trace of anything metallic." His furnaces at the pharmacy in Köping were not strong enough. Scheele appealed now to the Laboratorium Chymicum in Stockholm with its famous large furnaces.

25.2.4
A New Metal That I Called *Molybdœnum*

An authority for mining was established in Sweden in 1630 by King Gustavus II Adolphus. In the period 1634–1644 it was reorganized to a Royal Board of Mines [*Bergskollegium*]. In 1683 a laboratory for investigations in chemistry, mineralogy and metallurgy was founded and subordinated to the Royal Board. It was given the name Laboratorium Chymicum.

In 1727 Georg Brandt was appointed manager for the Laboratorium Chymicum with the duty to "analyze different ores and make chemical experiments of benefit for the noble metallurgy". Premises were made available in the Royal Mint. Under Brandt's leadership the Laboratorium

> Chymicum developed into a very important institution in European Science. Brandt also clearly saw the urgent need of education in chemistry, mining and metallurgy and his students included Axel Fredrik Cronstedt, Henrik Sheffer, Anton von Swab, Sven Rinman, Daniel Tilas, Bengt Qvist and Gustaf von Engeström. Many of these men later became famous scientists, active in the development of the Swedish mining and metallurgical industry and also active in the international work of discovering new elements. Brandt himself discovered the metal cobalt during his first years at the Laboratorium Chymicum. Cobalt minerals were important for coloring glass and china blue.

In 1778, while Scheele was wrestling with the problem of preparing a metal from the white *terra molybdœnœ*, Gustaf von Engeström was manager of the Laboratorium Chymicum and Peter Jakob Hjelm was responsible for the furnaces. Mary Weeks refers to a visit by an Englishman, E. D. Clarke, to Stockholm in 1799, when Hjelm was the manager of the laboratory. In his report he writes:

> I was received by a most intelligent man and very able chemist by the name of Hjelm, who permitted us to see the collection of minerals, belonging to the Swedish Crown. ... We could perceive that the Swedish chemists, celebrated as they justly are, carry on their works on a large scale: the furnaces used by Mr. Hjelm in the Royal Laboratory were of the size of those in our common blacksmiths' shops; and the rest of his apparatus was on a similar scale.

Even twenty years earlier, when Scheele contacted Hjelm, the furnace capacity was impressive and quite different from Scheele's own equipment. In 1781 Hjelm tried, at Scheele's suggestion, to reduce the oxide with carbon. To make sure of an intimate contact between oxide and reducing agent he stirred the pulverized oxide with linseed oil to a paste. When he heated the mixture in a closed crucible the oil was carbonized and on strong heating the oxide was reduced. Hjelm called this new "half metal" *molybdœnum*. When he determined its density he obtained the value 7.40. The density of pure molybdenum metal is however 10.22 g/cm^3. Thus Hjelm's metal was far from free from carbon. Today we know that molybdenum is a strong carbide former and a great deal of molybdenum carbide had been formed during the reduction experiments.

In 1781 Hjelm made a translation of Bergman's treatise on blowpipe analysis from Latin to Swedish. In this paper he also gave the first description of the experiments with reduction of *terra molybdœnœ*. Much later, in 1788, he gave a description in the *Transactions of the Royal Swedish Academy of Sciences*.

On 16 November 1781 Scheele wrote to Hjelm that he rejoices that we now have a new half-metal1) molybdœnum. He adds that already he "can hear the French seek-

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1) Half-metals or semi-metals were substances which resembled the "old" metals in color and density but which had differences in formability. After Georg Brandt's dissertation on the half-metals in 1735 and his discovery of cobalt, six semi-metals were known: mercury, bismuth, zinc, antimony, cobalt and arsenic. When new metals like molybdenum were discovered and prepared, they were often not malleable owing to the presence of impurities and because of that were called semi-metals.

ing to deny the existence of this new half-metal since they are not the discoverers of it". Here we can trace an early dispute over the priority to discoveries. Scheele's own generosity towards Hjelm is impressive. After having done all the laborious work with the preparation of molybdenum oxide, a fundamental achievement of great scientific importance, he accepts Hjelm as the discoverer of the new metal after having done "only" the reduction experiments. In later correspondence Scheele also writes that all the credit for the discovery of molybdenum is due to Hjelm.

25.3
Molybdenum Deposits in Our Time

25.3.1
Types of Minerals and Ores

There are many molybdenum-containing minerals in nature but only one of them, molybdenite, molybdenum disulfide, MoS_2 (Figures M36 and M37) has any economic importance. Typically, molybdenite occurs in an environment of silica-rich intrusive rocks, consolidated from magma beneath the surface of the earth.

Some of the ores are *secondary* from the molybdenum point view. This means that the main minerals are copper pyrites and other copper minerals They have been formed from copper-rich solutions containing small amounts of molybdenum, which have penetrated the rocks at high temperature and pressure. The solutions have been heated by magma. During the subsequent cooling the minerals have been formed as deposits along cracks in surrounding rocks.

Important examples of such ores are Bingham Canyon in Utah, USA, Sierita in Arizona, USA, and most importantly Chuquicamata in Chile. This mine is situated in Northern Chile on the western slopes of the Andes. It has an open pit, 2 · 3 km, with a depth of 800 m. and is one of the biggest copper mines in the world. About 600 000 tonnes of ore are mined daily.

There are large deposits with molybdenite as a *primary mineral* at Climax and Henderson in Colorado, Thomson Creek in Idaho, both in the USA, and Endako in British Columbia, Canada. These deposits are almost free from copper. An average value for the content of MoS_2 is 0.3%. The Climax mine was broken from 1924 to 1998 while the Henderson mine is still in production (Figure 25.1).

A very large deposit of the same type was recently discovered in Quartz Hill east of Ketchikan in Alaska. It contains 0.1% MoS_2.

In Knaben in Norway, in a slaty granite interwoven by quarts veins, a molybdenum ore with 0.15–0.20% MoS_2 is available. During World War I, German, British, French and Russian armament manufacturers competed to buy molybdenum from this single European source. The mining in Knaben has, however, stopped since the very big deposits in North and South America have been exploited.

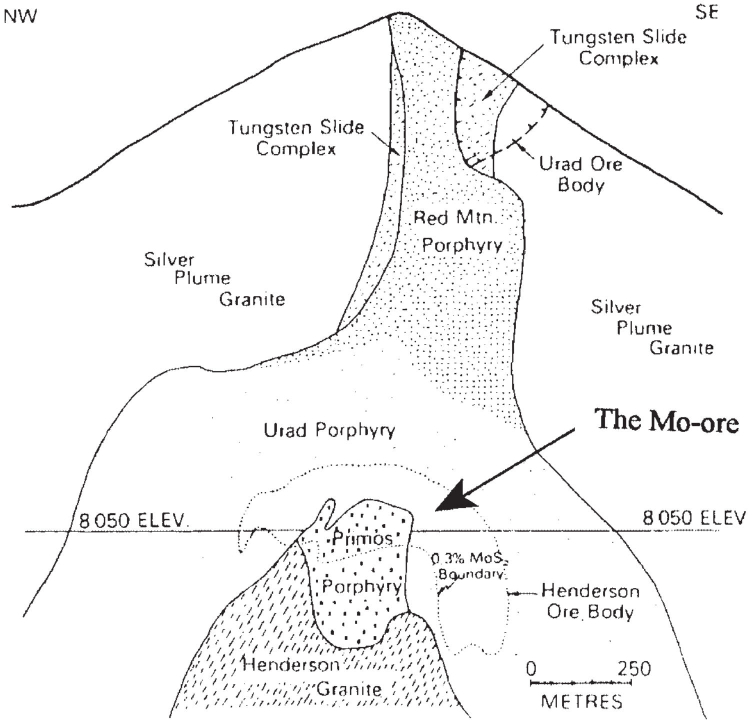

Figure 25.1 Vertical section through the Henderson deposit. (Reprinted with permission from *The Mineral Market, Molybdenum*, SGU, Geological Survey of Sweden, PM 1994:1 p. 32.)

25.3.2
World Resources, Mine Production and Ore Concentration

Molybdenum is, as mentioned, present as molybdenite MoS_2 as an associated sulfide in copper deposits and as the principal sulfide in large low-grade porphyry molybdenum deposits. The reserve base amounts to about 11 million tonnes (counted as molybdenum) in the whole world, half of which is in the USA. These resources are enough to supply world needs for the foreseeable future.

Mine production was 129 000 tonnes (of molybdenum) in the year 2000 [25.2]. The countries with the greatest outputs (thousand tonnes) were the USA (41.1), Chile (29.1), China (28.9), Peru (7.2), Mexico (6.9), Canada (6.83), Armenia (2.7), Russia (2.4) and Iran (1.6).

The large-scale use of molybdenum in modern industry rests on mass mining of large deposits of low-grade ores. The concentration of these in an economical way has been made possible by an effective ore dressing with flotation (see Chapter 1 Introduction). The separation processes are complicated, especially from Mo-containing copper ores, as in Chuquicamata. Different agents, specific for either copper sulfide or molybdenum sulfide, have been developed.

After crushing and grinding the ore is subjected to flotation and a combined Cu–Mo sulfide concentrate is obtained. In a second flotation process the two sulfides are separated and the copper concentrate goes to copper production.

The main part of the molybdenite concentrate is roasted to molybdenum oxide (see Figure 25.2) and is delivered as briquettes or oxide powder of technical molybdenum oxide. It is "technical" and not pure because the small content of gangue in the molybdenum sulfide concentrate stays in the oxide. In the roasting process the temperature has to be chosen carefully, high enough to change the sulfide to oxide, low enough to avoid vaporizing the MoO_3. Its vapor pressure is 1 mmHg (0.133 kPa) at 734°C and 10 mmHg (1.33 kPa) at 814°C.

During the roasting of Mo sulfide, sulfur dioxide is formed from which sulfuric acid can be produced in modern plants. If SO_2 is allowed to leave the chimney freely it has disastrous effects on the environment.

In the gases from the roasting of molybdenum sulfide the ore's content of the metal rhenium is present as rhenium oxide. This is an important source of this interesting metal, see Chapter 29 Rhenium.

The predominant source for molybdenum products is thus the molybdenite in ores. During recent years, smaller amounts of molybdenum (about 2% of the total Mo

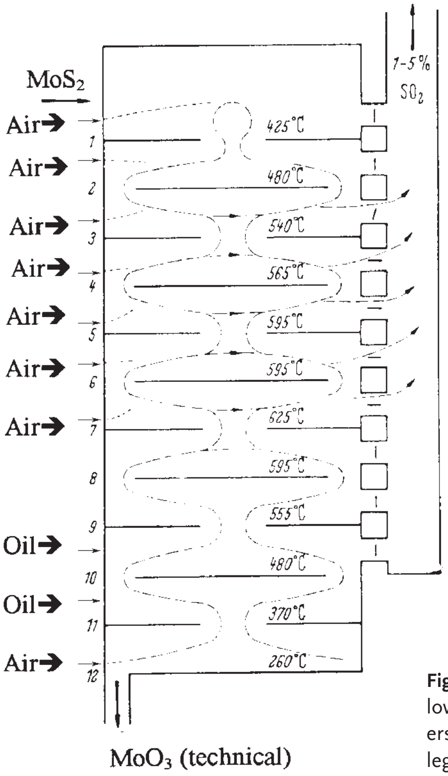

Figure 25.2 The roasting of MoS_2 to MoO_3. The lower part of the furnace is warmed by oil-burners. (Reprinted with permission of AB Ferrolegeringar, Stockholm, Sweden.)

production) have also been obtained by recycling catalysts used in the petroleum industry.

25.4
Manufacture of Molybdenum Metal and Alloys

25.4.1
Molybdenum Metal

Technical molybdenum oxide is purified from gangue in two different ways. One is sublimation. The other is dissolution in ammonia and filtering. On crystallization, ammonium molybdate is obtained, which is thermally decomposed to molybdenum oxide. Molybdenum metal powder is produced by reduction of pure molybdenum oxide with hydrogen gas in two steps. In the first stage molybdenum dioxide is produced at 600°C and in the second metal powder is obtained at 1100–1200°C. The processes are performed in tube furnaces through which boats, containing Mo oxide are pushed. Solid molybdenum metal is made by a powder metallurgy technique or by an arc melting process.

25.4.2
Ferromolybdenum

Ferromolybdenum is an alloy of iron and molybdenum. The most common manufacturing process is the aluminothermic one. Technical molybdenum oxide, ferrosilicon (75% Si), aluminum powder, slag former and iron filings are well mixed. On ignition an exothermic process starts. Ferromolybdenum with 65–75% Mo is manufactured in this way.

25.5
Modern Uses of Molybdenum

25.5.1
An Overview

Molybdenum sulfide is the raw material for the manufacture of a very diversified group of molybdenum alloys and chemicals, used for many purposes in a modern society. This is indicated by Figure 25.3.

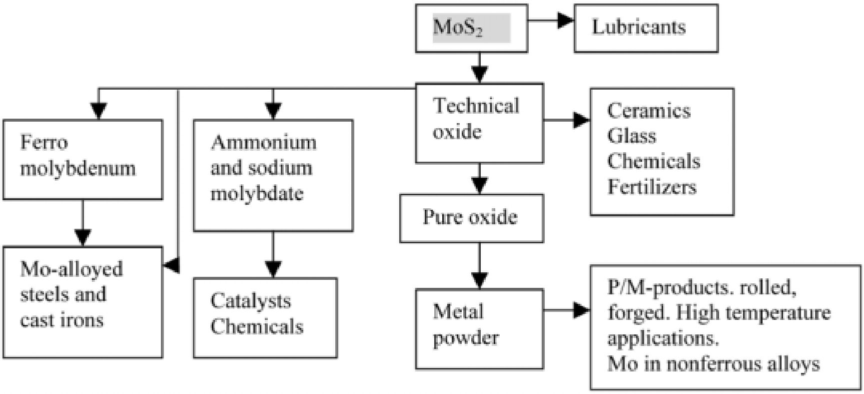

Figure 25.3 Fields of application for molybdenum and molybdenum products.

25.5.2
Some Specific Examples

25.5.2.1 An Important Alloying Element for Steel

75% of all molybdenum produced is used as an alloying element in steel. Molybdenum is added during manufacture in the form of MoO_3 powder or briquettes, or as ferromolybdenum. The latter is used in those melting processes, e.g. induction melting, which cannot reduce the oxide.

As an alloying element molybdenum has five different functions:

- It greatly improves the hardenability of low-alloy steels, which means that the hardening effect goes deeper into the steel material [25.3].
- After hardening of steel by quenching in water or oil the steel is hard but brittle. It is necessary to temper it at 200–500°C to obtain a good combination of hardness and toughness. Softening can be a big problem when the hardened and tempered steel is used at temperatures higher than the original tempering temperature. The presence of carbide-forming elements such as molybdenum (also Cr and V) in steel retards softening, and they also form fine carbides that produce a hardness increase at higher temperatures. This hardness increase is frequently referred to as secondary hardening.
- After tempering some steels are susceptible to temper embrittlement. Alloy steels are most susceptible, especially the chromium-nickel steels. A molybdenum content of 0.5% or less, however, reduces the susceptibility and Mo is an important alloying element added to steels to minimize temper embrittlement
- Molybdenum improves the wear resistance in tool steels, especially in high-speed steels. This again makes use of its tendency to form hard carbides.

- Austenitic stainless steels (see Chapter 24 Chromium) are very corrosion resistant but suffer from a tendency to pitting in salt water. Addition of molybdenum improves the resistance considerably.

25.5.2.2 **Molybdenum Metal in Special Applications**

In a non-oxidizing atmosphere it is possible to use molybdenum for high-temperature applications, as the melting point of the metal is 2623°C. In light bulbs molybdenum wire is used to carry the glowing tungsten filament. Molybdenum can even be used as the element wire in furnaces for high temperatures; however, it is important that the metal is protected by an inert gas atmosphere. If oxygen is present molybdenum oxide is formed and volatilizes so that the component is rapidly destroyed.

Molybdenum has a coefficient of expansion very similar to that of silicon and borosilicate glass. This allows molybdenum plates to be used to conduct heat away in glass components integrated circuits and thyristors.

Metal spraying with molybdenum powder, wire or strip is used for coating steel components. The layers reduce friction and improve wear performance.

25.5.2.3 **Molybdenum Silicide – A High-temperature Material**

A special molybdenum compound, molybdenum disilicide $MoSi_2$, has an interesting application. The compound is manufactured by powder metallurgy and, even at very high temperatures (1900°C), is very durable in air. In an oxidizing atmosphere a protective layer of silicon dioxide is formed on the surface. As the electric resistivity of the silicide is suitable it has been used as a resistance material in high-temperature furnaces ("*Kanthal Super*").

25.5.2.4 **Molybdenum Disulfide as a Lubricant**

MoS_2 is a black powder insoluble in most solvents. It crystallizes like graphite with hexagonal layer molecules MoS_2 infinitely extended in two dimensions (Figure 25.4). Within the layer the sulfur atoms are effectively close packed and the molybdenum atoms are situated in the octahedral holes. The layers are bound to each other by very weak van der Waals forces. Because of this the layers slip easily against each other and the sulfide has lubricant properties. It is an essential component in *solid lubricants* that can be used at much higher temperatures than conventional lubricants. They lubricate up to 350°C in air and 1200°C in vacuum or in an inert atmosphere. Molybdenum disulfide lubricants can also be suspended in special oils and used as lubricating aerosol sprays.

25.5.2.5 **Catalysts, Inhibitors and Other Chemicals**

Molybdenum normally has a valency of +6 but +4 and +5 are also known. The +4 state is, as we know, predominant in nature in molybdenite MoS_2. The capacity to change oxidation states makes molybdenum suitable as a catalyst for some reactions and an inhibitor for others. It catalyses different redox reactions. An important reduction that uses molybdenum as a catalyst is dehydrosulfurization, used to remove sulfur

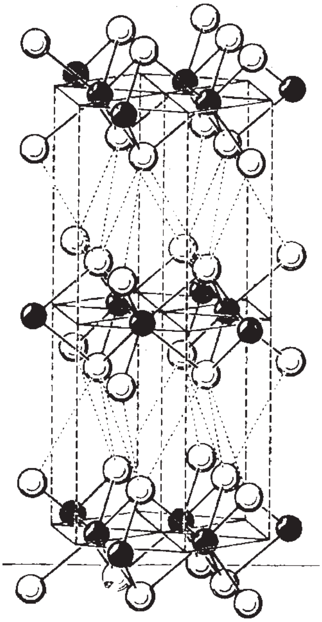

Figure 25.4 The crystal structure of molybdenum disulfide according to Hugo Strunz, *Mineralogische Tabellen*, 8.Auflage, Leipzig, 1982. Molybdenum atoms are dark, sulfur atoms light.

compounds from oil. Molybdate solutions are also used as catalysts in the production of formaldehyde from methanol – an oxidation process.

Sodium molybdate is used as an anodic corrosion inhibitor, effective against pitting corrosion, in a number of applications, such as in automobile anti-freeze products and in water cooling systems.

Chemicals containing ammonium molybdate and/or molybdenum oxide are used to reduce the smoke from burning PVC.

25.6
An Essential Trace Element for Life

There are very few examples of biological selection for functional purposes of elements with atomic number higher than 35. The outstanding exceptions are molybdenum and iodine.

Molybdenum is essential for the biological utilization of nitrogen from the environmental nitrogen cycle. Mo is a constituent of the enzyme *nitrogenase*, an enzyme used by bacteria to fix atmospheric nitrogen N_2 into organic nitrogen. Another enzyme containing molybdenum is *nitrate reductase*. This allows the reduction of nitrate to nitrite in plants and microorganisms. Nitrogenase and nitrate reductase are of great significance in nature as they are two of the most important channels for including nitrogen in biochemical circulation. In this connection, as with the catalyst function mentioned above, it is the cycling between molybdenum's +4 and +6 states that is involved.

The molybdenum requirement for adult men is 0.15–0.20 mg/day and cereals are the most important source.

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26
Tungsten

26.1 W
Facts about Tungsten

26.1.1 W
The Element

Symbol:	W
Atomic number:	74
Atomic weight:	183.84
Ground state electron configuration:	$[Xe]4f^{14}5d^46s^2$
Crystal structure:	Cubic bcc with $a = 3.165$ Å

26.1.2 W
Discovery and Occurrence

Discovery: C. W. Scheele prepared "tungsten acid" from scheelite in 1781. The Spanish brothers J. J. and F. d'Elhuyar prepared the same oxide from wolframite and were the first to isolate the metal tungsten in 1783.

Most important mineral: Scheelite $CaWO_4$ (Figures M38 and M39)
Wolframite (Fe, Mn) WO_4 (Figure M40)

Ranking in order of abundance in earth crust:	57
Mean content in earth crust:	1.25 ppm (g/tonne)
Mean content in oceans:	$1 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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26.1.3 W

Chemical Characterization

Tungsten has the highest melting point of any metal and, because of that, is used for the filaments of incandescent lamps. The metal is also used in tool materials. Modern high-speed steels retain their edge sharpness even after machining (turning, drilling) at high temperature. Tungsten contributes to this, as it is a strong carbide-forming element. Hard metal or cemented carbide is a P/M product (powder metallurgy), built up of very hard and wear-resistant tungsten carbide WC and cobalt for binding the carbide grains together. Cemented carbide is the largest end-use sector for tungsten.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
W^{VI} as in WO_3, $CaWO_4$, and WO_2Cl_2	$W(g) \rightarrow W^+(g) + e^-$	770	$W(g) + e^- \rightarrow W^-(g)$
W^{V} as in $[WF_6]^-$ and $[W(CN)_8]^{3-}$	$W^+(g) \rightarrow W^{2+}(g) + e^-$	170	−78.6
W^{IV} as in WO_2, WS_2 and WBr_4			
W^{III} as in $[W_2Cl_9]^{3-}$			
W^{II} as in WCl_2			

Standard reduction potential: $WO_4^{2-}(aq) + 4H_2O(l) + 6e^- \rightarrow W(s) + 8OH^-(aq)$ [alkaline solution]
$E^0 = -1.074$ V

Electronegativity (Pauling): 2.36

Radii of atoms and ions: (WebElements™)		
	Atomic:	135 pm
	Covalent:	146 pm
	W^{4+} (6-coordinate, octahedral):	80 pm
	W^{5+} (6-coordinate, octahedral):	76 pm
	W^{6+} (4-coordinate, tetrahedral):	56 pm
	W^{6+} (6-coordinate, octahedral):	74 pm

26.1.4 W

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
19 255 kg m^{-3} 19.26 g/cm^{-3}	9.55 cm^3	3695 K 3422 °C	5828 K 5555 °C	132 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
188	177	163	139	119

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$2.6 \cdot 10^{-6}$	$4.5 \cdot 10^{-6}$	$4.6 \cdot 10^{-6}$	$5 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
6	49	73	124	240	390

Mass magnetic susceptibility χ_{mass} at 293 K	$+4.0 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
411 GPa	161 GPa	306 GPa	0.28

26.1.5 W

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	35.2 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	800 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	850 kJmol^{-1}
Entropy S^0 at 298 K	32.64 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	16.0	24.3	25.8	27.0	32.3	34.7

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$W + O_2 \rightarrow WO_2$	–534	–496	–409	–323	–236
$2/3W + O_2 \rightarrow 2/3WO_3$	–509	–	–	–	–

26.1.6 W

Nuclear Properties and X-ray

Isotope range, natural and artificial 158–190

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half life	Decay mode	Decay energy Q
^{180}W	Stable	0.13	+0	–	–	–	–
^{182}W	Stable	26.3	+0	–	–	–	–
^{186}W	Stable	28.6	+0	–	–	–	–
^{183}W	Active	14.3	–1/2	0.1178	$1.1 \cdot 10^{17}$ y	–	–
^{184}W	Active	30.67	+0	–	$3 \cdot 10^{17}$ y	–	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{183}W
Reference compound	Na_2WO_4/D_2O
Frequency MHz (^1H = 100 MHz)	4.166
Receptivity D^P relative to ^1H = 1.00	$1.07 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.0613
Magnetogyric ratio, radT^{-1}s^{-1}	$-1.128 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
73	Ta	56.277
74	W	57.982
75	Re	59.718

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	169
17.37 keV ($MoK\alpha_2$)	94.8

Neutron absorption	Thermal neutron capture cross section	18.5 barns

26.2
Discovery

26.2.1
Jupiter's Wolf and the Wolf's Foam

Tin ores were mined in the German mountains in the 16th century. The ideal metallurgical reaction for tin manufacture was

$$SnO_2 + 2C \rightarrow Sn\ (\text{liquid}) + 2CO$$

The molten tin was covered with slag, formed from rock minerals and added slag former. For an economical result it was important that the tin content in the slag was low. Now and then disturbances occurred. Foam would appear on the surface of the melt and much valuable tin could stay in this foam as droplets. A *wolf* in the ore ate the tin. What the workmen believed was that the foam was the foam of a wolf, (*Wolf Rahm* in German). We now know that foam formation occurred when the tin ore also contained the mineral *wolframite* $(Fe,Mn)WO_4$. This mineral was unknown to the miners.

From antiquity, the metal tin has been connected with the planet Jupiter and had the same symbol. Early in the 16th century, Georgius Agricola in Bohemia was aware of the phenomenon of foam formation. He used the Latin expression *Spuma Lupi* (= the wolf's foam) to describe the effect of the strange mineral on the tin manufacturing process.

26.2.2
Tungstic Acid Appears

In 1761 the mineral that disturbed the tin production was subjected to chemical examination. J. G. Lehmann, known from the history of the chromium discovery, investigated a wolframite from Zinnwald (Cínovec in today's Czech Republic). When he melted the mineral sample in sodium nitrate, leached it in water and added hydrochloric acid he observed a white precipitate that gradually became yellow. He had in fact seen tungstic acid, but did not realize that there was a new element in it.

26.2.3-
The Mineral Tungsten

A heavy mineral containing the element tungsten was discovered in the Swedish province of Dalecarlia in 1750 and this started a vigorous search for an as yet unknown metal. Axel Fredrik Cronstedt, the discoverer of nickel, described the mineral in the *Transactions of the Royal Swedish Academy of Science* of 1751. “It is white-gray, nonmagnetic and heavy.” He noticed that the stone contained lime and an unknown *earth*. He introduced the name *tungsten* for the mineral (tungsten is Swedish and means *heavy stone*). Thirty years later Carl Wilhelm Scheele elucidated the composition of *tungsten*. Today the mineral has the name *scheelite* in honor to Scheele. The formula is $CaWO_4$.

26.2.4
Hunting Tungstic Acid

Scheele mentioned in a letter of 1780 to professor Torbern Bergman in Uppsala that he was engaged in investigating the mineral tungsten. He chose, with good intuition, an investigation technique different from what he had used when he was on the track of molybdic acid. It is true that the two metals are chemically similar but they are bound in quite different ways in their minerals. In today’s terms:

- molybdenite is molybdenum sulfide MoS_2
- scheelite is calcium tungstate $CaWO_4$

In 1781 Scheele published his results for the mineral *tungsten* in the *Transactions* of the Academy. The paper had the simple title “The components of tungsten” [26.1].

> Scheele had used two methods to isolate the unknown “acid”. In one the decomposition occurred with melting. The powdered mineral was mixed with potassium carbonate and the mixture was melted in an iron crucible. The solidified melt was leached in warm water. After filtering the filtrate was acidified with nitric acid. The new unknown “acid” was precipitated. It was again melted with potassium carbonate and the procedure was repeated. A pure white tungstic acid was obtained.
>
> The other method was “wet chemical”. The finely powdered mineral was treated with nitric acid. It was attacked and some of it was dissolved. The solution contained calcium nitrate. The insoluble residue was partly not attacked *tungsten* mineral and partly a yellow precipitate, formed in the reaction. Scheele thought that this was the anhydride of the tungstic acid. The yellow precipitate could be dissolved in ammonia. From this solution tungstic acid was precipitated with diluted nitric acid.

Now the situation with molybdic acid was repeated. Scheele had prepared the acid of a new metal but he was incapable of taking the last step: the final isolation of the element. His pharmacy did not have furnaces strong enough. This time he did not involve the Laboratorium Chymicum in Stockholm. The development continued in Spain.

26.2.5
The Seminary of Vergara in the Basque Country

In the north of Spain, near the Bay of Biscay, in the valley of the river Nervión, there are large deposits of iron ores, which, during the second part of the 19th century, became the base of an important steel industry, especially in the Bilbao area. The Basque provinces of Vizcaya and Guipúzcoa are still among the most important industrial zones in Spain, producing not only steel but also chemicals, paper, textiles and food,

In this Basque country a patriotic organization known as the *Sociedad Vascongada de los Amigos del Pais* (The Basque society of Friends of their country) was founded on Christmas Eve in 1764. It developed into a learned academy for the promotion of science, agriculture, industry, trade and arts. The members of this society were studious men of the nobility and clergy. During the first, more idealistic, period of its existence, the members used to meet every evening for general discussions and activities such as physical demonstrations and experiments, studies in mathematics, history, geography and practicing music.

Gradually the work became more practical and concentrated on supporting the exploitation of the natural resources of the Basque region of Spain. One very important result was the foundation in 1777 of an institute for art and science, the *Seminary of Vergara,* southeast of Bilbao (Figure 26.1). The seminary became the first institution in Spain for education and research in chemistry and metallurgy. And in the laboratories of the Seminary of Vergara the element tungsten was discovered.

Figure 26.1 The Seminary of Vergara.

The young French chemist *Joseph Louis Proust,* 23 years of age when the Vergara Seminary was founded, worked as a teacher at the seminary from the start. Perhaps it was here that he carried out some of the preparatory work and experiments for establishing the chemical law of definite proportions, called Proust's law. This states that the elements in a compound are all present in fixed proportions, regardless of how the compound is prepared. Proust's results became one of the keystones in Dalton's epoch-making atomic theory in 1808. In 1789 Proust became professor of chemistry in Madrid.

26.2.6
The Spanish Brothers Discover the New Metal

The Seminary started to send out young men to study chemistry in France, mineralogy at the Bergakademie Freiberg, and practical mining in Harz and Erzgebirge. Other important destinations were the Swedish iron and steel industry, the copper mine in Falun and Uppsala University. Two brothers with the family name d'Elhuyar, the older one Juan José and the younger Fausto, born in 1755 and 1756, were sent to Freiberg in 1778. They became ardent students of the great mineralogist and geologist A. G. Werner. After three years in Freiberg the younger brother Fausto returned to Vergara and became a teacher there. The older brother, Juan José, continued further north to Uppsala. During the spring term in 1782 he studied metallurgical chemistry for professor Torbern Bergman. During this time he also made a two-day visit to Scheele in Köping. It was just a short time after Scheele's publication "The components of tungsten". No doubt Juan José was informed of Scheele's work with tungsten and tungstic acid.

Mr. d'Elhuyar also visited the copper mine in Falun as can be seen from the mine visitors' book for 22 May 1782. He wrote his name "De Luyarte Espagnol".

In his diary for 1782, Bergman mentions two students from Spain, d'Elhuyar and de Virly. "They went privately through a course in higher chemistry and also lectures in assaying. They remained until the end of the term and obtained excellent results."

In 1954, Dr Stig Rydén at the Ibero-American Institute at the University of Gothenburg in Sweden wrote a description in Spanish of the visit of Jan José to Sweden [26.2].

When the brothers were reunited in Vergara they compiled their impressions. Was there some connection between

- The "wolf's foam" disturbing the tin manufacture in the German mountains
- The mineral wolframite that sometimes occurred with the tin mineral cassiterite, which the brothers brought from Zinnwald in Germany, and finally
- Scheele's *tungsten* and tungstic acid that Juan José had learned about in distant Sweden.

At the chemical laboratory at the Seminary of Vergara the two brothers now made a skilful analysis of the mineral wolframite and established its content of iron, manganese and a foreign "acid" (oxide). They formed the opinion that this oxide was identical with Scheele's tungstic acid.

The preparation of the new metal was made with a simple method. The yellow oxide was mixed with carbon powder and the mixture was heated to the highest temperature that could be obtained in the laboratory. After cooling and crushing it was possible to observe – with a magnifying glass – particles of metallic appearance. A new metal had been isolated. The year was 1783.

The new metal's density was determined to 17.6. Pure tungsten metal has a density of 19.3 g/cm^3. This shows that the metal obtained was not pure but was partly tungsten carbide. This metal is also a very strong carbide former. The density of tungsten carbide WC is 15.8 g/cm^3. A simple stoichiometric calculation shows that a mixture of 48.6% WC and 51.4% W has a density of exactly 17.6.

The brothers d'Elhuyar wrote immediately to Torbern Bergman in Uppsala and informed him of the discovery. In the 1784 spring issue of the *New Transactions of the Royal Swedish Academy of Sciences* Bergman wrote:

> At last I have something to mention about the mineral Tungsten, the elements of which I myself have – in Vol. III of my *Opuscula* – tried to make it probable that its yellow earth of acid character is metallic. This statement is now proved and there is no doubt at all about it. Signor D'Elhuyar from Spain, who in 1782 spent half a year in Uppsala, had on his return to his fatherland tungsten mineral at his disposal in a quantity big enough for making a reduction test. He prepared the yellow earth and obtained a regulus at the most severe fire. This metal has curious properties. Gravitas specifica is 17.6. ... It is just this metal that together with manganesium and iron forms the mineral that in Germany is called Wolfram and which is the reason for giving the new metal just the same name.
>
> As Signor d'Elhuyar has been appointed director for all Spanish smelteries in New Granada he has left Spain for America. His brother (Fausto), who has assisted him in the actual work with tungsten, continues to investigate the new metal. He also works with a new Mineralogy for Spain, arranged according to the elements. A publication about the new metal will come very soon in the *Journal de Physique*.

The two brothers' achievements were observed in their native country. The Spanish king, Charles III, was himself informed and he fully realized the importance of utilizing their skill and experiences for the Spanish colonies in the Western Hemisphere, rich as they were in minerals and precious metals. In 1784 Don Juan José was – as Torbern Bergman mentioned – sent to New Granada (Colombia) as director of the mines there. He successfully developed the mines and served also for many years as professor of mineralogy. He died in 1796, at the age of only 42, in the Santa-Ana mine outside Bogota.

In Freiberg a new method, amalgamation, for extracting precious metals from ores by means of mercury, had been developed. Don Fausto got the commission of the king in 1786 to study this method in Germany and Hungary and after that to leave for Mexico and the position of Director General of the Royal Assembly of Mines of Mexico. He and his wife arrived in Vera Cruz in September 1788. In Mexico City he built up a Mining School with well-equipped laboratories and effective assay furnaces. The school got a very good reputation. Baron Alexander von Humboldt had visited Mexico in 1803 and wrote that no city of the new continent presents scientific establishments so large and so substantial as the capital of Mexico. He mentions the School of Mines, directed by the learned Elhuyar.

In addition to leading the School of Mines, Don Fausto d'Elhuyar also made many inspection trips to mining centers. Not until 1821 did he return to Spain, and he died in 1833 at the age of 77.

26.2.7

A Tungsten Contribution of an Adventurer

Rudolf Erich Raspe was born in Hannover, Germany, in 1737 and in his younger days studied both science and languages in his home town and in Göttingen. He had a spectacular career and became professor of archaeology in Kassel. He was intelligent but unfortunately also dishonest. In fact the only description we have of his appearance is from a police report: "a red-haired man dressed in extravagant, gold-embroidered suits". He was arrested after he had stolen medals from a museum and pawned them. He escaped from the arrest, fled to England and stayed there and in Scotland for the rest of his life.

The baron Hieronymus von Münchhausen, 17 years older than Raspe, lived in the same town. The two men knew each other and both met Benjamin Franklin on his visit to Hannover. As a young man von Münchhausen had participated in the Russian war against Turkey and made himself well known for unbelievable stories of travelling, hunting and battles. These stories had fascinated Raspe. In his new home country Raspe made use of his gift for languages. He found it very easy to express himself and tell stories even in English. Now he remembered the tales of the bizarre baron and he wrote a book *Baron Münchhausen's Narrative of His Marvelous Travels and Campaigns in Russia"*, later translated into many languages.

Raspe kept his versatility and did not forget the science he had once acquired. He became interested in the minerals from Cornwall and started to give lectures in geology. When the d'Elhuyar brothers discovered tungsten in Vergara he was 46 years of age. The d'Elhuyars had used wolframite from the German mines. Raspe now provided wolframite from Cornwall and repeated the d'Elhuyars' experiments to prepare the metal. He also did the same experiments with scheelite and compared the different metal samples. He established that the two had about the same appearance, while the iron content was higher in the metal from wolframite. "If I am not mistaken the two metals are identical." Raspe also observed that tungsten metal is extremely hard. "It cuts glass like hardened steel. The metal ought to be suitable for manufacturing hard tools." It can be said that Rudolf Erich Raspe who collected Münchhausen's fantastic stories also foretold the new metal's fantastic success in the area of tool materials.

Sir Walter Scott, the author of *Ivanhoe*, became acquainted with Raspe and did not like him. In his novel *The Antiquary* Scott had a blackguard, Herman Dousterswivel, for whom Rudolph Erich Raspe was the model.

26.2.8
A Name for the New Metal

The d'Elhuyar brothers gave their metal the name *wolfromium* and this name has remained in large parts of the world. However, in France, England and the USA the Swedish name "tungsten" (heavy stone) became the basis for the element's name and also in fact in Spain (tungstène, tungsten, tungsten). Soon after the discovery, A. G. Werner in Freiberg proposed that the name should be *scheel or schelium* in honor of Scheele's pioneer work. During the 19th century the name question was discussed. Berzelius had now become the authority. He recommended the name wolfram and gave the element the symbol W. In his textbook *Lehrbuch der Chemie* he writes that the proposed name schelium is not good from the point of view of the Swedish language. He also states that "our compatriot's immortality has no need of such a support".

The element names tungsten and wolfram rapidly gained a foothold in their respective geographical areas. When the International Union of Pure and Applied Chemistry addressed the question in1960 it was shown that *tungsten, tungstène* and *tungstato* are so well established in the different countries that the name wolfram cannot replace them.

In all countries the symbol for the element tungsten or wolfram is, however, W in accordance with Berzelius' original proposal.

26.2.9
Scheelite Remembers Scheele

The name *tungsten* is no longer used for the mineral with the composition $CaWO_4$. C. C. Leonard in Heidelberg proposed in 1821 that the mineral name should be *scheelite* in order to remember Carl Wilhelm Scheele's epoch-making work on tungsten. This mineral name has been accepted. The *mineral name* "*tungsten*" is no longer used and must not be confused with the existing mineral *tungstenite* WS_2.

26.3
Tungsten in Nature

26.3.1
Tungsten Minerals

The minerals scheelite and wolframite, so important in the discovery of the element, also constitute the base for modern tungsten production.

Scheelite, $CaWO_4$, is present in epigenetic rocks, volcanic and sedimentary, formed in processes near the surface of the earth. In the ores the scheelite content is as a rule low, corresponding to, for example, 0.5% WO_3. The finding and identification of such small quantities is helped by the fact that scheelite fluoresces with a bluish-white light in UV radiation, (Figures M38 and M39). The scheelite mineral has a certain miscibility with the molybdenum mineral *powellite*, $CaMoO_4$. Some scheelite ores therefore also contain up to 8% MoO_3 (counted on the WO_3 content). This can be observed by a slight change of the color of the fluorescent light. Molybdenum in scheelite is as a rule a contaminant and reduces the value of the ore.

The minerals *ferberite* $FeWO_4$ and *hübnerite* $MnWO_4$ are completely miscible and occur in practice as the mineral *wolframite* $(Fe,Mn)WO_4$ (Figure M40). The mineral is found preferentially in veins or in pegmatites.

26.3.2
Tungsten Deposits

Tungsten resources are geographically widespread, see Figure 26.2. The reserves are estimated at about 2 million tonnes (contained tungsten) of which one-third is in China. Significant reserves are also available in Canada, Russia and the USA. In Europe, Portugal and Austria have the biggest reserves.

Throughout the world the ore types are distributed so that 55% are based on wolframite while 45% contain scheelite, so there is roughly a 1:1 relation. In the eastern hemisphere, wolframite dominates still more with a wolframite:scheelite ratio of 2.5:1.

> The most important of the Chinese deposits are situated in the southeast, in Jiangxi province. The background to the discovery of these big wolframite deposits in Jiangxi is described in a story. A short time before World War I a young Chinese, Mr. Li, came as a student to the Imperial School of Ore Dressing in London. He was given an assignment to study the tin deposits in Cornwall and develop methods to separate wolframite and cassiterite, a task closely connected to the very beginning of tungsten discovery. Through this study he became very accomplished at identifying wolframite. On his return to China, Mr. Li, well educated as he was from the famous London school, was sent out prospecting for tin ore. He then discovered the big wolframite deposits in Jiangxi province.

26.3.3
Production Technique for Tungsten Concentrate

Tungsten ore is usually won by underground mining, After careful crushing and grinding, the ore is suspended in water in a mixer. Flotation is carried through in steps. At first, contamination, for instance copper minerals, can be “lifted” with special flotation agents. Then specific agents for the tungsten mineral are added and the valuable mineral is separated. This dressed ore can contain 65–85% WO_3 and this concentrate is one of the big trade products for tungsten.

No	Deposit	No	Deposit	No	Deposit
1	Tungsten, North West Territories, Canada	8	Yxsjöberg, Sweden	15	Sangdong, South Korea
2	Mount Pleasant, New Brunswick, Canada	9	Mittersill, Salzburg, Austria	16	Ham Hung, North Korea
3	Climax, Colorado, USA	10	Uludag, Turkey	17	Jiangxi Province, China
4	Tasna, Bolivia	11	Turnuy, Caucasian, Russia	18	Hermyingyi, Burma
5	Barra Verde, Rio Grande do Norte, Brazil	12	Ingitschke, Uzbekistan	19	Mae Hong Son, Thailand
6	Panasqueira, Portugal	13	Choltoson, Transbajkal, Russia	20	King Island, Tasmania, Australia
7	Salau, Dept. Arège, France	14	Vostok, Maritimskoje, Russia	21	Mount Carbine, Queensland, Australia

Figure 26.2 Important tungsten deposits in the world. (Reprinted from SGU PM 1989:5. Theme Wolfram, p. 36. Geological Survey of Sweden. With permission.)

26.3.4
The World Production from Mines

The W content of the ores varies from mine to mine in the range of 0.1 to 2%. The production of ores and concentrates varies greatly according to demand and price, and some mines have shut down. The price level is the reason for closing the Canadian mines although the country has about 15% of the total world tungsten reserves.

In the year 2000 the total production in all mines of the world was not far from 40 thousand tonnes (contained tungsten). Of this China accounted for about 80% (see Table 26.1).

Table 26.1 World mine production of tungsten in 2000

Country	Production, tonnes (contained W)	Percentage of total
China	30 000	80.2
Russia	3500	9.35
Austria	1600	4.3
Portugal	750	2.0
North Korea	700	1.9
Bolivia	380	1.0
Uzbekistan	200	0.5
Other countries	280	0.75
World total	37 400	100

Figures taken from ref. [26.3].

26.4
Chemistry at Work With Tungsten Products

The chemistry of tungsten is complex. The metal has different oxidation states in compounds, the most usual being +6. The yellow oxide WO_3 is an important example. In alkaline water solutions the hexavalent element is present as tungstate ion WO_4^{2-}.

The industrial chemical treatment of tungsten concentrate uses scheelite, either concentrated scheelite or synthetic scheelite, manufactured from woframite concentrates. In this latter case wolframite is treated with sodium hydroxide or sodium carbonate to form sodium tungstate. Dissolution in water and filtering removes the hydroxides of iron and manganese. Addition of calcium chloride to the filtrate precipitates calcium tungstate – synthetic scheelite.

Scheelite, natural or synthetic, is attacked by hydrochloric acid in an autoclave. An almost insoluble residue of $WO_3 \cdot xH_2O$, contaminated by silicates from the gangue, is obtained. On treatment with ammonia this oxide-hydrate is dissolved to form a colorless solution and purified by filtration. After evaporation a white substance crystallizes, ammonium *paratungstate* APT (or *ammonium parawolframate* APW) with the formula $(NH_4)_{10}H_{10}W_{12}O_{46}$. APT has been an important substance in the worldwide trade in tungsten products. When this compound is ignited pure WO_3 is formed.

Tungsten powder is obtained by reduction of WO_3 with hydrogen gas at a temperature of 800°C. The very hard, wear-resistant, tungsten carbide WC is prepared by reaction between W powder and carbon powder at a temperature above 1600°C. Tungsten carbide WC has a density of 15.72 g/cm^3 and a Vickers hardness of 2350.

26.5
Metallurgy and Powder Metallurgy at Work with Tungsten Products

26.5.1
Ferrotungsten

Ferrotungsten with 70–85% W is the main alloying addition to steel baths during the manufacture of tungsten steels. It is manufactured from scheelite or wolframite concentrate either by carbon reduction at high temperature in an electric furnace or by reduction with aluminum or aluminum/silicon in a metallothermic process. Because of its high melting temperature ferrotungsten cannot be tapped as a melt from the furnace. Instead the solid button is removed from the cold furnace, crushed down to a mean size of 6 mm (about the size of a peanut), suitable for addition to the steel baths.

26.5.2
Cemented Carbide or Hard Metal Produced With Powder Metallurgy

The production of cemented carbide starts with milling a mixture of tungsten carbide powder and cobalt powder together with polyethylene glycol PEG (a lubricant for the following pressing operation). The milling is carried out for 15–50 h using cylpebs of hard metal in alcohol as a milling liquid. The milling is carried out to mix the components thoroughly and to give the tungsten carbide the desired grain size. After evaporating the milling liquid the hard metal powder is pressed (compacted) into a body suitable for sintering. During this process, performed in hydrogen gas, the lubricant vaporizes, the binding metal dissolves some tungsten carbide and melts to a binding phase. This leads to *pore closure* at 1350°C. Finally the furnace is filled with argon and the temperature is increased to 1450°C. This creates the final density of the cemented carbide tool.

26.6
Modern Uses of Tungsten and Tungsten Products

26.6.1
General Applications

After their discovery, the d’Elhuyar brothers wrote that “no use has yet been found for the new metal but we must not conclude from this that it is entirely useless”. This was an under-statement! The physical properties of the metal have made it very useful in a modern society. The melting point is the highest of all elements, 3422°C. Above 1650°C it also has the highest tensile strength of all metals. Its electrical and thermal conductivity are good, 30% and 40% respectively of the values for copper. The metal can easily be melted into glass as it has the same low coefficient of thermal expansion as boron silicate glass. The metal has also a very low specific heat, which, in combination with the good heat conductivity, results in rapid heating and cooling. The very high density of the metal also opens up for some important applications. The sports goods industry has started to use the heavy metal in golf clubs and golf ball cores. Heavy alloys for armaments and for weights and counterweights have high contents of tungsten, as do alloys for heat sinks and radiation shielding. Tungsten composites (e.g. 96% W and 4% polymer) are also used as a "green" alternative for lead in bullets and shot. For cores in small caliber ammunition tungsten-nylon and tungsten-tin have been tested as alternatives to hazardous lead–antimony alloys.

26.6.2
In Service for Lighting

The high melting point and low vapor pressure make tungsten wire very suitable for filaments in incandescent lamps. Millions of homes all over the world are nowadays lit by lamps in which the white-hot wire is made of pure tungsten. In his fascinating book *Uncle Tungsten* [26.4] Oliver Sacks has devoted one chapter to an essay on "Light for the Masses". It ends with a description of bulbs with tungsten filaments and molybdenum supports.

A similar application is filaments in X-ray tubes. Tungsten wire is also used for electrodes in high-temperature applications such as TIG welding (*t*ungsten *i*nert *g*as) and in spark plugs.

26.6.3
Tungsten in Tool Materials

The tendency of tungsten to form hard, wear-resistant, carbides is used for advanced tool steels and for cemented carbides, hard metals.

26.6.3.1 High-speed Steels

> *F. W. Taylor* (1865–1915) was an American engineer who is best known as the father of scientific management in industry. From 1898 to1901 he was a consultant at Bethlehem Steel and, through his contacts with the manufacturing industry, he realized the importance for productivity of machining properties. Together with *White*, another American, he worked on the development of better tool steels. In 1898 they discovered and patented a hardening process for high-carbon steels (1.85% C) alloyed with 8% tungsten and 4% chromium. By using an austenitizing temperature of 1200°C they could give the steel unsurpassed effectiveness during machining. This steel was introduced in 1900 at the world exhibition in Paris. During the 20th century a whole family of high-speed steels has been developed.

Modern high-speed steels are alloyed with strong carbide-forming elements, such as W, Mo, V and Cr. A carbon content of about 1% results in the formation of carbides in the steelmaking process. Two important high-speed steels are shown in Table 26.2.

Table 26.2 Composition of two high-speed steels

Grade AISI	Composition %					
	C	Cr	Mo	W	Co	V
M2	0.85	4.2	5.0	6.4	–	1.8
M42	1.08	3.8	9.4	1.5	8.0	1.2

Tools of hardened and tempered high-speed steels retain their edge sharpness even after the machining (turning, drilling) has increased the edge temperature very much. Thus it is possible to perform the cutting operation at high speed – hence the name "high-speed steel".

26.6.3.2 Cemented Carbide

Hard metal is neither a hard metal nor a special steel. Hard metal or *cemented carbide* is a P/M product (powder metallurgy), built up of very hard and wear-resistant tungsten carbide WC (shown as gray grains in Figure 26.3) and cobalt for binding the carbide grains together (white in the figure). The combination gives the product not only hardness and wear resistance but also a certain toughness. Cemented carbide is the largest end-use sector for tungsten, used as a tool material for wire drawing, mining and stone cutting, and oil and gas drilling. The greatest application of all nowadays, however, is for machining (turning, milling and drilling) in the engineering industry, including automotive and aircraft manufacturing. In modern tools for machining steel WC is partly replaced by titanium carbide TiC. Titanium carbide and nitride are also used as coating of the tool materials to improve the machining properties.

The German electrical bulb manufacturer Osram produced tungsten wire for the lamps and used diamond dies for the drawing. They were expensive and in the early 1920s the company looked for alternatives, which led to the invention of the cement-

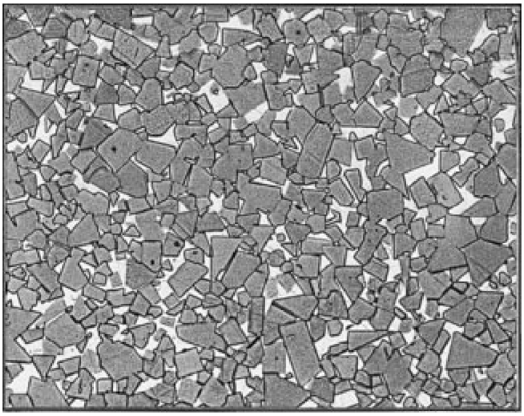

Figure 26.3 Microstructure of WC–Co hard metal with a coarse grain size of 4 μm.

ed carbide. The Krupp group introduced the product commercially under the name of Widia (“like diamond”).

The hardness of the cemented carbide (Figure 26.4) depends on:

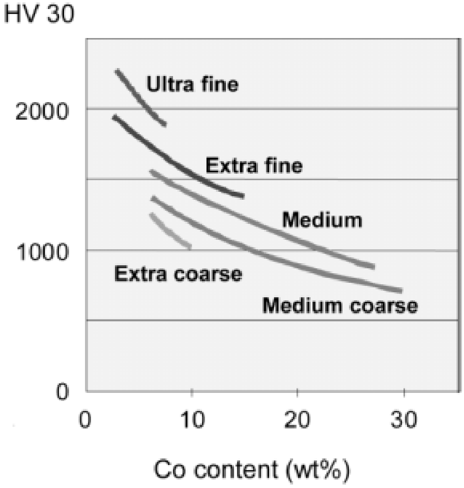

Figure 26.4 Hardness as a function of the cobalt content and WC grain size. The designations “ultra fine” etc. are connected to the WC grain size, as indicated in Table 26.3. (Reprinted from *Understanding Cemented Carbide* with permission of SANDVIK Hard Materials, Sweden.)

- the cobalt content of the cemented carbide. The higher the Co-content, the lower the hardness;
- the grain size of WC. The finer the WC grain size, the greater the hardness.

The classification system for WC grain size is shown in Table 26.3.

Table 26.3 WC grain size classifications and designations

Designation	**Mean grain size μm**
Ultra fine	<0.5
Extra fine	0.5–0.9
Fine	1.0–1.3
Medium	1.4–2.0
Medium coarse	2.1–3.4
Coarse	3.5–5.0
Extra coarse	>5.0

26.7
Tungsten in Life

The concentration of tungsten in natural waters is very low and the element is nontoxic. Until recently tungsten was supposed to have no biological role at all. A few enzymes containing tungsten have, however, been found in anaerobic bacteria, especially *clostridium*. In these, tungsten assists in reduction/oxidation reactions such as CO_2 fixation. It is a mystery why nature uses tungsten and not molybdenum for these purposes.

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27
Manganese

27.1 Mn
Facts about Manganese

27.1.1 Mn
The Element

Symbol:	Mn
Atomic number:	25
Atomic weight:	54.94
Ground state electron configuration:	$[Ar]3d^5 4s^2$
Crystal structure:	Cubic bcc with $a = 8.91$ Å

27.1.2 Mn
Discovery and Occurrence

Discovery: The mineral pyrolusite has been known since antiquity. Decisive contributions to the elucidation of the chemistry of pyrolusite were made by C. W. Scheele. The element was isolated in 1774 by J. G. Gahn in Falun, Sweden, and he is considered to be the discoverer of manganese.

Most important mineral: Pyrolusite MnO_2 (Figure M41), manganite MnO(OH), other oxide minerals and in manganese-containing iron ores. Manganese is present in quantity as nodules on the ocean floor (Figure M42).

Ranking in order of abundance in earth crust:	12
Mean content in earth crust:	950 ppm (g/tonne)
Mean content in oceans:	$2 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	0.2 ppm
Content in a man's body (weight 70 kg):	14 mg

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27.1.3 Mn

Chemical Characterization

Manganese is a gray-white, brittle metal. It is an important component of many types of steel. Ferromanganese, containing about 78% manganese, is used in steelmaking. High Mn contents make steels extra wear resistant and difficult to work. Safes, for example, are made of manganese steel containing about 12% manganese. Manganese dioxide (MnO_2) occurs native as pyrolusite and is prepared artificially. It is used as a depolarizer in dry cell batteries. Manganese is an important trace element in life and has a role in photosynthesis.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Mn^{II} as in MnO, MnS, and $MnSO_4$	$Mn(g) \rightarrow Mn^+(g) + e^-$	717	$Mn(g) + e^- \rightarrow Mn(g)$
Mn^{III} as in MnO(OH)	$Mn^+(g) \rightarrow Mn^{2+}(g) + e^-$	1509	–
Mn^{II} and Mn^{III} in Mn_3O_4	$Mn^{2+}(g) \rightarrow Mn^{3+}(g) + e^-$	3248	
that is $Mn^{II}[Mn^{III}]_2O_4$	$Mn^{3+}(g) \rightarrow Mn^{4+}(g) + e^-$	4940	
Mn^{IV} as in MnO_2 and MnF_6^{2-}	$Mn^{4+}(g) \rightarrow Mn^{5+}(g) + e^-$	6990	
Mn^{V} as in $Na_3MnO_4 \cdot 10H_2O$	$Mn^{5+}(g) \rightarrow Mn^{6+}(g) + e^-$	9220	
Mn^{VI} as in MnO_4^{2-}	$Mn^{6+}(g) \rightarrow Mn^{7+}(g) + e^-$	11 500	
Mn^{VII} as in Mn_2O_7 and $KMnO_4$			

Standard reduction potential:	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	$E^0 = +1.51$ V
	$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	$E^0 = +1.23$ V
	$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	$E^0 = -1.18$ V

Electronegativity (Pauling): 1.55

Radii of atoms and ions:	Atomic:	140 pm
(WebElements™)	Covalent:	139 pm
	Mn^{2+} (6-coordinate, octahedral):	81 pm
	Mn^{2+} (8-coordinate):	110 pm
	Mn^{2+} (4-coordinate, tetrahedral):	80 pm
	Mn^{3+} (6-coordinate, octahedral):	72 pm
	Mn^{4+} (6-coordinate, octahedral):	67 pm
	Mn^{4+} (4-coordinate, tetrahedral):	53 pm
	Mn^{5+} (4-coordinate, tetrahedral):	47 pm
	Mn^{6+} (4-coordinate, tetrahedral):	39.5 pm
	Mn^{7+} (6-coordinate, octahedral):	60 pm
	Mn^{7+} (4-coordinate, tetrahedral):	39pm

27.1.4 Mn

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
7470 kg m^{-3} 7.47 g cm^{-3}	7.35 cm^3	1519 K 1246 °C	2334 K 2061 °C	479 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	298 K	373 K	573 K	973 K
7	7.8	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$21.7 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	298 K	573 K	973 K	1473 K
–	1380	1600	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K $+121 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
199 GPa	80 GPa	129 GPa	0.24

27.1.5 Mn
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	14.5 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	220 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	281 kJmol^{-1}
Entropy S^0 at 298 K	32.00 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	–	26.32	31.5	38.9	46.0	21.1

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Mn + O_2 \rightarrow 2MnO$	−726	−697	−624	−551	−469
$3/2Mn + O_2 \rightarrow 1/2Mn_3O_4$	−642	−604	−518	−435	–
$Mn + O_2 \rightarrow MnO_2$	−465	−428	−338	–	–

27.1.6 Mn
Nuclear Properties and X-ray

Isotope range, natural and artificial	46–66

Naturally occuring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{55}Mn	Stable	100	−5/2	3.468

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{55}Mn
Reference compound	$KMnO_4/D_2O$
Frequency MHz (^{1}H = 100 MHz)	24.789
Receptivity D^P relative to ^{1}H = 1.00	0.179
Receptivity D^C relative to ^{13}C = 1.00	1020
Magnetogyric ratio, radT^{-1}s^{-1}	$6.645 \cdot 10^7$
Nuclear quadropole moment, barn	0.33

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
24	Cr	5.405
25	Mn	5.888
26	Fe	6.391

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	271
17.37 keV (MoKα_2)	33.5

Neutron absorption **Thermal neutron capture cross section** 13.3 barns

27.2
Discovery

27.2.1
“Braunstein” for Coloring – and Discoloring – of the Glass Melt. Transforms Copper to Silver!

Glass making is an applied high-temperature chemistry that has been used for at least 5000 years. Glass is a silicate melt containing alkali oxides. For special purposes additions are made of calcium, magnesium, lead, boron and aluminum oxides.

The technique of coloring glass was discovered early. Cobalt dissolved in the glass melt gives a blue color, colloidal particles of gold or copper make the glass ruby-red. If the glass melt contains divalent iron Fe^{2+} a bluish-green color appears. Addition of an oxidizing agent converts the iron to trivalent Fe^{3+}. This ion has a much weaker yellowish color, so the glass seems to be colorless and purified. One of the earliest oxidizing agents used for purifying glass melts in this way was *pyrolusite*, *Braunstein*, *Magnesia nigra*. In his book *Pirotechnia* published in 1540, *Vannocio Biringuccio* [27.1] speaks of a German “half mineral”, Braunstein. “It does not melt and it is unusable for metal making”. However, it does have one special quality. A small quantity added to molten glass purifies the glass and makes it colorless. This special property of pyrolusite was the reason for giving it the name *sapo vitri* – glass soap.

In *Pirotechnia* there is a description of how treatment with *Braunstein* can make the glass melt both colorless and strongly colored. Large additions make the glass “wonderful violet”. Without knowing the true chemical nature of *Braunstein* the glassworkers had discovered the different characteristic colors of the element manganese in higher oxidation states.

The different colors of water solutions of the “Braunstein metal” confused chemists during the 17th and 18th centuries, and they spoke about the “chameleon mineral”. In 1774 Scheele claimed that if pyrolusite is melted with sodium hydroxide, the solution after leaching with water had a blue color. It changed to red after addition of extra pyrolusite and to green after adding ferrous (divalent) iron. Not until the beginning of the 19th century was the chemistry of the different manganese acids clarified. In 1820 J. G. Forchhammer in his doctor’s dissertation in Copenhagen showed that manganese is an element with several oxidation states and colors – green in solutions with trivalent manganese and red in permanganate solutions.

Metallurgy is like glass-making chemistry at high temperatures and it has been of great importance in the discovery of elements, especially metals. Ancient metallurgy was of course not carried out to discover new elements but to make metals and alloys for tools, weapons and *objets d'art*. In the history of element discoveries, however, we often meet metallurgical furnaces and processes.

As the final step in metal manufacture, carbon reduction of the oxide to a metal, a melt (*regulus)* or a metal powder led to the uncovering of the element, which could then be identified (silver copper, lead). If the metal was so strongly bound to oxygen that reduction with carbon was impossible (aluminum, titanium), chemical and mineralogical methods had to be used for identification long before the isolation of the metal itself was possible. In the spirit of alchemy, metallurgy was also used in attempts to transform metals into nobler variants, iron to copper, copper to silver, silver to gold. It was in work of this type that the third remarkable property of *Braunstein* was discovered. It could transform copper into silver!

It was early known that red copper became yellow and similar to gold after melting with *galmeja,* a zinc carbonate (we now know that the product was brass). In Roman chemistry it also became known that fusion of copper with *Braunstein* gave a white alloy, similar to silver. The *Braunstein* or pyrolusite for this "silver making" was mined on the south coast of the Black Sea in present Turkey.

27.2.2
***Braunstein*, Pyrolusite, What Is It in Reality?**

Although pyrolusite has been used since antiquity its composition was still unknown in the 16th and 17th centuries. Some sort of an iron ore was a guess. The elusive substance was also given many names: *Braunstein,* pyrolusite, magnesia, magnesia nigra, manganese, manganesium.

When systematic chemical experiments became possible in the 18th century, what pyrolusite is became clear. That work resulted in the discovery of several elements.

The German chemist J. H. Pott made a comprehensive investigation of pyrolusite around 1740 and prepared manganese hydroxide and also some manganese salts. But it was not clear to him that he had an unknown metal in his bottles. He thought that pyrolusite was an alkaline earth although similar to alum. This was incorrect, but one very important result came out of Pott's experiments. Pyrolusite is not an iron ore.

27.2.3
Early Attempts to Find the Metal in Pyrolusite

Sven Rinman (1720–1792) was a prominent metallurgist in Sweden (section 8.7.2). In 1756 he tried to isolate a metal from pyrolusite. He first roasted it and mixed it with charcoal and slag former. After intense heating for 22 minutes he got a small metallic ball. The metal was brittle and looked like bismuth in the fractures. Again, it was not iron! A magnet did not attract the metal. Rinman was really on the track of the new metal but did not have time to follow up his discovery.

In 1774 G. Keim wrote a dissertation *De dubis metallis* [About doubtful metals], in which he accounted for reduction experiments with pyrolusite. He wrote: "I took one part of the powdered pyrolusite and two parts of black flux and melted the mixture at high temperature. On casting the melt I got a regulus, bluish-white and brittle."

Keim's metal could not be dissolved in pure acids, concentrated or dilute, but could be in a mixture of hydrochloric and nitric acids. No doubt Keim had manganese metal in his crucible. The work on *De dubis metallis* had, however, been carried out at the University of Trnava in present-day Slovakia and the dissertation attracted very little attention. Keim's work has scarcely been even a footnote in the history of the discovery of manganese.

27.2.4
The Pyrolusite Chemistry Clears Up

Professor Torbern Bergman in Uppsala was skeptical of Pott's presumption that pyrolusite had something in common with alum. He therefore requested Scheele to set about investigating the mineral pyrolusite.

27.2.4.1 Who Was Carl Wilhelm Scheele?

Carl Wilhelm Scheele (1742–1786) was born in Stralsund in present-day Germany, then in Swedish Pomerania, where his father was a brewer. Scheele is looked upon as one of the greatest chemists of all time. As an experimentalist it is difficult to find his equal. Who taught and supervised him? Which university had the honor of sorting out this genius? Where did he prepare his doctoral thesis and where did he become professor?

Scheele's life is remarkable. When – at the age of 33 – he was elected as a member of the Royal Swedish Academy of Sciences, he had not taken any university degree at all. His title was *pharmaciæ studiosus*, "student of pharmacology". Two years later, in 1777, Scheele obtained his sole university degree as a pharmacist. He was then already a chemist with a worldwide reputation and the examination day took the form of a homage to Carl Wilhelm Scheele from the Collegium medicum.

From his youth he had worked in different pharmacies and studied chemistry "the practical way". At the age of 15, Carl Wilhelm began to work in the Unicorn pharmacy in Gothenburg, where he had a clerk by the name of Grünberg as instructor and teacher. From him he borrowed textbooks of chemistry and pharmacology and was allowed to make his own experiments in the well-equipped pharmacy. After eight years in these positive surroundings, Scheele's immensely diligent study had yielded results. Carl Wilhelm left Gothenburg as a very clever chemist.

After brief employments in pharmacies in Malmö and Stockholm, in 1770 he came to the Upland's Arms pharmacy in Uppsala, now named "The Lion". His time there, 1770–1775, was of great importance both for himself and also for the science of chemistry. He came in contact with professor Torbern Bergman (1735–1784) at the university and with Johan Gottlieb Gahn (1745–1818), later the discoverer of manganese. Scheele's first publication about fluorspar and its acid (in 1771) attracted professor Bergman's attention and he discovered the qualifications of the pharmacy assistant. The three, Bergman, Gahn and Scheele (Figure 27.1) became friends for life and were able to work on and solve many difficult chemical problems. And it was Bergman who proposed that Scheele ought to analyze pyrolusite.

Figure 27.1 Johan Gottlieb Gahn, Carl Wilhelm Scheele and Torbern Bergman (the likeness to the original persons can be questioned). (Reprinted from the booklet "Of the meteor family" published by AB Ferrolegeringar, Stockholm. With permission.)

From 1775 to his death in 1786 he was pharmacist in the small town of Köping in central Sweden (Figure 27.2).

During his time in Uppsala, Scheele discovered hydrofluoric acid and the elements oxygen and nitrogen. There he also investigated pyrolusite, leading to the discoveries of the elements chlorine and manganese and – incidentally – also barium. In Köping Scheele made thorough investigations of tungsten acid and molybdenum oxide, leading to the discoveries of the element tungsten (by the d'Elhuyar brothers in Spain) and of molybdenum (by Hjelm in Stockholm). He also made many discoveries in organic chemistry.

Scheele did not have a long life, dying at the age of 46. Certainly his health had suffered as a result of his discovery of both hydrofluoric acid and chlo-

Figure 27.2 Scheele's pharmacy and residence in Köping.

rine in badly ventilated laboratories. However, he lived long enough to see his achievements valued. Several foreign Academies elected him as a member. Frederick the Great of Prussia invited him to Berlin and the Academy of Sciences there. He was also offered positions in England and in Italy. However, as mentioned, he stayed in Köping to the end of his life.

27.2.4.2 **Scheele's Investigation of Pyrolusite**

Professor Torbern Bergman had requested Scheele to investigate pyrolusite and he did so. In 1774 he published his results in an important paper [27.2]. This was of great importance in the history of element discoveries and for chemistry as a whole.

A very short summary of the results is given in Table 27.1. On the left Scheele's expressions are used and on the right the corresponding facts in modern chemical terminology.

Scheele's investigation confirmed that pyrolusite is not an iron mineral and that it has nothing in common with alum. Instead the mineral contains an unknown metal with the ability to "take up and give off phlogiston" in distinct quantities, that is a metal with different states of oxidation. It explained the perplexing color variations observed.

This important investigation resulted, directly or indirectly, in the discovery of three new elements:

- *manganese,* the main element of pyrolusite, which Gahn in Falun, after a proposal from Scheele, prepared by reduction of pyrolusite (see below);
- *chlorine,* which Scheele discovered in the reaction between pyrolusite and hydrochloric acid;

- *barium*, which Scheele himself did not isolate although he paved the way for the discovery. He found and characterized heavy spar, barite, and its oxide, a "new earth" in his experimental work with a pyrolusite contaminated with barium.

Table 27.1 Scheele's observations on pyrolusite in 1774

Expressions according to Scheele[a]	Modern chemical terms
Pyrolusite is a mineral with a large tendency to take up phlogiston[b]	Pyrolusite is an oxidizing agent
On reaction with some acids, e. g. hydrochloric acid, pyrolusite is saturated with phlogiston and its solution becomes colorless	On reaction with acids that can be oxidized, e.g. hydrochloric acid, pyrolusite is reduced and its solution becomes colorless
Regarding acids containing sulfur, pyrolusite is easily dissolved by those rich in phlogiston, thus also by volatile sulfuric acid[c]. On distillation of the solution obtained, no volatile sulfuric acid is emitted	The oxidizing agent pyrolusite reacts easily with and dissolves in the reducing agent sulphurous acid. During the reaction SO_2 and the sulfite ions are oxidized to sulfate ions. On distillation of the solution obtained, no volatile sulfur dioxide is emitted
Pyrolusite cannot give a colorless solution with any acid without taking up phlogiston. If there is a lack of phlogiston the solution becomes blue or red	Pyrolusite cannot give a colorless solution with any acid without being reduced. If the acid is not a reducing agent or if a reducing agent is not added the solution becomes blue or red
If charcoal is added to a melt of pyrolusite the melt takes up phlogiston from the charcoal and becomes colorless. Added saltpeter takes up phlogiston from the colorless metal and the melt becomes colored again	If charcoal is added to a melt of pyrolusite the tetravalent manganese is reduced to divalent, and the melt becomes colorless. Added saltpeter oxidizes manganese and the melt becomes colored again

[a] Scheele used the Swedish designation *brunsten* (German *Braunstein*). In this table the international name pyrolusite is used.

[b] Scheele was an adherent of the phlogiston theory all his life. Yet it has been said that he was an "antiphlogistic practitioner" as he showed that iron, copper, and mercury form more than one oxide each. He was in fact the first to show that one metal can have different oxidation states.

[c] Volatile sulfuric acid is sulfurous acid H_2SO_3, containing SO_2.

Yet after the many investigations of pyrolusite and Scheele's brilliant research, manganese metal remained officially undiscovered!

27.2.5
Finally an Accepted Metal in Pyrolusite

Torbern Bergman, who was informed of Scheele's results, thought that they strongly indicated that an unknown element with *metallic spirit* was hidden in the mineral pyrolusite.

In his pharmacy in Uppsala, Scheele's working place at that time, there was no furnace available effective enough to reduce a metal from pyrolusite. But Scheele's good friend J. G. Gahn in Falun had such a furnace. Scheele prepared a sample of pure pyrolusite and asked Gahn to use his "hell-furnace". Gahn succeeded and obtained a *regulus* of a metal, which Scheele investigated. It was free from iron and when it was dissolved in sulfuric acid an inflammable gas was evolved. The element manganese had been discovered and the year was 1774.

This reduction of pyrolusite gave Gahn a place in the history of element discovery. Gahn but not Rinman or Keim. Why? Of course Gahn's careful work was the basis of the success. But a contributory factor was his co-operation with Carl Wilhelm Scheele and Torbern Bergman. Their great scientific authority supported the acceptance of Gahn as the discoverer by the whole chemical world.

Ten years after Gahn's reduction, Peter Jacob Hjelm (the discoverer of molybdenum) gave an exhaustive description of the method [27.3].

> Ten years have already elapsed since Joh. Gottlieb Gahn, member of the Royal Board of Mines, first of all brought forth an individual Metal out of Braunstein. The second name of the mineral, Magnesia Nigra, was the reason to call the new metal Magnesium. Assessor Gahn immediately informed his friends orally of the method, which gave a Regulus. They found his information correct and spread news to their friends within the country and abroad. In all places the method was verified. But as no description has been published it has happened that some people, unaware of the details and the important tricks of the operation, have failed and not succeed with the reduction. The result has been that Gahn's original information has been questioned. The main reason for the failures is, however, that people have not been capable of making the correct use of the available scattered notes about the reduction method.
>
> In this connection I made some time ago a reduction of Magnesia Nigra in a conventional testing forge and I had all success that could be expected. In the light of those circumstances described above I thought I ought to give the following description:
>
> It is necessary to procure a pure Braunstein, first of all free from iron. ... After it has been finely ground an amount of 1/2 lod (6.7 g) is mixed with water or better a combustible liquid such as oil or molten tallow in so small amount that the mixture is neither too thin nor too dry. This mixture is placed in the crucible and a teaspoon of fine charcoal or coal from blood is stirred into it. ... In less then one hour at high temperature I got a metallic Regulus as a round grain, well and evenly molten, weighing 1/4 lod. This Regulus was not drawn by the magnet.

This description was also published in German in Crells Ann. 1787.

27.2.6
A Name for the New Metal

It was not easy to agree on a name for the discovered metal. When Bergman had been convinced of the existence of a metal in the *Braunstein* and of the possibility of isolating it, he gave the element the name *magnesium*, no doubt because the mineral name was *magnesia nigra* (*Braunstein*). To avoid the risk of confusion with *magnesia alba* some people started to use an old designation from Albertus Magnus, *mangane-*

sium, as an alternative to Bergman's metal name magnesium. It was, however, too long. In Germany the masculine word *Braunstein* was used for the mineral and the same word, but the neuter, became the designation for the metal. *Johann Friedrich John* (1782–1847), professor of chemistry in Berlin, proposed in 1807 the element name *mangan*. At this time Berzelius was the authority. He compared the metal names calcium and magnesium (Davy isolated Ca and Mg by electrolysis of melts in 1808) and suggested that that it would be logical to use the name manganium for the *Braunstein* metal but accepted, for practical reasons, the name mangan in Swedish and Mangan in German. It became manganese in English.

27.2.7
Manganese in Iron Ores

P. J. Hjelm continued to take a great interest in manganese. In 1778 he debated a thesis with Torbern Bergman as his opponent. He showed that manganese always occurs with iron in iron ores, in both magnetite and hematite. In the blast furnace process manganese is reduced in parallel with iron and is always present as a component in steel. Even unalloyed steels, to which no manganese is added, have a manganese content of some tenths of a percent.

27.3
Manganese Deposits in Our Time

27.3.1
Manganese Minerals

Hundreds of manganese minerals are known. Pyrolusite MnO_2 is essential. Two others, manganite MnO(OH) and hausmannite Mn_3O_4 are likewise important, while rhodochrosite $MnCO_3$ and braunite $3Mn_2O_3 \cdot MnSiO_3$ are of less importance, see Table 27.2.

Table 27.2 Manganese minerals

Mineral	Formula	Crystal system	Color	Streak color (rubbing on a porcelain surface)
Pyrolusite Figure M41	MnO_2	Tetragonal	Dark steel-gray	Brownish-black
Manganite	MnO(OH)	Orthorombic	Black	Brownish-black
Hausmannite	Mn_3O_4	Tetragonal	Brownish-black	Reddish-brown to brown
Rhodochrosite	$MnCO_3$	Rhombohedral	Rose-red or pink to gray	White
Braunite	$3Mn_2O_3 \cdot MnSiO_3$	Tetragonal	Black, gray	Black

27.3.2
Manganese Ores

Iron ores with high manganese content, 5 to 35%, are designated manganiferous ores. They were important in earlier times. Real manganese ores nowadays are ores with a manganese content of at least 35%. They are usually sedimentary and weathered and contain oxide-type manganese minerals.

World resources are very large but distributed irregularly. The reserves (known and workable ore bodies) are estimated to 670 Mtonnes (metal content). Of this amount South Africa provides 55% and Ukraine 20%. If instead the reserve base is considered (known ore bodies that may be worked at some future time) the total amount is enormous 5000 Mtonnes, of which 80% is in South Africa. Two very big deposits are Hotazel in the Kalahari desert in South Africa near the border with Botswana and Groote Eylandt at Carpentaria Bay in Australia.

27.3.3
Mine Production of Manganese

Manganese world mine production for the year 2000 is reported in Table 27.3 [27.4].

Table 27.3 World mine production of manganese in 2000

Country	Production (metal content) Thousand tonnes	% Mn in ore
South Africa	1578	30–48
Ukraine	930	30–35
Brazil	920	30–50
Gabon	804	45–53
China	800	20–30
Australia	787	37–53
India	590	10–54
Ghana	287	30–50
Kazakhstan	280	20–30
Mexico	156	27–50
Other countries	147	–
Total	7279	–

27.3.4
Manganese Nodules in the Ocean

On the floor of the ocean, at a depth of approximately 4000 m, so-called manganese nodules may be found (Figure M42). They are manganese and other metal oxides and clay. Nodules of economic interest contain 25–30% Mn, 1.5% Ni, 1.2% Cu, 0.3% Co and 0.05% Mo. The diameter of the nodules is on average 50 mm but the size varies (see Figure M42). The quantity of nodules is huge. One estimate is that it corresponds to 700 billion tonnes of manganese. Important localities with 300 million tonnes manganese are found in the Pacific Ocean between the West Coast of the USA and the Hawaiian Islands. However, recovery will be very difficult and expensive and the nodules are looked upon as resources of manganese, nickel and copper for the future.

27.4
Manufacture of Some Manganese Products

27.4.1
Ferromanganese

A very large part, 85–90%, of the total manganese consumption goes to steel manufacture The manganese is added to the steel furnaces as ferromanganese, an alloy with about 80% Mn and 0.5–8% C. Ferromanganese with high carbon content is manufactured by reduction with coke in blast furnaces or, more usually nowadays, in electrical low shaft furnaces. Manufacture of ferromanganese with low carbon content is carried out by silicothermic reduction in electrical furnaces.

An alternative alloy is silicomanganese with, for example, 70% Mn, 15% Si and 2% C. Increased silicon content lowers the carbon content. Special grades for addition in stainless-steel production contain up to 30% Si and a very low C content.

The world production of ferromanganese in the year 2000 was 3780 thousand tonnes of which 75% was made in electric furnaces and 25% in blast furnaces. The worldwide production of silicomanganese is almost as large as the ferromanganese production, so in 2000 a total of 7000 thousand tonnes were produced of the two manganese alloy types. China made 27% of the total, Ukraine 14, South Africa 11, France 7, Norway 7 and Japan 6%. [27.4].

27.4.2
Manganese Metal

Manganese metal is produced at a temperature of 35°C and pH 8 in an electrolytic cell from a catholyte containing manganese sulfate $MnSO_4$ and ammonium sulfate. Manganese deposits are removed as small plates from the cathode sheets of stainless steels by bending and hammering. A metal with 99.9% Mn is obtained. It is used for manufacturing special manganese chemicals and as an alloying metal in aluminum and copper alloys.

27.4.3
Manganese Dioxide[1)]

Manganese dioxide MnO_2 is used for dry-cell batteries and for electronic materials such as ferrites. As mentioned above manganese dioxide is found in nature as the mineral pyrolusite and this natural manganese dioxide (NMD) is used for some standard cells. Very few ores are, however, suitable for preparing NMD for dry cells, but such ores are found in Gabon, Brazil and a few other countries. Improved oxide grades are obtained synthetically. One manufacturing method is chemical, giving CMD, e.g. by thermal decomposition of manganese nitrate. The main technique, however, is the anodic oxidation of manganese ions. The product, electrolytic manganese dioxide (EMD), is a black powder with a density of 4.0–4.3 g/cm^3. In the whole world about 200 thousand tonnes each of NMD and CMD+EMD are produced per year. 30% of the synthetic manganese dioxide (EMD) is accounted for by Japan although the country must rely on imported manganese ore. Other big producers of EMD are China (25%) and the USA (20%).

27.5
Uses of Manganese and Manganese Products

27.5.1
Manganese in Steel

All iron ore contains manganese. As raw iron (pig iron) and steel are manufactured, manganese goes into the product. Thus even unalloyed steel has a manganese content of some tenths of a percent. In modern steel making, however, manganese is used as an alloying element. Manganese has the ability to bind sulfur as manganese sulfide MnS. Otherwise, if the Mn content is too low, iron sulfide is formed, which melts at red heat and destroys the adhesion between the grains in the steel structure. The steel will crack as it suffers from “hot shortness”. Because of this, many modern structural steels, intended for welding, are given a manganese content of 1.6%. The growing group of HSLA steels (High Strength Low Alloyed) are micro-alloyed with about 0.05% niobium, vanadium or titanium. Weldable HSLA steels have a manganese content of 1.0–1.8%. Stainless steels also contain about 1% Mn. In a special group of stainless steels the nickel content is partly replaced by 4–16% Mn.

“Hadfield steel” is an old steel but still in modern use. It takes its name from its 19th-century British inventor Sir Robert Hadfield. The composition is 13% Mn, 1% Cr and 1.25% C. This steel gets harder when it is used as a wear-resistant material in jaw-crushers, teeth for earth-moving equipment, railway points, etc.

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1) In this and other sections information [27.5] from The International Manganese Institute, Paris, has been used. With permission.

27.5 2
Manganese in Aluminum and Copper Alloys

Aluminum sheets for facing buildings and many other applications get increased strength by alloying with 1% Mn. Manganese is also used as the alloying metal in some copper alloys (special brass, manganese bronze) and is the main component in an alloy for bimetallic strips in temperature-control equipment in cars (72% Mn, 18% Cu, 10% Ni).

27.5.3
Battery Applications

Dry-cell batteries, flashlight batteries, are important applications for manganese. Its dioxide is used as a depolarizer The batteries, Lechlanché cells, are still closely similar to Georges Leclanché's original invention (1866). The electrolyte is a paste of ammonium chloride and zinc chloride, a zinc can is the anode and a carbon rod, surrounded by manganese dioxide, the cathode. During work (discharge) hydrogen is released at the cathode – a gas film is formed on the electrodes and cuts off the current. The role of manganese dioxide is to oxidize the hydrogen to water. Hence the reactivity of the dioxide is very important. NMD can be used in standard cells while EMD or CMD are required for high-performance cells.

An alternative to the Leclanché cell is the *alkaline* MnO_2 *zinc cell* with an increased service life (introduced in the 1950s). The cathode is an MnO_2/C powder mixture on the inside wall of a steel container, the anode is zinc powder and the electrolyte is potassium hydroxide.

27.5.4
Other Uses of Manganese Chemicals

Manganese chemicals are used in many applications, a few of which are mentioned below.

- Potassium permanganate is produced by anodic oxidation of manganate according to the equation $MnO_4^{2-} \rightarrow MnO_4^- + e^-$. It is a powerful oxidizing agent with bactericidal properties that makes it suitable for *treating wastewater and purifying drinking water.*
- Manganese-ethylene bisdithiocarbamate, "Maneb", is used as an agricultural *fungicide* for controlling crop and cereal diseases.
- Methylcyclopentadienyl manganese tricarbonyl (MMT) is added as an *anti-knock agent* to gasoline. This use, replacing lead, is important for the environment.
- Manganese sulfate is used in *fertilizers and in animal feed.*
- Manganese phosphate is used as a coating on steel acting as a *lubricant carrier* and improving wear resistance.
- Ferrite is a ceramic material with the general formula $MO \cdot Fe_2O_3$ where M may be manganese, iron, cobalt, nickel or zinc. Ferrite is magnetic with poor electrical con-

ductivity. This combination makes the material suitable for magnet cores for high frequencies within circuit boards in television and computer technology. Large amounts of manganese oxides, carbonates and even the metal are used for these applications.

27.6
Manganese in Life

About the presence of manganese in the human body and in plants and soil it can be said that too much or too little spoils everything; just enough but not too much is a rule for manganese – as for most things in this world.

27.6.1
A Toxic Element ...

Professional exposure via inhalation can result in disease in the pulmonary system or the central nervous system. It is mainly the industrial use of manganese dioxide that is dangerous. Therefore it is important to have effective exhaust ventilation and to reduce exposure times. Threshold limit values for airborne manganese in dust and fumes have been introduced in many countries. One example is a maximum of 2.5 mg manganese/m^3 in total dust and a maximum of 1 mg manganese/m^3 in the very fine fraction of dust (particles <0.001 mm).

27.6.2
... but Essential for Life

Manganese is an essential trace element in life. The element has been adopted by nature because of its tendency to appear in different oxidation states. Its best-known role is in photosynthesis. The enzyme that oxidizes water to O_2 contains a cluster of four manganese atoms and six oxygen atoms (corresponding to Mn_2O_3). In the process it is rearranged in a particular way that prepares for the later formation of oxygen. When O_2 has left, a cluster of 4 Mn atoms with 4 O atoms (corresponding to MnO) remains, as shown to the right in Figure 27.3.

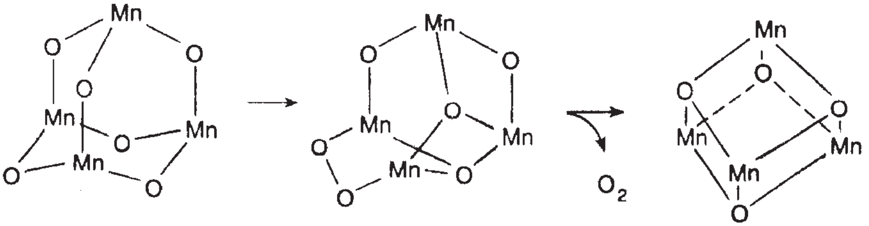

Figure 27. 3 Manganese in photosynthesis [27.6]. A cluster of four manganese atoms is thought to rearrange and oxygen is evolved.

The manganese content of soils can vary widely. A deficiency in most crops is indicated by an overall chlorosis (chlorophyll deficiency), e.g. gray spots on the leaves of oats. In such cases manganese sulfate provides an efficient remedy.

Manganese is essential to ensure the health of humans and animals, and the human body contains about 14 mg manganese. Manganese deficiency leads to different diseases, including impaired growth and depressed reproductive functions. A dietary uptake of 3 mg/day seems to be necessary. Nuts, cereals, dried fruits, meat, fish and seafood are important sources. A curiosity is that tea is very rich in manganese, ten times more than cereals.

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28
Technetium

28.1 Tc
Facts about Technetium

28.1.1 Tc
The Element

Symbol:	Tc
Atomic number:	43
Atomic weight:	98
Ground state electron configuration:	[Kr]$4d^5 5s^2$
Crystal structure:	Hexagonal hcp with $a = 2.74$ Å, $c = 4.39$ Å

28.1.2 Tc
Discovery and Occurrence

Discovery: The element was first produced by irradiation of molybdenum in an atomic reactor. The new metal was identified in 1937 by E. G. Segrè and C. Perrier in Palermo. The metal was given its name technetium, as it was the first element manufactured in a technical way.

Most important mineral: No Tc-minerals of importance are known. In 1988, however, minute Tc quantities were detected in a deep molybdenum mine in Colorado.

Ranking in order of abundance in earth crust:	89–92
Mean content in earth crust:	–
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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28.1.3 Tc
Chemical Characterization

Technetium is a radioactive, silvery gray metal that tarnishes slowly in moist air. The chemistry of technetium is related to that of rhenium. In medical practice different Tc compounds are used. One is sodium pertechnetate $Na^{99m}TcO_4$. The radioactive isotope is absorbed in tumors that can later be located by radioactive detection.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Tc^{IV} as in TcO_2 and $TcCl_4$	$Tc(g) \rightarrow Tc^{+}(g) + e^{-}$	702	$Tc(g) + e^{-} \rightarrow Tc(g)$
Tc^{V} as in $TcOCl_3$	$Tc^{+}(g) \rightarrow Tc^{2+}(g) + e^{-}$	1470	–53
Tc^{VI} as in TcF_6 and $TcOCl_4$	$Tc^{2+}(g) \rightarrow Tc^{3+}(g) + e^{-}$	2850	
Tc^{VII} as in Tc_2O_7 and TcO_3Cl			

Standard reduction potential:	$TcO_4^{-}(aq) + 8H^{+}(aq) + 7e^{-} \rightarrow Tc(s) + 4H_2O(l)$	$E^0 = +0.472$ V
	$TcO_2(s) + 4H^{+}(aq) + 4e^{-} \rightarrow Tc(s) + 2H_2O(l)$	$E^0 = +0.272$ V
Electronegativity (Pauling):	1.9	
Radii of atoms and ions:	Atomic:	135 pm
(WebElements™)	Covalent:	156 pm
	Tc^{4+} (6-coordinate, octahedral):	78.5 pm
	Tc^{5+} (6-coordinate, octahedral):	74 pm
	Tc^{7+} (6-coordinate, octahedral):	70 pm
	Tc^{7+} (4-coordinate, tetrahedral):	51pm

28.1.4 Tc
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
(11 500) kg m^{-3} (11.5) g cm^{-3}	(8.6) cm^3	2430 K 2157 °C	4538 K 4265 °C	–

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
–	51	50	50	–

Coefficient of linear expansion K^{-1} 100 K	293 K	500 K	800 K
–	–	–	–

Resistivity nΩm 78 K	298 K	393 K	573 K	973 K	1473 K
–	200	226	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+31 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	—	–

28.1.5 Tc
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	23 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	550 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	677 kJmol^{-1}
Entropy S^0 at 298 K	–
Molar heat capacity Cp at 298 K	–

28.1.6 Tc
Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 88–113

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{98}Tc	$4.2 \cdot 10^6$ y	–	(+6)	—	β^-	^{98}Tc→^{98}Ru	1.796 MeV
^{97}Tc	$2.6 \cdot 10^6$ y	–	+9/2	—	EC or β^+	^{97}Tc→^{97}Mo	0.320 MeV
^{99}Tc	$2.1 \cdot 10^5$ y	–	+9/2	5.685	β^-	^{99}Tc→^{99}Ru	0.294 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{99}Tc
Reference compound	$KTcO_4/D_2O$
Frequency MHz (^{1}H = 100 MHz)	22.508
Receptivity D^P relative to ^{1}H = 1.00	–
Receptivity D^C relative to ^{13}C = 1.00	–
Magnetogyric ratio, radT^{-1}s^{-1}	$6.046 \cdot 10^7$
Nuclear quadropole moment, barn	–0.13

Characteristic X-radiation

Z	Element	Kα_2 keV
42	Mo	17.374
43	Tc	18.251
44	Ru	19.150

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	167
17.37 keV (MoKα_2)	20.6

Neutron absorption **Thermal neutron capture cross section** –

28.2
Discovery

28.2.1
Element 43 Is Wanted

When the element hafnium was discovered in 1923 only five empty places remained in the periodic table, as shown in Figure 28.1. Two of the missing elements, 43 and 75, belonged to the manganese group. The former had also been called "eka-manganese" and the latter "dwi-manganese" in Mendelejev's system. They ought to be found in localities typical for manganese and they could be expected to resemble manganese in chemical reactions.

X-ray spectroscopic investigations[1] had begun to be used regularly at this time and they showed clearly that element 43 was missing between 42 molybdenum and 44 ruthenium. It was astonishing that it had not already been found, as manganese and its compounds had been so thoroughly investigated.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	**43**	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La*	Hf	Ta	W	**75**	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	**85**	Rn
7	**87**	Ra	Ac*															

Figure 28.1 Unfilled places for elements 43, 75, 85 and 87 in the periodic table in the year 1923. Among the lanthanides 61 was also unknown. This is not shown in the figure.

28.2.2
An Elusive Shadow

Many attempts had been made to find the element, many scientists had thought they had succeeded and many different names were given to the "newcomer" in the periodic table. Some different steps in this laborious story are briefly described in Table 28.1, using information from ref. [28.1].

---

[1] For X-ray investigations and Moseley's law see section 10.7 in Chapter 10, Blowpipe and Spectroscope

Table 28.1 Different names for element 43 after many "discoveries"

Year	Name Proposal	Discovery and discoverers	Comments
1877	Davyum	S. Kern reported (*Chem News*, 1877, 36, p.4, 114, 155–56) that he had found a new element between Mo and Ru. He named the new metal in honor for of the great English chemist Sir Humphry Davy.	The atomic weight of Kern's "new metal" was determined as 154. That excluded it from a position between Mo and Ru.
1896	Lucium	P. Barrière (Chem News, 1896, 74, p.159, 212, 214) was awarded a French patent for his new metal with the atomic weight 104. He described it as "a novel illuminating body".	The specialist of spectral analysis, professor W. Crookes, showed that lucium was contaminated yttrium.
1908	Nipponium	M. Ogava (J. Coll. Sci. Imp. Univ. Tokyo, 1908, 25 No 15–16; CA 1909, p. 403, 1730–31) thought he had isolated a new element from the mineral molydenite. The metal had the atomic weight ca. 100 and properties similar to manganese. Ogava gave the element the name of his home country and the symbol Np.	Spectroscopic investigation with X-rays did not find any lines characteristic for a new element.
1924	Moseleyum	C. H. Bosanquet and T. C. Keeley made many X-ray investigations of manganese minerals and hoped to be able to identify lines from element 43. (Phil.Mag. 1924, 14, p. 145–47). All results were negative. They were however original enough to propose that eka-manganese, one day discovered, should be given the name moseleyum with the symbol Ms.	R. Hamer in Science, 1925, 61, p. 208–209 appealed for support for the proposal. Whenever and by whomever the element 43 was discovered the name moseleyum should be reserved for it as a memorial to the young British physicist, who found the relation between the atomic number of an element and its X-ray frequency.
1925	Masurium	Walter Noddack and Ida Tacke	See text

28.2.3
Arduous and Almost Impossible

In 1922, the German scientists Walter Noddack and Ida Tacke started a very systematic search for elements 43 and 75. During this work they found each other and "Fräulein Chemikerin" Ida Tacke became Mrs. Noddack. The geochemical analysis of the situation and the collection of minerals, planned and accomplished on an international scale, are described in Chapter 29 Rhenium. The chemical investigations were carried out in Berlin, partly at the physical-chemical institution at the university, partly at the Physico-Technical Testing Institute (Physikalisch-Technische Reichsanstalt). The material was concentrated by an advanced chemical treatment, separating a number of different elements such as niobium and tantalum, followed by formation of sulfides containing element 43, which was supposed to be present. Another technique used was sublimation. The different end products were examined by X-ray analysis. Otto Berg at the Siemens & Halske company took part in the work as an expert in spectroscopic investigations.

The group investigated, for example, platinum ores from Siberia and ores from Scandinavia, containing rare earth minerals such as gadolinite $Be_2FeY_2Si_2O_{10}$ and fergusonite $Y(Nb, Ta)O_4$. Tantalum–niobium ores containing the mineral columbite $(Fe,Mn)(Nb,Ta)_2O_6$ were also collected and examined.

In 1925 [28.2] they published a paper about a sample (several milligrams), extracted from 1 kg columbite ore. This concentrate was said to contain 5% of element No 75 and 0.5% of element No 43. In proof of that the X-ray data reported in Table 28.2 were given.

Table 28.2 Results from X-ray spectroscopic investigation of a concentrate prepared from a columbite ore

element 43	**wavelengths in Å** **Kα_1**	**Kα_2**	**Kβ_1**		
measured	0.672	0.675	0.601		
calculated	0.6734	0.6779	0.6000		
element 75	**Lα_1**	**Lα_2**	**Lβ_1**	**Lβ_2**	**Lβ_3**
measured	1.4299	1.4407	1.235	1.2048	1.216[a)]
calculated	1.4306	1.4406	1.2355	1.2041	1.2169

a) Uncertain

Element No 43 they named *masurium* after the region of Masuria in the German province of Eastern Prussia (now Mazury in Poland), from where Walter Noddack originated. Rhenium they named after the river Rhine and the home region of Ida Tacke. The rhenium discovery could be verified, but not the masurium discovery. No evidence of masurium was given besides the three X-ray lines in Table 28.2. Was masurium the final erroneous conclusion in the dramatic story of the discovery of eka-manganese, element 43?

A new, unexpected insight into the chemistry of element 43 was eventually gained, which resulted its final discovery.

28.2.4

To Discover an Element That Does Not Exist!

> Professor E. O. Lawrence gave us a piece of molybdenum plate which had been bombarded for some months by a strong deutron beam in the Berkeley cyclotron. The molybdenum has also been irradiated with secondary neutrons which are always generated by the cyclotron.

So starts a paper in 1937 [28.3] by E.G. Segrè and C. Perrier at the university in Palermo, Italy, a paper that is regarded as the announcement of the real discovery of element 43. Lawrence was the inventor of the cyclotron; Segrè, visiting him in Berkeley, was a specialist in the chemistry of radioactive elements and Perrier was a mineralogist and colleague to Segrè.

Visiting the radioactive molybdenum plate in its protective container Segrè must have had the following reactions in his thoughts:

$$_{42}\mathrm{Mo} + {}_{1}\mathrm{H} \rightarrow {}_{43}(\text{Eka-Mn}) + {}_{o}\mathrm{n} \quad \text{(irradiation with deutrons } {}^{2}_{1}\mathrm{H})$$
$$_{42}\mathrm{Mo} + {}_{o}\mathrm{n} \rightarrow {}_{43}(\text{Eka-Mn}) + {}_{-1}\beta \quad \text{(irradiation with neutrons } {}^{1}_{0}\mathrm{n})$$

Returning to Palermo, Segrè and Perrier started an investigation of the molybdenum plate.

> 200 mg of the Mo plate was dissolved in aqua regia. The solution was very radioactive. Manganese and rhenium compounds were added as carriers. The two scientists could show that the radioactivity followed these elements in chemical reactions. They supposed that they had element 43 in their beakers. They observed that the new element in particular reacted like rhenium, indicating that the new element was more similar to rhenium than to manganese.
>
> During the work with the new element, and in cooperation between Segrè and Seaborg, several isotopes of the new element, all radioactive, were found. Most of them are very short-lived. The most long-lived disintegrates with β-radiation and is transformed to ruthenium. This occurs with a half-life of 4.2 million years. If technetium had been present at the time of the creation of the earth 4.3 billion years ago, the element would have disappeared almost entirely.

Thus all the searches for element 43 would have failed for the simple reason that the element is not present in the earth's crust in measurable concentrations.

In 1924, Bosanquet and Keeley had made abortive attempts with their X-ray spectroscopic methods (Table 28.1) to find technetium in manganese minerals. In the light of the facts revealed later, their failure ought to be looked upon as the result of good experimental technique and scientific honesty. Should now their name proposal *moseleyum* be accepted?

28.2.5
Finally a Name for Element 43

During the discovery time the element name “masurium” had been established and some generations of chemistry students learned the rigmarole

manganese, masurium, rhenium

In 1946, Segrè and Perrier proposed the name *technetium* with the symbol Tc for the element they had discovered. The fact that technetium was the first element that had been prepared in a technical way lay behind the choice of name, from the Greek *technikos* (artificial). At a meeting in Amsterdam in September 1949 the *International Union of Chemistry* changed its name to the *International Union of Pure and Applied Chemistry*. On the same occasion the old name *masurium* Ma was officially replaced by the new name *technetium* Tc for element 43. In 1951 J. C. Hackney published a review of the chemical properties of the now established element technetium [28.4].

28.2.6
Was Masurium Element 43?

In 1988, Pieter van Assche at the Belgian nuclear research institute in Mol examined the work of Noddack, Tacke and Berg in detail [28.5]. At first he emphasized a statement in 1934 of Ida Tacke herself: “It is conceivable that with the irradiation of heavier nuclei with neutrons these nuclei decay into several larger fragments; these fragments can turn out to be isotopes of known elements, but not neighbors of the irradiated elements.” This is really a forecast of nuclear fission, discovered four years later by O. Hahn, Lise Meitner, and F. Strassman. How is it possible that this important statement from Tacke was ignored? One reason, van Assche says, was the publication in 1925 of the discovery of rhenium and masurium [28.2]. Because the masurium discovery could not be confirmed the work was seriously discredited.

Commenting on the element discovery, van Assche notes that the element masurium had been reported only in samples containing considerable quantities of uranium while no masurium had been found in samples free from uranium. He concluded that element 43 could in fact have been present as a result of the radioactive decay of uranium. If so, Noddack, Tacke and Berg really were the discoverers of element 43.

Fathi Habashi at the Department of Mining and Metallurgy in the Université Laval in Quebec, Canada, took up this theme in 1994 [28.6] and claimed that van Assche’s suppositions cannot be supported. Habashi refers to Kenna [28.7] who gave a general review of the discovery of technetium and Kuroda [28.8] who reported looking for technetium in African uranium-rich pitchblende. In one sample they found that this ore contains 2.1–2.5 $\cdot$ 10^{-10} g Tc (isotope 99) per kg. Noddack’s best experiment to detect masurium was made with 1 kg columbite with 2% U. Kuroda calculates that the amount of masurium must have been only about 1.3 $\cdot$ 10^{-11} g which is, by a factor of 50, smaller than the amount that would have been marginally detectable. Element 43 was not present in detectable amounts for Noddack, Tacke and Berg in 1925 and they did not discover it. But much higher technetium concentrations have been present on the earth – at least in Africa. When the Oklo[1] phenomenon, a spontaneous nuclear fission reactor, occurred in Gabon 2000 million years ago it produced technetium in amounts that gave far greater concentrations than those found in uranium bearing ores today. The technetium produced in this way has decayed because the isotope with the longest life ^{99}Tc has a half-life of 4.2 million years.

The year 1925 is unique in the history of the discovery of the elements. Rhenium was discovered and accepted, masurium was reported and rejected. Rhenium was the last element discovered with conventional chemical methods. Technetium was the first man-made element, promethium the second (1944). The transuranic elements, discovered in the second half of the 20th century, are all “artificial”.

28.2.7
Technetium in Weighable Quantities

In 1946 a molybdenum plate with a weight of 4 kg was irradiated with neutrons in a reactor at Oak Ridge in the USA. After chemical treatment 0.1 mg of Tc metal could be isolated and plated by electrolysis onto a copper foil. The first full gram of technetium was isolated in 1952 by treatment of a concentrated solution of waste products from a nuclear reactor.

28.3
Technetium – Properties and Uses

28.3.1
The Isotopes

Radioactive elements have no stable isotopes. Among the natural elements, polonium (atomic number 84) and heavier ones are radioactive. Technetium with its atomic number 43 is the lightest of all elements having no stable isotopes. Another light such element is 61 promethium. Technetium has 26 unstable and 11 metastable (isomer) isotopes, all radioactive [28.9]. Details of the three most long-lived isotopes and two metastable (m) isotopes, important for tracer work, are collected in Table 28.3.

---

[1] For the Oklo reactor see chapter 52.

Table 28.3 Long-lived isotopes and tracer isotopes of technetium. The designation m stands for "metastable". Metastable (or isomeric) refers to an excited state of an isotope that lives a longer time than expected before decaying.

Isotope	Half-life	
^{97}Tc	$2.6 \cdot 10^6$	years
^{98}Tc	$4.2 \cdot 10^6$	years
^{99}Tc	$2.1 \cdot 10^5$	years
^{95m}Tc	61	days
^{99m}Tc	6.0	hours

Besides transmutations induced by neutrons, protons and neutrons giving technetium, several radioactive isotopes have also been identified among the fission products of uranium in nuclear reactors.

28.3.2
From the Nuclear Reactor to the Human Body – The Medical Uses of Technetium

The gap below manganese in the periodic table provided a sufficiently strong scientific motive for the laborious work of finding a new element to fill the empty space. Much chemical and physical knowledge was also acquired. Today the metal technetium is available in quantities that are small but possible to handle. But can this element, with its background in the terrible environment of the interior of a nuclear reactor, have any use at all in daily life?

It is astonishing to note that technetium has an important medical application. In 1954 E. J. Baumann and his co-workers [28.10] injected a solution, containing a Tc isotope into rats with tumors. After two hours the Tc concentration in the tumors was 11–30 times higher than in the blood. Since 1964 a diagnostic technique is used in which the isotope ^{99m}Tc with a half-life of six hours is injected in the human body. The radioactive isotope is absorbed in tumors that can later be localized by radioactive detection. The selection of ^{99m}Tc is justified by the fact that the half-life is low and that the isotope is not a β-emitter. The isotope can thus perform its medical function with minimal secondary effects for the patient.

In medical practice different Tc compounds are used. One is sodium pertechnetate $Na^{99m}TcO_4$. After the investigation the substance is eliminated from the body via the kidneys (urine).

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29
Rhenium

29.1 Re
Facts about Rhenium

29.1.1 Re
The Element

Symbol:	Re
Atomic number:	75
Atomic weight:	186.21
Ground state electron configuration:	[Xe]$4f^{14}5d^{2}6s^{2}$
Crystal structure:	Hexagonal hcp with $a = 2.76$ Å, $c = 4.46$ Å

29.1.2 Re
Discovery and Occurrence

Discovery: The existence of rhenium was predicted in 1871 by Mendelejev, who named it *dvi-manganese*. Walter Noddack, Ida Tacke and Otto Berg discovered rhenium in Berlin in 1925.

Most important mineral: Re-sulfide is present in some molybdenum ores, 2 mg Re per tonne MoS_2. The element evaporates as volatile oxide when the Mo sulfide is roasted to MoO_3.

Ranking in order of abundance in earth crust:	81
Mean content in earth crust:	$7 \cdot 10^{-4}$ ppm (g/tonne)
Mean content in oceans:	$4 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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29.1.3 Re

Chemical Characterization

Rhenium is a rare, silvery white metal. It tarnishes slowly in moist air but resists corrosion and oxidation fairly well. Rhenium is used as an important component in superalloys for blades in turbine engines and this is the major use today. In particular, alloys with 3–6% Re, produced as single crystals, have very good properties.

Oxidation states:

Re^{II} as in ReI_2
Re^{III} as in Re_2O_3 and Re_3Cl_9
Re^{IV} as in ReO_2 and $ReBr_4$
Re^{V} as in Re_2O_5, $ReOF_3$, and ReF_5
Re^{VI} as in $ReCl_6$ and $ReOBr_4$
Re^{VII} as in Re_2O_7, ReO_3Cl, and ReF_7

Ionization energy (kJ mol^{-1}):

$Re(g) \rightarrow Re^{+}(g) + e^{-}$	760
$Re^{+}(g) \rightarrow Re^{2+}(g) + e^{-}$	1260
$Re^{2+}(g) \rightarrow Re^{3+}(g) + e^{-}$	2510
$Re^{3+}(g) \rightarrow Re^{4+}(g) + e^{-}$	3640

Electron affinity (kJ mol^{-1}):

$Re(g) + e^{-} \rightarrow Re(g)$
–14.5

Standard reduction potential:

$ReO_4^{-}(aq) + 8H^{+}(aq) + 7e^{-} \rightarrow Re(s) + 4H_2O(l)$ $E^0 = -0.368V$
$ReO_2(s) + 4H^{+}(aq) + 4e^{-} \rightarrow Re(s) + 2H_2O(l)$ $E^0 = +0.251$ V

Electronegativity (Pauling): 1.9

Radii of atoms and ions:
(WebElements™)

Atomic:	135 pm
Covalent:	159 pm
Re^{4+} (6-coordinate, octahedral):	77 pm
Re^{5+} (6-coordinate, octahedral):	72 pm
Re^{6+} (6-coordinate, octahedral):	69 pm
Re^{7+} (6-coordinate, octahedral):	67 pm
Re^{7+} (4-coordinate, tetrahedral):	52 pm

29.1.4 Re
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
21 020 kg m^{-3} 21.02 g cm^{-3}	8.86 cm^3	3459 K 3186 °C	5869 K 5596 °C	137 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
52	49	47	44	45

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
–	$6.2 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
26.2	172	249	397	635	844

Mass magnetic susceptibility χ_{mass} at 293 K	$+4.56 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
465 GPa	176 GPa	433 GPa	0.32

29.1.5 Re
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	33.1 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	705 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	770 kJmol^{-1}
Entropy S^0 at 298 K	36.86 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	18.0	25.48	26.9	29.1	34.6	37.3

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Re + O_2 \rightarrow ReO_2$	–380	–345	–255	–	–

29.1.6 Re
Nuclear Properties and X-ray

Isotope range, natural and artificial 160–192

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{185}Re	Stable	37.4	+5/2	3.172	–	–	–
^{187}Re	Active	62.6	+5/2	3.220	$4.4 \cdot 10^{10}$ y	β^-	0.0027 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{185}Re	^{187}Re
Reference compound	$KReO_4/D_2O$	
Frequency MHz (^{1}H = 100 MHz)	22.525	22.752
Receptivity D^P relative to ^{1}H = 1.00	0.0519	0.0895
Receptivity D^C relative to ^{13}C = 1.00	296	512
Magnetogyric ratio, radT^{-1}s^{-1}	$6.106 \cdot 10^7$	$6.168 \cdot 10^7$
Nuclear quadropole moment, barn	2.2	2.1

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
74	W	57.982
75	Re	59.718
76	Os	61.487

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	176
17.37 keV (MoKα_2)	98.4

Neutron absorption	**Thermal neutron capture cross section**	90 barns

29.2
Discovery

29.2.1
Where Should Elements 43 and 75 Be Looked For?

As is described in the technetium chapter Mendelejev's eka-manganese and "dwi-manganese", the elements 43 and 75, were still undiscovered at the beginning of the 1920s. The German scientists Walter Noddack (1893–1960) and Ida Tacke-Noddack (1896–1978) tried to analyze the situation logically. Which elements could No 43 and 75 be expected to follow in minerals and rocks. For the ambitious scientists it was not enough to simply say that the unknown elements ought to be found together with manganese. They contended that manganese extraction had been going on for so long and investigations of manganese compounds had been so carefully done that if No 43 and 75 had been hidden with manganese they should have been discovered long ago. Two types of minerals attracted their interest, two minerals containing a large number of rare elements, namely platinum ores on the one hand and columbite on the other.

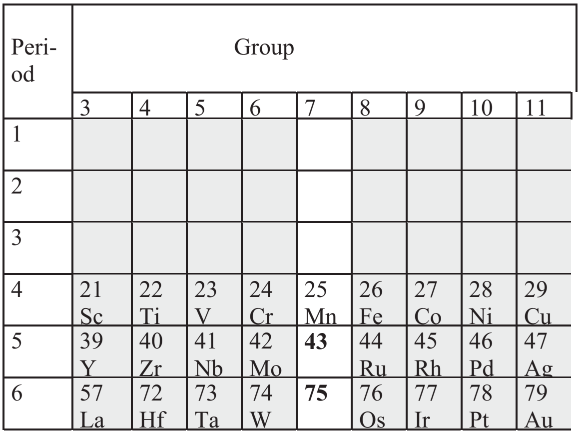
River gravel, for example from the Ural Mountains, was at this time an important initial material for platinum extraction. Before weathering the rock is composed of olivine stones in which veins of chromite are present. In these chromite veins platinum metals are present as grains and spots. In the weathered product, platinum metals (groups 8–10) are found along with Cu, Ag and Au from group 11.

Columbite contains niobium and tantalum as oxides in minerals that form a continuous series between the two end minerals *niobite* (Fe,Mn)(Nb,Ta)$_2$O$_6$ and *tantalite* (Fe,Mn)(Ta,Nb)$_2$O$_6$.

These minerals are accompanied by other very complex minerals containing yttrium, cerium, erbium, uranium, thorium, titanium, zirconium and tungsten, i.e. elements in groups 3, 4, 5 and 6.

A research project, concentrated on columbite minerals to the left and on platinum ores to the right (Figure 29.1), ought to locate the elements 43 and 75 and make a discovery possible.

With the final result available it is easy to be wise and note that when the two scientists made their analysis and found group 6 of interest they specifically mentioned tungsten and tungsten minerals but not molybdenum. And in the end it turned out to be some molybdenum ores that contained element 75 in considerable quantities. But nothing was known of that at the beginning of the 1920s.



Period	Group								
	3	4	5	6	7	8	9	10	11
1									
2									
3									
4	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
5	39 Y	40 Zr	41 Nb	42 Mo	**43**	44 Ru	45 Rh	46 Pd	47 Ag
6	57 La	72 Hf	73 Ta	74 W	**75**	76 Os	77 Ir	78 Pt	79 Au

Figure 29.1 The elements around the undiscovered elements 43 and 75

29.2.2
The River Rhein but not the Region Masurien

Walter Noddack and Ida Tacke (Mr. and Mrs. Noddack) started systematic experimental attempts to find elements 43 and 75 in 1922. They worked partly at the physical-chemical institution at the University of Berlin, partly at the Physico-Technical Testing Institute (Physikalisch-Technische Reichsanstalt). Otto Berg at Siemens & Halske took part in the work as an expert on spectroscopic investigations.

From platinum ore Walter and Ida extracted a quantity of ca. 1 mg of a white oxide. They supposed it was an oxide of the eka-manganese variant 75. Otto Berg found X-ray spectroscopic lines that he thought could be assigned to both elements 75 and 43. In May 1925 a gadolinite was investigated and its content of what they supposed to be element No 75 was highly enriched. During X-ray investigation of this concentrate they observed and measured five lines in the L-series of the spectrum and the three scientists felt justified in asserting that they had discovered element 75. The same element was also isolated from a columbite. Now they announced the discovery not only of element 75 but also of element 43. They called one of the elements (43) masurium with the symbol Ma. The name was chosen from the region of Masurien in the province of East Prussia (in those days German Ostpreussen, today Mazury in Poland). The other (75) was called rhenium Re after the river Rhine (Rhein in German).

Now a battle broke out, a battle that culminated in 1927 [29.1]. One group of critics (Loring and Druce) claimed that they themselves had found element 75 in manganese salts. A second group (Dolejsek and Heyrovsky) also asserted that element 75 was present in manganese salts. For their analysis they used the polarographic method, invented by Jaroslav Heyrovsky (1890–1967), a technique for which he was awarded the Nobel Prize in 1959. The concentration methods used by the two groups were repeated on several different samples of crude manganese sulfate in the University of Wisconsin [29.1]. In no case was an end product obtained in which rhenium could be identified.

Half of the results of Noddack and Tacke were accepted in Germany. In 1929 rhenium was approved as element 75 by the German commission for atomic weights, and the atomic weight 188.71, determined by the discoverers, was inserted in the official table of atomic weights. The masurium discovery was, however, not approved.

29.2.3
A Worldwide Search for Rhenium

The period between the discovery in 1925 and the approval in 1929 was a laborious time. At the end of 1926 the Noddacks had ca. 2 mg rhenium at their disposal. It was a meager result for all their strenuous work. Could they now mobilize energy and funds for continued research? It was of the greatest importance that the *Notgemeinschaft der Deutschen Wissenschaft* [Emergency Action for German Science] then assigned 30 000 RM, a large sum of money, for the Noddacks' rhenium research. It made possible expeditions to Scandinavia and to Russia where they could look out for and buy minerals and rocks believed to contain rhenium. Places visited in Scandinavia are indicated on the map, Figure 29.2. [29.2].

The mineral samples they found are rare and contain very low contents of rhenium.

Some examples from their analysis are given in Table 29.1.

Table 29.1 Rhenium contents in some ores and minerals found by the Noddacks

Locality	Ore/mineral type	Re content, ppm
The Urals	Platinum ore	0.8
Finland	Biotite, (K,Al,Mg) silicate	0
Fichtelgebirge		
Germany	Pyroxene, (Mg,Al) silicate	0.002
Iveland, Norway	Thortveitite, Y silicate	0.6
Arendal, Norway	Columbite, $(Fe,Mn)(Nb,Ta)_2O_5$	0.2
Arendal, Norway	Gadolinite, (Fe,Be,Y) silicate	0.03

From the large samples of gadolinite and columbite they brought back to Berlin a quantity of 120 mg rhenium was prepared in the autumn 1927. The difficulties remained to prepare the new metal in quantities large enough that its mechanical properties could be examined. An agreement was made with Siemens & Halske that the company would pay the expenses of preparing the first full gram of rhenium. At this stage the very important observation was made that some molybdenum ores have

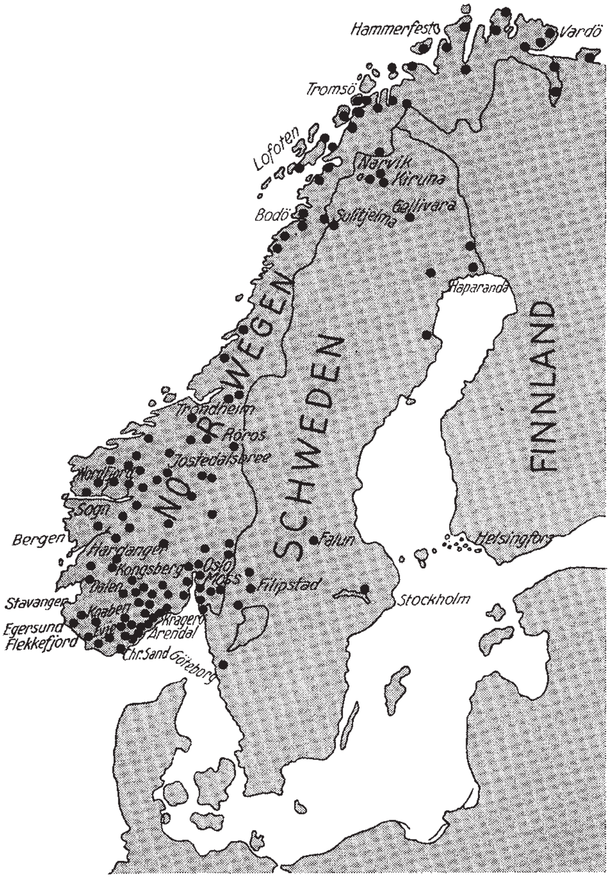


Figure 29.2 Mineral deposits in Scandinavia in which Ida and Walter Noddack looked for rhenium

higher rhenium contents than the other ore types investigated. This is shown in Table 29.2.

Table 29.2 Rhenium contents in molybdenite MoS_2

Locality	Re content, ppm
Telemarken, Norway	21
Japan	10
Bolivia	0.05
Siberia	0.6
Colorado, USA	1.8

With renewed support from *Notgemeinschaft*, Walter and Ida Noddack could take home a considerable quantity of molybdenum ore from Norway. Its rhenium content was 2–4 mg per kg. The ore was treated at the tantalum factory of Siemens & Halske, and the one gram goal agreed upon was reached in the summer 1929. The Noddacks now possessed the large rhenium quantity of 3 g.

29.2.4

High Concentrations of Rhenium are Unexpectedly Found at Home!

Ida and Walter Noddack's labors on rhenium were published and particularly noted by German chemists. The Leopoldshall Chemical Factory near Magdeburg had a department at Mansfeld, in which cobalt, nickel, and molybdenum were extracted from ores intended for copper manufacture. W. Feit, a technician working there, was informed about rhenium's tendency to follow molybdenum and he asked himself: "Is rhenium present at some stage in my own molybdenum processing?" He concentrated a molybdenum residue and handed it over to Walter Noddack and his wife. An X-ray spectrogram showed a rhenium content that the two scientists thought could not be possible. Mr. Feit then developed a method for extracting rhenium from a complex sulfide sludge.

The sludge, containing copper, molybdenum, nickel, iron, vanadium and rhenium, was dried and then allowed to weather in air for several months. This treatment oxidized the sulfides to sulfates. The weathered sludge was leached with water. Concentration by evaporation led to precipitation of the sulfates of calcium, copper and nickel. Ammonium sulfate was added to the mother liquor and nickel ammonium sulfate precipitated. Vanadium and molybdenum were then precipitated as polyphosphates. After filtering the solution contained the rhenium originally present in the complex sludge. Potassium chloride was added and impure potassium perrhenate was precipitated. Very pure $KReO_4$ was obtained by recrystallization.

Using this method the annual production of potassium perrhenate $KReO_4$ at the beginning of the 1930s increased to ca. 120 kg. The metal rhenium had ceased to be the Noddack family's small private element.

Wilhelm Feit was now the center of attention among rhenium scientists. Encouraged by this he continued to investigate the new element [29.3].

29.3

Rhenium Sources in Modern Times

The main rhenium sources are:
- the complex Chuquicamata-type copper molybdenum ores in Chile and Peru
- molybdenite deposits in Arizona, New Mexico and Utah
- complex copper ores in Kazakhstan, Russia, Canada and other countries.

The reserves are estimated at 2400 tonnes, half of them in Chile. The reserve base (known ore bodies that may be worked at some future time) are quite large: in the USA, 4500 tonnes, in Chile, 2500 tonnes and in the whole world 10 000 tonnes.

The total world rhenium production in mines is estimated [29.4] at 28 400 kg for the year 2000, although this figure is uncertain. A value of 12 600 kg is included for the USA, although the production figure is secret. It has been calculated from the official values for MoS_2 production in the USA. The US consumption of rhenium in 2000 (from domestic sources and import) was 32 000 kg, a considerable quantity considering that a production goal of 1 g was reached only 71 years earlier.

29.4
Modern Techniques for Manufacturing Rhenium

Rhenium tends to occur with molybdenum in sulfide ores. Molybdenum and probably also rhenium are present in these as sulfides MoS_2 and ReS_2. A large part of the world's molybdenum comes from copper mines (Figure 29.3). The crushed ore is enriched by flotation so that, at the end, a molybdenum sulfide concentrate with 50% Mo and 0.3% Cu is obtained. The rhenium content of the ore is present in this concentrate. In a roasting process the sulfides are oxidized to oxides, MoO_3 and Re_2O_7.

Rhenium with its highest oxidation number +7 corresponds to Re_2O_7. This oxide has a property that is important for the modern production of rhenium. It is very volatile, with a boiling point of 350°C. Molybdenum oxide MoO_3 has a boiling point of 1151°C but starts to sublime at 750°C. During the roasting process with the maxi-

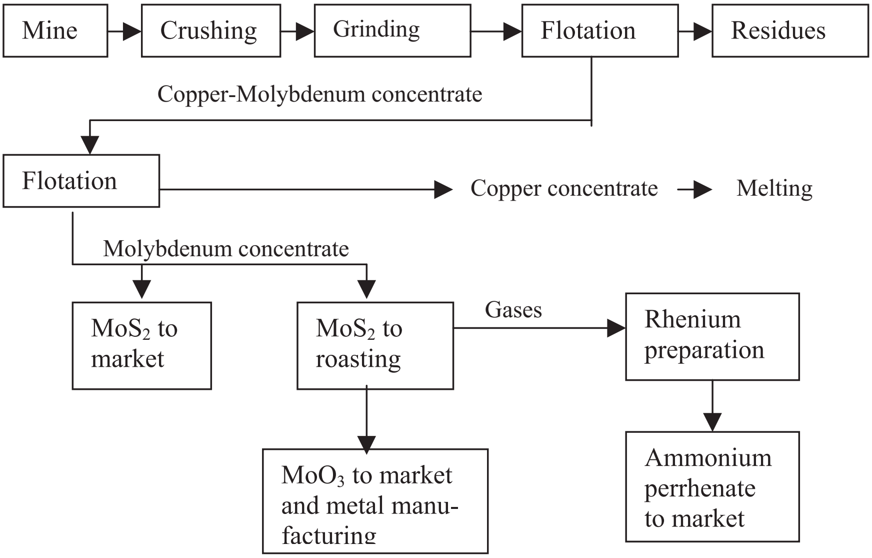


Figure 29.3 Preparation of rhenium products from a complex copper–molybdenum ore

mum temperature ca. 625°C and a temperature at the furnace exit of 425°C (see Figure 25.2 in Chapter 25 Molybdenum) the molybdenum oxide stays in the solid phase while the rhenium oxide will be vaporized. When the roast gases are cooled the solid Re oxide is leached in water and further purified by an ion-exchange technique. Ammonia is added to the pure concentrated eluate and ammonium perrhenate is crystallized. Reduction with hydrogen gives rhenium powder, which, after compacting and sintering in hydrogen gas above 1000°C, forms solid metal that can be manufactured into rhenium foil and wire.

29.5
Uses of Rhenium

Rhenium, alloyed with platinum, was used in petroleum-reforming catalysts in the production of high-octane hydrocarbons, used for lead-free gasoline. This special use is expected to decline as other less-expensive catalysts become available. However, other catalytic functions of rhenium in organic chemistry and medical techniques are still important.

Rhenium has some outstanding properties. It has the highest melting point, 3186°C, of all metals except tungsten, and so is a refractory. Its high modulus of elasticity, 465 GPa (iron 210, molybdenum 330, tungsten 400) results in very good mechanical stability, rigidity and low creep at high temperature. These properties have made rhenium an important component of superalloys (chromium, nickel, cobalt, iron alloys) for blades in the turbine engine industry and this is today the major use. In particular, alloys with 3–6% Re, produced as single crystals, have very good properties for jet engines in aircraft. This fact suggests good future prospects for rhenium as the number of large aircraft can be expected to increase.

Rhenium is an ideal metal for use at very high temperatures, which makes it suitable for rocket motors. Complicated geometries can be fabricated using chemical vapor deposition CVD (see section 18.6.7). Rhenium is deposited on the exterior of a mandrel, which is afterwards removed chemically.

The compatibility of rhenium with platinum metals makes interesting combinations possible. Ultramet in the USA [29.5] developed a CVD method of depositing thick iridium films on rhenium. The combined iridium/rhenium structure permits liquid rocket operation at temperatures exceeding 2200°C.

The thrust chamber is the heart of all liquid propellant rocket engines. It receives the propellant from the injector, burns it in the combustion chamber, accelerates the gaseous combustion products and ejects them from the chamber to provide thrust. The material used in rocket thrust chambers, up to a thrust of 445 N, is iridium/rhenium. The chambers are fabricated by forming an inner wall of iridium for oxidation resistance and a structural outer shell of rhenium. As rhenium has a density of 21 g/cm^3 its volume has to be restricted. The same performance as solid iridium/rhenium can be achieved with an advanced composite. The composite consists of an inner wall of iridium and a structural outer shell of carbon/carbon. An intermediate thin layer of rhenium, 0.25–0.5 mm, binds the Ir and C/C layers together.

Other applications are rhenium–tungsten alloys in X-ray tubes and rotating X-ray anodes. Rhenium–molybdenum alloys are superconductors at a temperature of 10 K.

29.6
The Biological Role of Rhenium

As rhenium is a very rare element it gives no environmental problems in nature and seems to have no biological role in living systems. There are no reports of the metal or its compounds being toxic.

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30
Cobalt

30.1 Co
Facts about Cobalt

30.1.1 Co
The Element

Symbol:	Co
Atomic number:	27
Atomic weight:	58.93
Ground state electron configuration:	$[Ar]3d^74s^2$
Crystal structure:	α-Co cubic fcc with $a = 3.54$ Å, ε-Co hexagonal hcp with $a = 2.51$ Å, $c = 4.07$ Å. Transition $\alpha \rightarrow \varepsilon$ at 417°C

30.1.2 Co
Discovery and Occurrence

Discovery: Cobalt minerals were used in antiquity to give blue coloring to glass and pottery. The Swedish chemist Georg Brandt (1694–1768) investigated the "color cobalts" and found a new element that he named cobalt. He was also the first to isolate cobalt in the metallic state in 1735.

Most important mineral: Skutterudite $(Ni, Co)As_3$
Cobaltite CoAsS (Figure M43)
Linnaeite $(Co, Ni)_3S_4$

Ranking in order of abundance in earth crust:	30
Mean content in earth crust:	25 ppm (g/tonne)
Mean content in oceans:	$2 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	$32 \cdot 10^3$ years
Mean content in an adult human body:	0.02 ppm
Content in a man's body (weight 70 kg):	1.4 mg

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30.1.3 Co

Chemical Characterization

Cobalt is a metal with magnetic properties similar to those of iron. Its salts give glass a beautiful deep-blue color. Cobalt-based alloys have long been used in the manufacturing industry. An addition of 20% cobalt to chromium–nickel-based alloys, used for turbine blades and burner lines in aircraft engines, improves the high-temperature properties. Cobalt powder is an important component in cemented carbides (hard metals). Cobalt is also an essential element for life and important for humans and animals. It is present mainly in the form of vitamin B_{12}. The artificially produced isotope ^{60}Co is used as a source of intense g-radiation. It is used in industry and in radioisotope therapy.

Oxidation states:

Co^{II} as in CoO, CoS, and CoF_2
Co^{III} as in Co_2O_3
and $Co_2(SO_4)_3 \cdot 18H_2O$
Co^{II} and Co^{III} as in Co_3O_4
that is $Co^{II}[Co^{III}]_2O_4$

Ionization energy (kJ mol^{-1}):

$Co(g) \rightarrow Co^{+}(g) + e^{-}$	760
$Co^{+}(g) \rightarrow Co^{2+}(g) + e^{-}$	1648
$Co^{2+}(g) \rightarrow Co^{+}(g) + e^{-}$	3232
$Co^{3+}(g) \rightarrow Co^{4+}(g) + e^{-}$	4950

Electron affinity (kJ mol^{-1}):

$Co(g) + e^{-} \rightarrow Co^{-}(g)$
−63.7

Standard reduction potential:

$Co^{3+}(aq) + e^{-} \rightarrow Co^{2+}(aq)$ $E^0 = +1.92$ V
$Co^{2+}(aq) + 2e^{-} \rightarrow Co(s)$ $E^0 = -0.277$ V

Electronegativity (Pauling): 1.88

Radii of atoms and ions:
(WebElements™)

Atomic:	135 pm
Covalent:	126 pm
Co^{2+} (4-coordinate, tetrahedral):	72 pm
Co^{2+} (6-coordinate, octahedral):	79 pm
Co^{2+} (6-coordinate, octahedral, high spin):	88.5 pm
Co^{2+} (8-coordinate):	104 pm
Co^{3+} (6-coordinate, octahedral):	68.5 pm
Co^{3+} (6-coordinate, octahedral, high spin):	75 pm

30.1.4 Co

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
8900 kg m^{-3} 8.90 g cm^{-3}	6.62 cm^3	1768 K 1495 °C	3200 K 2927 °C	421 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
130	105	89	69	53

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$6.8 \cdot 10^{-6}$	$13 \cdot 10^{-6}$	$15 \cdot 10^{-6}$	$15.2 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
9	56	95	197	480	885

Mass magnetic susceptibility χ_{mass} at 293 K	–
Magnetic characterization	Ferromagnetic

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
205 GPa	77 GPa	202 GPa	0.33

30.1.5 Co

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	16.2 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	375 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	425 $kJmol^{-1}$
Entropy S^0 at 298 K	30.04 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	13.9	24.8	29.7	37.0	40.5	40.5

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$2Co + O_2 \rightarrow 2CoO$	–428	–397	–330	–256	–182
$3/2Co + O_2 \rightarrow 1/2Co_3O_4$	–390	–355	–265	–	–

30.1.6 Co

Nuclear Properties and X-ray

Isotope range, natural and artificial	50–72

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**
^{59}Co	Stable	100	–7/2	4.627

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{59}Co
Reference compound	$K_3[Co(CN)_6]/D_2O$
Frequency MHz (^1H = 100 MHz)	23.727
Receptivity D^P relative to ^1H = 1.00	0.278
Receptivity D^C relative to ^{13}C = 1.00	1590
Magnetogyric ratio, $radT^{-1}s^{-1}$	$6.332 \cdot 10^7$
Nuclear quadropole moment, barn	0.42

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
26	Fe	6.391
27	Co	6.915
28	Ni	7.461

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	322
17.37 keV ($MoK\alpha_2$)	41.4

Neutron absorption	Thermal neutron capture cross section	37.5 barns

30.2
Discovery

30.2.1
Blue Glass and Pottery, Known to the Ancients

Blue glazed pottery dated 2600 BC and Persian blue glass beads from 2200 BC have been found, the blue color in both cases coming from cobalt. Chemical analyses show, however, that blue coloring was often achieved with copper. Among all the glass articles found in Tutankhamen's tomb (from 1343 BC) and investigated in 1927, almost all were colored with copper, only one contained cobalt. Cobalt blue has accompanied handicrafts and artistry through the centuries: Greek glass, Chinese pottery during the Tang and Ming dynasties, Venetian glass, blue pigment in painting. The old technique, coloring with cobalt, was very practical and functioned without any knowledge of the active substance in the additive used. Certainly many put the question: *What is the cobalt in cobalt blue?*

30.2.2
Kobolds – Demons in the Lower Regions

At the end of the 14th century a new mineral was discovered in Erzgebirge on the border between Bohemia and Saxony. When it was subjected to metallurgical processes the metallurgists observed fumes that were harmful to health. The mineral contained arsenic. According to an old Germanic tradition the *Kobolds* were evil subterranean gnomes, who enjoyed obstructing and destroying the miners work. No doubt the evil ghosts were present in this new mineral and made it worthless.

30.2.3
The Worthless Can Be Valuable

During the next century it was discovered in Bohemia that the worthless mineral contained the same substance that, from time out of mind, had been used for coloring glass and china blue. Before using this Bohemian mineral it was roasted (heated in air) to remove the arsenic. The sublimed arsenic was sold to the pharmacies. The roasted ore was mixed with sand. This mixture was called *safflor*. A similar product was called *zaffer* (perhaps derived from sapphire). For the growing glass industry in the 16th century, *zaffer* was an important additive. In his book *Pirotechnia* Vannoccio Biringuccio (see Chapter 2 About Matter) in 1540 mentions: “Zaffer cannot be melted but it dissolves in the melted glass and gives it a blue color. If too much is added the glass becomes black”.

Why did the glass become blue? No one knew. The answer came with the discovery of the element cobalt.

30.2.4
Why Did Glass become Blue?

Riddarhyttan, with its extensive ore deposits, is situated in the province of Vestmanland in central Sweden [30.1]. During the 17th century interest had been concentrated on copper but from 1680 both supply and quality were low. At this time the pharmacist Jurgen Brandt lived and worked in Stockholm. He had developed a method of utilizing poor copper ores, so he sold his drugstore and bought Riddarhyttan in 1690. In 1696 a new copper deposit was discovered, which made the new owner and his wife Catharina very optimistic. There was, however, one big problem. The copper ore was mixed with, as they thought, sulfide of arsenic. Later on it was established that the strange mineral was cobaltite CoAsS. In Riddarhyttan another cobalt mineral, free from arsenic, seems to have been present too, namely linnaeite Co_3S_4.

Catharina and Jurgen had a son in 1694. He was christened Georg and became the discoverer of the metal cobalt. At an early age he began to help his father with chemical experiments. As an adult he started to study mathematics at Uppsala University and decided to continue with chemistry, mining and metallurgy. Then he had to go abroad, as no higher education was available in Sweden. He became the holder of a scholarship from the Royal Board of Mining and Metallurgy, so he could start his European studies. First he visited professor Boerhave in Leiden (The Netherlands). This man was well known through the book *Elementa Chemie* and for his teaching. Brandt continued to Reims (France) and in 1726 he became a Doctor of Medicine there. He never practiced as a physician but the doctor’s degree was a valuable sign of his learning.

On his way back to Sweden, Georg Brandt made a thorough visit to the mines in Harz in Germany and he gave the Royal Board a description of the mining there (see Figure 30.1).

> Organization of a royal Board of Mining and Metallurgy [Bergskollegium] had been started in Sweden in 1630 by King Gustavus II Adolphus. In 1683 a laboratory for the science of chemistry, mineralogy and metallurgy was founded and subordinated to the Royal Board. It was given the name “Laboratorium Chymicum”.
>
> Back in Sweden Georg Brandt was employed in 1727 at the Laboratorium Chymicum, still as the holder of a scholarship but in fact as the laboratory manager. Not until 1748 was he formally appointed manager of the laboratory with the duty to “analyze different ores and make chemical experiments of

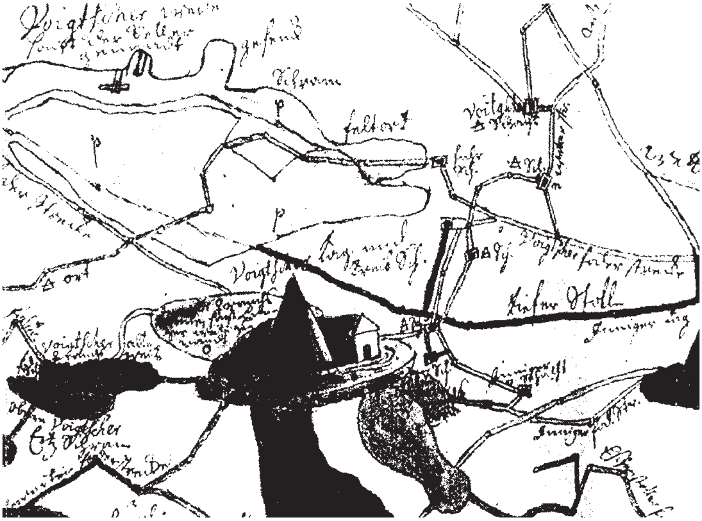


Figure 30. 1 A detail from Brandt's mine maps from Harz, drawn by hand and given to the Royal Board together with a travelling report.

> benefit to the noble metallurgy". Already in 1727 premises for the laboratory were made available in the Royal Mint. Under Brandt's leadership the Laboratorium Chymicum developed into a very important institution in European science. Brandt also clearly saw the urgent need of education in chemistry, mining and metallurgy and his students included Axel Fredrik Cronstedt, Henrik Sheffer, Anton von Swab, Sven Rinman, Daniel Tilas, Bengt Qvist and Gustaf von Engeström, many of whom later became famous scientists.

Georg Brandt had acquired knowledge of many things during his European studies including *safflor* (*zaffer*), known to have the ability to give glass a beautiful blue color. Brandt decided to find out why *zaffer* turned glass blue. He investigated samples in his laboratory, and with all the resources available it was simple for Brandt to isolate an unknown oxide. He reduced it with carbon at a high temperature and obtained a new metal, which he named *Cobalt* after the old German name Kobolds for the gnomes in the mountains. However, it is not quite clear what material Brandt used when he discovered cobalt. It may have been minerals from Riddarhyttan or Loos – or even from Germany.

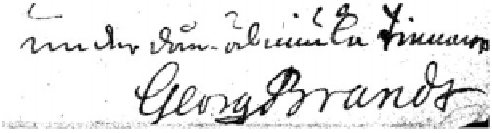
Brandt states in his *Diarium Chymicum* 1741:

> There are six kinds of metals and I have shown in my dissertation on the half-metals which I presented to the Royal Academy of Sciences in 1735 that there are also six kinds of half-metals[1]. The same dissertation shows that, through my experiments, I had the good fortune to ... be the first discoverer of a new half-metal namely cobalt regulus, which had formerly been confused with bismuth.

---

[1] The six "half-metals" were according to Brandt mercury, bismuth, zinc, antimony, arsenic, and cobalt. Half-metals resemble the metals in color and weight but are not malleable.

Brandt's signature under the Diarium 1741 has been preserved and is reproduced in Figure 30.2:



[illegible]
Georg Brandt

Figure 30.2 Georg Brandt's signature.

There has been some confusion about the discovery year for cobalt. As Brandt himself says that he gave this information to the Academy in 1735, this is often considered to be the discovery year.

In 1748, Brandt published the results of further investigations of the new element. This time he used the mineral linnaeite Co_3S_4 from the mine of his childhood in Riddarhyttan as raw material. He succeeded in preparing of a *regulus* of the metal and he reported the element's magnetic properties.

Georg Brandt's death on 29 April 1768 attracted attention from the entire scientific world. One biographer wrote: "He was one of the ablest chemists of his time" [30.2].

30.2.5
A Cobalt Mine World-famous for Nickel

In 1736, two brothers, Henric and Olof Kahlmeter, both working for The Royal Board of Mining and Metallurgy journeyed to Lapland, in the far north of Sweden. On their way back they passed the province of Helsingland. They had heard of a bismuth mine in Loos and they wanted to examine it, especially as they knew from Georg Brandt's investigations that bismuth could be mixed with the new metal cobalt. Was it possible that cobalt was available there? They stayed three weeks for investigations and they brought samples home with them to the Laboratorium Chymicum. And the examination gave a positive result: "The samples give a wonderful blue color."

Henric Kahlmeter returned to Loos and started mining the cobalt ore. Initially the ore was exported as such for making z*affer* in other countries. After a direct order from governmental authorities domestic *color-cobalt* manufacturing started near the mine in 1744.

30.3
Cobalt Deposits

30.3.1
Cobalt Minerals

Cobalt minerals are mainly sulfides, but some are also arsenides. Data for important minerals are collected in Table 30.1.

Table 30.1 Important cobalt minerals and their properties

Mineral	Formula	Color/Luster	Streak	Hardness Mohs	Density g/cm^3
Linnaeite Cobalt sulfide	$(Co, Ni)_3S_4$	Gray to white. Metallic	Black	4.5–5.5	4.8
Skutterudite Cobalt arsenide	$(Ni, Co)As_3$	White to silver. Metallic	Black	6	6.5–6.8
Cobaltite Cobalt iron arsenic sulfide	$(Co,Fe)AsS$ Figure M43	White to silver gray. Metallic	Dark gray	5.5	6.0–6.4

30.3.2
Cobalt Ores

Most cobalt is obtained as a by-product of copper–nickel mining and refining. The nickel content in ores can be 1.5% while the cobalt content is 0.15%.

Magmatic nickel-copper ores containing cobalt are known in the Sudbury region in Canada and in the Kambalda district in Australia. Sedimentary copper–cobalt ores constitute, from the economic point of view, the most important cobalt deposits. The ores in the Copper Belt of the Democratic Republic of Congo (DRC, formerly Zaire) and Zambia (Figure 30.3) belong to this type of deposit.

Nickel–cobalt-containing laterite[2] ores are available in Cuba, New Caledonia, Papua New Guinea and the Philippines.

A large nickel–copper–cobalt sulfide ore deposit is under development at Voisey's Bay in Labrador, Canada. Nickel–cobalt mixed sulfides at Moa Bay, Cuba, are also important. Similar ores are mined and refined in Jinchuan in China.

A cobalt–arsenic ore is known in the "Cobalt Belt" in Idaho, USA, but the mine in Blackbird was closed in 1959. Plans for new mining and cobalt production in Idaho have been reported.

[2] Laterite is a reddish residual soil, developed in humid tropical and subtropical regions. It contains iron, aluminum and other metal hydroxides. The *Laterite* soil group was dropped in a terminology revision in 1949 and classified as *Orthox* within the group of *Latosols* [30.3]. The designation is, however, still in use.

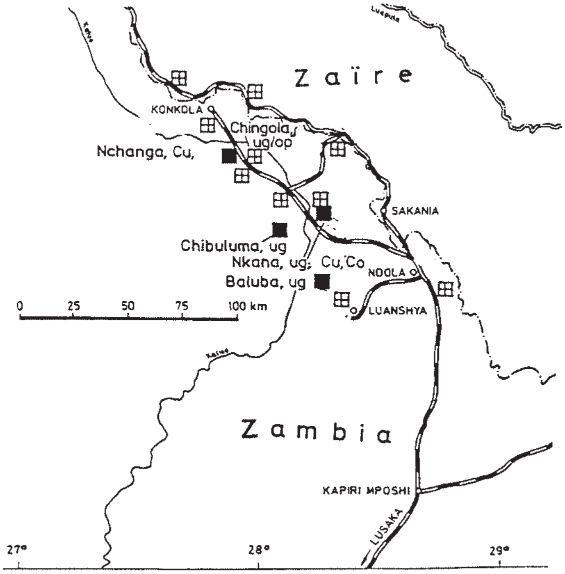


Figure 30.3 Map of the Copper Belt in north-western Zambia. The Copper Belt runs parallel to the boundary between the DRC and Zambia between the towns of Ndola and Konkola. (Reprinted with permission from SGU (Geological Survey of Sweden) PM 1992:1. Theme Cobalt.)

In Russia, nickel–cobalt sulfide and laterite ores are mined; in South Africa, cobalt is obtained as a significant by-product from platinum mines.

The production of cobalt ores and concentrates is increasing from new deposits in Australia, the DRC and Uganda. In addition many projects for cobalt mining are in the development stage in Africa, the Asia/Pacific region and North America.

30.3.3
Cobalt Reserves

Cobalt reserves (known ore bodies that may be worked) in the world are estimated to 3.2 million tonnes (cobalt content) [30.4]. An estimate of the reserve base (known ore bodies that may be worked at some future time) gave 10 million tonnes, of which the DRC accounts for 25%. Most of this large reserve base is in nickel-bearing laterite deposits and in sedimentary copper deposits of DRC and Zambia. In addition millions of tonnes of speculative cobalt resources exist in manganese nodules on the ocean floor.

30.3.4
The Production in Mines

World mine production by country in 2000 is shown in Table 30.2 [30.4].

Table 30.2 World mine production of cobalt in the year 2000

Country	Production (cobalt content)	
	Tonnes	% of total
DRC	7000	21
Australia	5600	17
Canada	5280	16
Zambia	4600	14
Russia	3600	11
Cuba	2350	7
Morocco	1300	4
New Caledonia	1100	3
Brazil	900	2.5
South Africa	585	1.8
Botswana	320	1.0
Kazakhstan	300	0.9
China	200	0.6
Zimbabwe	125	0.4
Total (rounded)	33 000	100

30.4
Manufacture of Cobalt Products from Ores and Concentrates

30.4.1
Production Technique

After concentration of the ores by flotation or by gravity methods the metal can be manufactured using techniques selected with reference to the actual ore type. Only a few examples are schematically described here. For details see ref. [30.5].

Copper-cobalt ores from the DRC are roasted in a fluidized-bed furnace to convert sulfides to soluble oxides. After leaching with sulfuric acid, copper is removed by electrolysis. Cobalt is precipitated from the electrolyte as hydroxide. The hydroxide is redissolved, and the cobalt is obtained as metal in an electrolytic process.

Nickel sulfide concentrates can be treated by *flesh melting* (see Chapter 31 Nickel) to give a *matte* with for instance 10% Ni, 2% Cu, 0.4% Co, 33% Fe, 30% S. In the Sherrit–Gordon process (Canada) the matte is leached with ammonia in autoclaves at high temperature and under a pressure of oxygen. This converts the sulfides to sulfates and cobalt and nickel to soluble ammine complexes. In further autoclave processes cobalt powder is produced. by reduction with high-pressure hydrogen.

In the INCO process the matte is crushed and a nickel alloy is magnetically separated. This fraction also contains the cobalt. The alloy is melted and granulated, and the nickel is volatilized as $Ni(CO)_4$ in the *carbonyl process*. The residue is dissolved and cobalt obtained as cathode plates in an electrolytic process.

Laterite ore concentrates are leached with sulfuric acid in a high-temperature, high-pressure process. Nickel and cobalt from the solution are finally separated by solvent extraction. From the cobalt fraction the metal is precipitated as sulfide. After refining and redissolving, the cobalt is again isolated electrolytically. An alternative is precipitation of oxalate. Then the oxide is formed in a calcination process. A high-temperature reduction with hydrogen gas gives *cobalt powder*.

Arsenic-containing concentrates (from cobaltite ores) are roasted in a fluidized bed at 700°C to remove most of the arsenic as As_2O_3. After leaching with hydrochloric or sulfuric acid the purified leach solution can be used for electro-extraction of cobalt or for precipitation of cobalt as carbonate.

30.4.2
Cobalt Metal Production

Metallic cobalt is, as mentioned above, produced as *cobalt powder* and *cobalt cathode sheets*. Mined ore is as a rule refined in the country of origin. Examples are:

- cobalt–nickel laterite ores in China, mined and refined to cobalt cathodes and powder in Juanxi province
- domestic sulfide and laterite ores in Russia, refined in different places within that big country: Monchegorsk on the Kola Peninsula, Norilsk in Siberia, Orsk and Verkhiny Ufaley in the Ural Mountains
- On the other hand many joint ventures have been built up with mining in one country and metal manufacturing in another. Two examples:
  - Australian concentrate from mines in Western Australia are exported to Finland for treatment at the Harjavalta refinery.
  - Nickel–cobalt laterites and mixed sulfides, mined in Moa Bay, Cuba, are refined in Fort Saskatchewan, Alberta, Canada.

The world refinery capacity was in 2000 estimated at 60 000 tonnes cobalt per year [30.4] of which the DRC has 28%, Finland 16, Russia 13, Canada 8, Zambia 8, Norway 7, Australia 6 and China 3%.

30.5
Uses of Cobalt

About 65% of the total consumption of cobalt is for alloys and powder metallurgical (P/M) products:

- high-temperature alloys
- wear-resistant alloys
- tool steels
- alloys for permanent magnets
- cemented carbides, in which cobalt is a binding metal

Other important end products include catalysts, pigments, cobalt oxides for glass and glaze coloring and cobalt salts as fertilizers.

30.5.1
Alloys and Cemented Carbides

Cobalt-based alloys have for a long time been used in the manufacturing industry. *Stellite alloys* containing cobalt–chromium and cobalt–chromium–tungsten were patented at the beginning of the 20th century. They have now been further developed for use as tools and for hard facing. Chromium–nickel-based alloys are used in aircraft engines for turbine blades and burner lines. An addition of 20% cobalt improves the high-temperature properties.

Cobalt powder is an important component in cemented carbides (hard metals). The product and its use of cobalt are described in Chapter 26 Tungsten.

The three elements iron, nickel and cobalt are special because they are *ferromagnetic*. In these materials the atoms are grouped together into *domains* – small regions in which all the magnetic moments are parallel. In such a metal the domains are normally directed randomly and their magnetic effects cancel. If a specimen is placed in a magnetic field the domains are lined up, and the metal, especially iron, becomes a very strong magnet. A piece of steel – unlike soft iron – can keep the magnetism when the field is removed. This is typical for a hard-magnetic material. What makes a metal ferromagnetic? The answer is that if the inter-atomic distances are of the right magnitude the formation of domains is possible. This does not happen if the atoms are too large or too small. The atoms of Fe, Co, and Ni are of the right size.

Above a certain temperature, the Curie temperature, the ferromagnetic properties are lost. Cobalt is a ferromagnetic metal with a remarkably high Curie temperature as can be seen from Table 30.3.

Some special cobalt-containing alloys are:

- Alnico alloys in permanent magnets with e.g. 10% Al, 18% Ni, 12% Co, 6% Cu and 54% Fe. See further samarium-cobalt magnets in chapter 17 Rare Earth Metals;
- the dental alloy *Vitallium* containing 64% Co, 30% Cr and 5% Mo. It is used for cast denture base and bridgework;

- low expansion alloys, *Invar*, iron–nickel alloys with up to 25% cobalt, used for connections to borosilicate glass equipment;
- thin films of complex cobalt-containing alloys applied by PVD or sputtering onto substrate surfaces and used for *magnetic recording*.

Table 30.3 The Curie temperatures of "normal" ferromagnetic metals[a)]

Metal	Curie temperature °C
Iron	770
Cobalt	1115
Nickel	354

a) Special metals, alloys and intermetallic compounds with ferromagnetic properties are described in Chapter 17 Rare Earth Metals.

30.5.2
Catalysts

The element cobalt is inclined to form complexes and to bind different ligands to these complexes. This makes the metal suitable as a catalyst. An important industrial process using cobalt as a catalyst is the removal of sulfur from oil by hydrodesulfurization. In this case the catalyst is composed of an inert carrier material, alumina, and a mixture of cobalt and molybdenum oxides. The organically bound sulfur is removed as hydrogen sulfide, which is neutralized. The oil can then be delivered with very low sulfur content. This has been of great importance for the environment in our population centers.

Since cobalt can change between the oxidation states +2 and +3 the element is an effective catalyst for oxidation reactions. The element is in fact an additive to nearly all catalysts for oxidation reactions in organic chemistry, for instance in the oxidation of toluene to benzoic acid. Co_3O_4 and $LaCoO_3$ are also used as components in catalysts for the oxidation of CO in automobile exhaust gases.

30.5.3
Coloring and Decolorizing – Glass, Paints, Aluminum Cladding

Addition of cobalt oxide to a glass melt and to enamel provides a blue color. The original use of *safflor* or *zaffer* for decorative reasons, known for many centuries, is thus of importance even today, although in slightly modified form. What is new is that a glass with 0.5% Co is very suitable for welders' goggles and that glass with a few milligrams of Co per kilogram is used for camera lenses.

Cobalt can also be used for decolorizing glass. Iron oxide in the glass gives a yellow color. Addition of a balanced amount of cobalt gives a blue color. The complementary effects – yellow and blue – create an impression of colorless glass.

For anodized aluminum sheets for cladding houses, coloring with cobalt acetate gives a yellow to brown color with good stability.

Many cobalt pigments are used in oil paintings: cobalt blue – a silicate, Thenard's blue – an aluminate, cobalt violet – a phosphate.

30.5.4

A Moisture Detector and an Invisible Ink

Silica gel is often used as a drying agent, as for instance in laboratory desiccators. It is a porous, granular form of silica, synthetically manufactured from sodium silicate. Microscopic pores attract and hold moisture by physical adsorption. Cobalt chloride mixed with the gel gives it the blue color of anhydrous chloride $CoCl_2$. When the gel has adsorbed moisture, pink (almost invisible) cobalt chloride hexahydrate $CoCl_2 \cdot 6H_2O$ is formed. This indicates that the drying agent is saturated with moisture. Warming removes the moisture and restores the blue anhydrous chloride. The same reactions were used in invisible ink for sending secret messages. The hexahydrate was dissolved in water (addition of a little glycol made the solution colorless). Writing on paper was invisible but heating revealed the message.

30.5.5

Collecting Solar Energy

Black cobalt oxide Co_3O_4 is used as a coating on high-temperature solar collectors and for this purpose is superior to black chromium coatings, often used. Co_3O_4 can be applied by plating, by pyrolysis of cobalt salts or simply by use of paints containing cobalt oxide. More sophisticated methods are also used, e.g. vacuum deposition.

30.5.6

Radioactive Cobalt

Cobalt in nature consists of one single isotope, ^{59}Co. By irradiation with neutrons in a nuclear reactor the radioactive isotope ^{60} Co is obtained. It is a strong γ-radiator with a half-life of 5.27 years. This radiation is of the same type as X-rays, and for this reason ^{60}Co is used against cancer in "cobalt therapy", a special form of radiotherapy. The radiation is also used for sterilizing medical equipment.

In radiotherapy the radiation energy destroys tumor cells that are later replaced by fresh tissue. Two different methods of treatment are available: cobalt therapy and treatment with X-rays, generated in linear accelerators. The latter equipment is technically very sophisticated and complicated. It can be used only in large hospitals with advanced expertise, both medical and technical. In contrast, cobalt therapy is simple and suitable for small hospitals and medical services in developing countries. For cobalt therapy the active ^{60}Co radiation source is enclosed in a lead capsule. The powerful radiation is directed against the patient's tumor through an aperture.

The γ-radiation from ^{60}Co is also used for materials testing, e.g. to indicate pores in welds. Testing with the isotope can use simpler and less-expensive equipment than corresponding investigations using a conventional X-ray technique. Isotope testing is especially suitable in those cases when available space is limited, for example when faults must be detected in air engine components directly in the aircraft. Radiation from ^{60}Co is also used for determining the thickness of thin strips of steel that are rolled in a cold rolling mill. The radiation passes through the strip while rolling is going on. If the intensity of radiation passing through the strip is too low then the strip is too thick. With an automatic electronic system the roll-nip can be adjusted.

30.6
Cobalt in Life

30.6.1
Risks with Cobalt

Occupational cobalt poisoning is caused primarily by inhalation of dust. Prolonged exposure to cobalt powder may produce allergic sensitization and chronic bronchitis. Because of that a TLV (Threshold Limit Value) of 0.1 mg/m^3 is prescribed for cobalt powder.

Within the EU a large number of substances have been investigated for their influence on health. Cobalt metal and its oxide and sulfide have not been classed as carcinogenic even though some experiments with animals may indicate that. The International Agency for Research into Cancer (IATC) obtained similar results, but the substances were given an observation status.

30.6.2
Essential for Life

Cobalt is an essential element for life and important for humans and animals. It is present mainly in the form of vitamin B$_{12}$ (see Figure 30.4). Bacteria in the body may

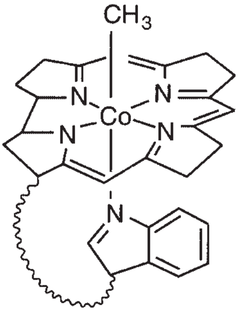


Figure 30. 4 Structure of vitamin B$_{12}$.
In the vitamin the cobalt content is 4.4%.

manufacture this compound. However, in humans this process is ineffective because it takes place only in the colon, from where very little uptake into the blood is possible [30.6]. A daily supply of vitamin B_{12} in the diet (meat, fish, eggs and dairy products), is therefore necessary.

In animals vitamin B_{12} is synthesized more efficiently in the gut, and ruminant animals such as cows and sheep can manufacture this vitamin for their own use.

Lack of vitamin B_{12} leads to the blood disease pernicious anemia, with deterioration of the cells in bone marrow responsible for replacing blood. In the end serious anemia can arise. A lack of vitamin B_{12} may also lead to disturbances in the nervous system.

As mentioned, some animals can produce their own vitamin B_{12}. This does of course presuppose the intake of enough cobalt in the diet. Where there are deficiencies in soils, top dressings containing cobalt sulfate are added.

If, in spite of that, the animals show symptoms of anemia, salt licks, “cobalt licks”, containing 0.1% of cobalt as sulfate are offered to the “patients”.

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31
Nickel

31.1 Ni
Facts about Nickel

31.1.1 Ni
The Element

Symbol:	Ni
Atomic number:	28
Atomic weight:	58.69
Ground state electron configuration:	[Ar]$3d^8 4s^2$
Crystal structure:	Cubic bcc with $a = 3.52$ Å

31.1.2 Ni
Discovery and Occurrence

Discovery: Axel Fredrik Cronstedt discovered the element in 1751 in a cobalt mine at Loos in Helsingland in central Sweden.

Most important mineral: Pentlandite $(Ni,Fe)_9S_8$
Pyrrhotite $Fe_{1-x}S$ a magnetic pyrite, nickeliferous, with up to 5% Ni
Garnierite (nepouite) $(Ni,Mg)_6(OH)_8Si_4O_{10}$
Gersdorffite NiAsS (Figure M44)
Annabergite $Ni_3(AsO_4)_2 \cdot 8H_2O$

Ranking in order of abundance in earth crust:	23
Mean content in earth crust:	84 ppm (g/tonne)
Mean content in oceans:	$5.6 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	0.1 ppm
Content in a man's body (weight 70 kg):	7 mg

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31.1.3 Ni

Chemical Characterization

Nickel is a malleable and ductile metal, ferromagnetic up to 354°C. Iron meteorites contain metallic iron with up to 20% nickel. The main nickel source is the mineral pentlandite. Pure nickel metal is used as protective coatings on steel and copper components. Some of the most important nickel-containing alloys are German silver, Invar and Monel metal. Nickel was used as coinage in nickel–copper alloys for several thousands of years. The US 5-cent coin (whose nickname is "nickel") contains 25% nickel. The important group of austenitic stainless steel (used in all types of corrosive environments and also on our kitchen sinks) contains, as well as 18% chromium, also 8% nickel. Finely divided nickel absorbs 17 times its own volume of hydrogen and is used as a catalyst in many processes, including the hydrogenation of oils. Nickel contact dermatitis, nickel allergy, is well recognized and is more usual among women than men. Persistent eczema may occur after sensitization by nickel-containing components such as nickel-plated earrings. Recent studies have indicated that sensitization can be avoided by using alloys resistant to corrosion by sweat.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ni^{II} as in $Ni(OH)_2$, NiS	$Ni(g) \rightarrow Ni^+(g) + e^-$	737	$Ni(g) + e^- \rightarrow Ni^-(g)$
and $Ni[CN)_4]^{2-}$	$Ni^+(g) \rightarrow Ni^{2+}(g) + e^-$	1753	–112
Ni^{III} as in NiO(OH) an $NaNiO_2$	$Ni^{2+}(g) \rightarrow Ni^{3+}(g) + e^-$	3395	
	$Ni^{3+}(g) \rightarrow Ni^{4+}(g) + e^-$	5300	

Standard reduction potential: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \quad E^0 = -0.257$ V

Electronegativity (Pauling): 1.91

Radii of atoms and ions:	Atomic:	135 pm
(WebElements™)	Covalent:	121 pm
	Van der Waals	163 pm
	Ni^{2+} (4-coordinate, tetrahedral):	69 pm
	Ni^{2+} (4-coordinate, square-planar):	63 pm
	Ni^{2+} (6-coordinate, octahedral):	83 pm
	Ni^{3+} (6-coordinate, octahedral):	70 pm
	Ni^{3+} (6-coordinate, octahedral, high spin):	74 pm

31.1.4 Ni

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
8902 kg m^{-3} 8.90 g cm^{-3}	6.59 cm^3	1728 K 1455 °C	3186 K 2913 °C	444 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
113	94	83	67	71

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$6.6 \cdot 10^{-6}$	$13.4 \cdot 10^{-6}$	$15.3 \cdot 10^{-6}$	$16.8 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
5.5	62	103	225	400	–

Mass magnetic susceptibility χ_{mass} at 293 K	–
Magnetic characterization	Ferromagnetic

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
200 GPa	80 GPa	181 GPa	0.32

31.1.5 Ni
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	17.2 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	377 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	430 $kJmol^{-1}$
Entropy S^0 at 298 K	29.87 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	13.6	26.07	34.9	32.2	38.9	38.9

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$2Ni + O_2 \rightarrow 2NiO$	–423	–387	–301	–215	–115

31.1.6 Ni
Nuclear Properties and X-ray

Isotope range, natural and artificial	52–76

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**
^{58}Ni	Stable	68.08	+0	–
^{60}Ni	Stable	26.22	+0	–
^{61}Ni	Stable	1.14	–3/2	–0.7500
^{62}Ni	Stable	3.63	+0	–
^{64}Ni	Stable	0.93	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{61}Ni
Reference compound	$Ni(CO)_4 + C_6D_6$
Frequency MHz (^1H = 100 MHz)	8.936
Receptivity D^P relative to ^1H = 1.00	$4.09 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.234
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-0.2395 \cdot 10^7$
Nuclear quadropole moment, barn	0.162

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV
27	Co	6.915
28	Ni	7.461
29	Cu	8.028

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	49.1
17.37 keV ($MoK\alpha_2$)	47.4

Neutron absorption	**Thermal neutron capture cross section**	4.51 barns

31.2
Discovery

31.2.1
"Cobalt That Has Lost Its Soul"

When Swedish miners in the 18th century were on the lookout for cobalt stones for blue coloring purposes they sometimes found yellowish-red minerals in locations where cobalt could be expected. But, added to glass, these minerals did not give the typical deep-blue color. It was said that "some cobalt has lost its soul".

31.2.2
A Copper Ore Without Copper!

Miners in Germany now and then found reddish-brown stones, often with green spots. Was it copper? When this stone was dissolved in nitric acid it gave, like copper, a green color. But surprisingly it was not possible to make copper from the ore. Therefore it was given the disparaging name *Kupfernickel*. The ore was a false copper ore. The suffix "nickel" came from a spiteful dwarf, Nicolaus, who transformed copper into something worthless, thus to "nickel".

31.2.3
The Discovery of Nickel

The mine in Loos had attracted great attention in Sweden. It had been known as a bismuth mine but interest had obviously increased since 1736, when cobalt deposits were discovered there. Cronstedt (see below) had finished his studies with Georg Brandt in 1748 and he was certainly well aware of cobalt and of the Loos mine. He himself and The Royal Board were interested to know whether any other valuable minerals could be found. In 1751, Cronstedt visited Loos and did indeed find a new mineral. He investigated it both in Loos and in the Laboratorium Chymicum in Stockholm. In contrast to the cobalt minerals it gave a green color when dissolved in nitric acid. At first he drew the same conclusion as the German miners: "I have found a copper mineral." He placed a piece of iron in the solution and expected red copper to precipitate on the iron surface. He was very astonished when the reaction did not occur. No copper! In that case, what metal was present in the solution?

He made another observation with the new mineral. After weathering, green spots had been formed on the mineral surface. He scraped the green stuff off and roasted it to oxide at red heat. This he mixed with charcoal and heated in a crucible to a high temperature. A metal with no resemblance to copper was formed. The metal was white and had slight magnetic properties.

In the same year, 1751, Cronstedt also investigated *Kupfernickel* from Freiberg in Germany, isolated a metal from it and found exactly the same properties as in the metal from Loos. After further studies of the physical, chemical and magnetic properties of his new metal he published the discovery in the *Transactions of The Royal Swedish Academy of Sciences* in 1751 and 1754 and he proposed the name *nickel* for the new element.

It is interesting to notice that two Swedes, Brandt and Cronstedt, who each discovered a new element and chose their names, did not hesitate to select the negatively loaded names cobalt and nickel. In our modern technological society the names of these metals have clearly positive connotations because of their functions in important alloys.

Opinions differ about which mineral in Loos Cronstedt used for his nickel discovery. Was it

- *NiAs, nickeline red nickel, "Kupfernickel"?* A copper-red mineral that may also contain Sb, Fe, Co and S
- *NiAsS, gersdorffite?* A silver-white to steel-gray mineral that also can contain iron and cobalt
- $(Ni,Co)_3(AsO_4) \cdot 8H_2O$, *annabergite?* An apple-green mineral

Cronstedt himself describes the mineral as *Niccolum ferro et cobalto arsenicatis et sulphuratis*. This may indicate that it was gersdorffite that Cronstedt had found on his visit to Loos in 1751. Erland Grip [31.1] says that "...in gersdorffite from Loos in 1751 the Swedish chemist A. F. Cronstedt discovered the element nickel".

Cronstedt's discovery was soon accepted in many countries. It can, however, be difficult to accept discoveries made by unknown and young persons. At the time of his discovery, Cronstedt had not yet reached the age of 29. So there were dissenting opinions. The French chemists B. G. Sage and A. G. Monnet asserted that Cronstedt's nickel was nothing but a mixture of cobalt, copper, iron and arsenic. As a matter of fact, the first nickel did contain iron, cobalt and arsenic as contamination. Professor Torbern Bergman in Uppsala carried out extensive separation work and produced nickel in a pure form from Cronstedt's contaminated metal. He published his results in 1775, strongly confirming that nickel really was a new element and giving Cronstedt priority in its discovery. This was strong confirmation. In 1796, William Nicholson published the book *First Principles of Chemistry*. About nickel he writes there:

> This metallic substance has not been applied to any use; and the chief attention of those chemists who have examined it has been directed to obtain it in a state of purity; which however has not been accomplished. ... Nickel has

> been thought to be a modification of iron. ... So long as no one is able to produce this metal from pure iron or copper, and to explain in an intelligible way the process by which it can be generated, we must continue to regard it as a peculiar substance, possessing distinct properties. The general opinions of chemists concur in admitting the force of this reasoning.

In the 19th century the new metal was, however, accepted without reservations. It became used in many applications, especially once electricity made the electroplating of nickel on steel and copper possible. The greatest increase in production came at the beginning of the 20th century, when stainless steels and "superalloys" with high nickel content could be produced in electric furnaces.

220 years after the discovery of nickel a memorial was set up in Loos. The Royal Swedish Academy of Sciences and International Nickel INCO in Canada supported the creation of this memorial. At the unveiling in 1971 P. J. R. Butler, chairman of INCO's board said:

> Axel Fredrik Cronstedt through his discovery not only founded an industry but also a modern technology. Without nickel there would be no jet aircraft, no chemical industry as we understand it today, no possibilities of space flight and no moon landings.

A painting of the sculpture is shown in Figure 31.1

Axel Fredrik Cronstedt – a remarkable man! What was his background and how did he accomplish his success?

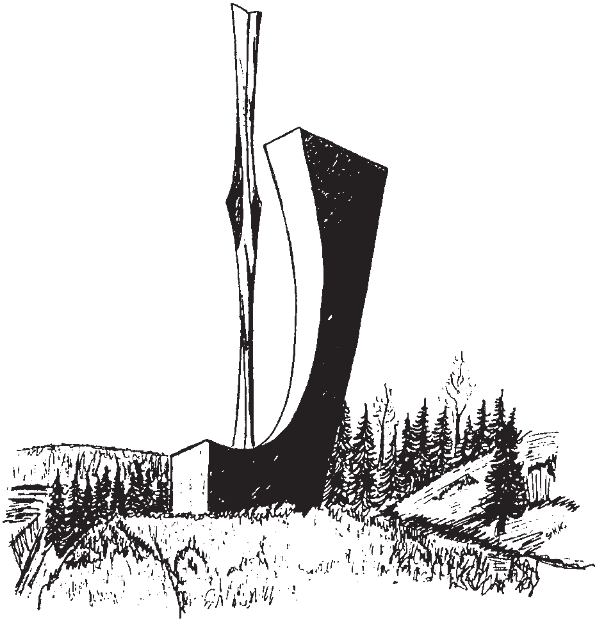

Figure 31. 1 The nickel memorial in Loos. "Form for nickel". Painting by Sven Hugo Karlsson of Olof Hellström's sculpture.

31.3
A. F. Cronstedt – An Individual Chapter in the History of Chemistry and Mineralogy

31.3.1
A Short, Active Life

Axel Fredrik Cronstedt (Figure 31.2) was born on 23 December 1722 in the Södermanland province, south of Stockholm in Sweden. In contrast to Georg Brandt he did not belong to a family of miners. His father was lieutenant-general Gabriel Cronstedt and a military education and career was also planned for the young Axel Fredrik. Instead he devoted his energetic talents to chemistry, mineralogy and mining. He finished his career as inspector of mines and died in 1765, only 43 years old. Cronstedt made very important achievements within three areas:

- the description of mineralogy in a new, systematic way
- the discovery of the element nickel
- the development of chemical analysis with the blowpipe.

The first two points are outlined in this chapter. Blowpipe analysis was described in Chapter 10 Blowpipe and Spectroscope.

Figure 31.2 A medallion of A. F. Cronstedt.

31.3.2
Preparation for Big Tasks

Axel Fredrik soon demonstrated his interest for and ability in mathematics and science. At the end of the 1730s in Uppsala he began to study chemistry and mineralogy with J. G. Wallerius, Sweden's first professor of chemistry. There he became acquainted with Sven Rinman, who was some years older. Rinman was already employed by the Royal Board of Mining and Metallurgy (Bergskollegium) and he aroused Cronstedt's interest in a career in mining. This contact with the man who later on was called "the father of Swedish mining and metallurgy" was very important to the young Axel Frederik. Cronstedt followed Rinman and also obtained a post with the Board and at the Laboratorium Chymicum. In 1744–45 he visited the silver mine in Sala and learned about mining and the metallurgy of lead and silver. From 1746 to 1748 he studied assaying and chemistry with Georg Brandt.

31.3.3
A New Mineralogical System

Before Cronstedt, minerals had been characterized only by more or less unimportant "outer" properties[1].

In the new system minerals were classified according to their composition, determined by chemical analysis. He summarized his new views in a book 1758, which in 1770 was translated into English with the title *Attempt at Mineralogy or the Arrangement of the Mineral Sphere*.

The translator was *Gustaf von Engeström* (1738–1813), Brandt's successor as manager of the Laboratorim Chymicum.

It seems strange that in the middle of the 18th century it was possible to build a system based on chemical analysis. For a chemist in the 21st century, used to spectral analysis, X-ray fluorescence analysis and atomic absorption spectrophotometry, it is difficult to understand how, at that time, it was possible to say much about the composition of a specific mineral, but in Sweden it was possible. The method was *blowpipe analysis*, described in Chapter 10 Blowpipe and Spectroscope.

In 1820 Berzelius wrote "Cronstedt, the founder of the chemical system of mineralogy, a man who by his acuteness in that science rose so far above his age that he was never correctly understood by it, used the blowpipe to distinguish between minerals".

The attitude to mineralogy introduced by Cronstedt, that the chemical composition should be determined, became firmly established from then on.

31.4
Were the Chinese First to Discover Nickel?

An alloy called *packfong*, containing nickel, was known long before the element nickel was discovered in Sweden. The name *packfong* means "white copper" and is used to distinguish the alloy from *tongfong*, red copper. The white metal was used for jewelry and knick-knacks but also for a number of practical things such as spoons, plates and snuffboxes. Knowledge of the real composition of *packfong* was certainly not available.

In 1768, an official of the Swedish East India Company, the *super-cargueure* Petter Johan Bladh, obtained a shipment of partly "raw", reddish *packfong*, partly "refined",

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[1] The "unessential" outer properties of the minerals later on became very important. The different crystal forms and their symmetry relations became the basis for the growing geometric crystallography, developed in France by *René Haüy* (1743–1826).

white *packfong*. Mr. Bladh contacted Gustav von Engeström who, since 1768, had been the manager of the Laboratorium Chymicum. Bladh wanted help from the famous laboratory to find out what *packfong* really was. The answer from the laboratory was clear and simple. The reddish, "raw" alloy is composed of copper and nickel with some contamination from cobalt. The alloy becomes white and genuine *packfong* by addition of zinc. In connection with this investigation it was made clear that the original ore contained a complex nickel–copper sulfide mineral and was mined in Yunnan in the south of China. Using some metallurgical technique the "raw" copper–nickel alloy was first produced. This was transported to Canton, where it was remelted and alloyed with zinc. In this process the alloy became white and real packfong. The alloy corresponds to the material that today is called German silver or argentine. Its main components are copper (65%) and zinc (20%) and it is thus a brass. As it also contains nickel (15%) it is often called nickel brass. The good mechanical properties of this alloy make it suitable as material for springs. However, the alloy is most well known for its use in many articles, such as knives, forks and spoons, that are silver plated after manufacture.

The Chinese were pioneers in the manufacture and utilization of nickel alloys. But they did not discover the element nickel. That discovery was made by Axel Fredrik Cronstedt.

31.5
Nickel Occurrence

31.5.1
Nickel Minerals and Ores

Nickel minerals are mainly sulfides, along with some arsenides, silicates and hydroxides. The white to gray colored *gersdorffite* NiAsS was the mineral in which Cronstedt discovered the new element nickel. Figure M44 shows gersdorffite together with the green secondary mineral *annabergite* $Ni_3(AsO_4)_2 \cdot 8H_2O$. The mineral was a part of Bengt Reinhold Geijer's (see section 17.4.1.2) collection, donated to the Swedish Museum of Natural History in 1831.

The copper-red nickeline "Kupfernickel", an arsenide, was of importance in the pre-industrial time (Figure M45). Neither of the two minerals has any economic importance nowadays.

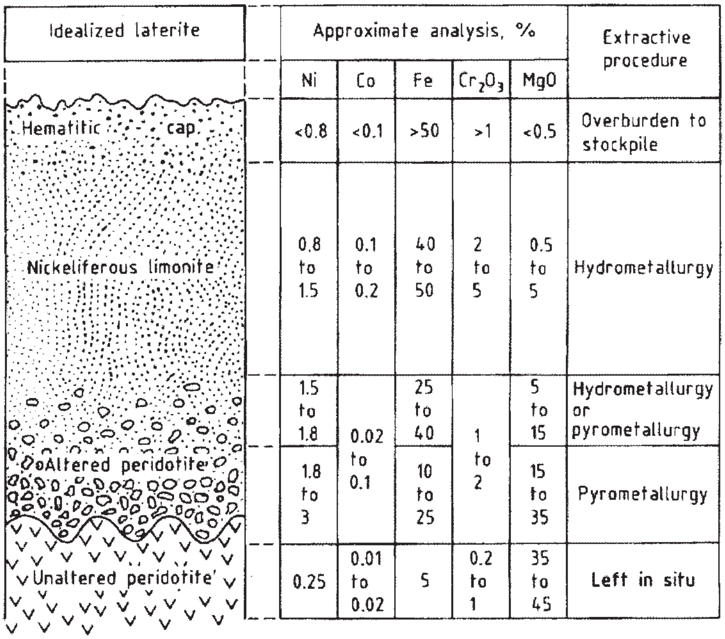
The ionic radius of divalent nickel (Ni^{2+} 0.69 Å) is similar to that of divalent iron (Fe^{2+} 0.77 Å) and magnesium (Mg^{2+} 0.71 Å). Therefore the three elements substitute for one another in minerals.

There are two main types of nickel ore. *Sulfide ores* occur as massive ore bodies or impregnated in cracked or fragmented rock (breccia). Nickel sulfides and copper sulfides are both present and typical percentages are 1–2% Ni and 3% Cu. The sulfide ores often contain cobalt, and sometimes platinum metals as well.

The most important nickel sulfide mineral is *pentlandite* $(Ni,Fe)_9S_8$ a mineral that is formed at great depth in the interior of the earth by magmatic activity or by hydrothermal alteration. The mineral is gray to white and has a metallic luster and black streak. Ores based on pentlandite account for 60% of world nickel production. The mineral *pyrrhotite* (FeS to Fe_7S_8) often occurs with pentlandite, and contributes substantially to the sulfur dioxide problem for the environment during the production of nickel from ores.

The other type is *oxide ores,* especially the *laterite ores.* Garnierite and nickeliferous limonite are important components of these. In the concentration zone, where garnierite has been formed, the nickel content can be 2–3.5%.

When superficial rocks with even a low nickel content are weathered in humid tropical and subtropical regions, nickel and iron are dissolved and the solution passes to lower strata. Nickel is precipitated as a *nickeliferous limonite* (Fe,Ni)O(OH) with about 1% Ni. This is not a true mineral but a mixture of similar hydrated oxide minerals. On its way to lower strata the solution reacts with the magnesium-rich periodite, the composition of which is altered. Hydrated nickel–magnesium silicates, apple-green or pale green, with high nickel content, 2–3% are formed. A group name for these silicates is *garnierite,* a mineral aggregate with the formula $(Ni,Mg)_6(OH)_8Si_4O_{10}$, see Figure 31.3. Garnierite and nickeliferous limonite are components in the *nickel laterite ores.*



Approximate analysis, %					Extractive procedure
Ni	Co	Fe	Cr_2O_3	MgO	
<0.8	<0.1	>50	>1	<0.5	Overburden to stockpile
0.8 to 1.5	0.1 to 0.2	40 to 50	2 to 5	0.5 to 5	Hydrometallurgy
1.5 to 1.8	0.02 to 0.1	25 to 40	1 to 2	5 to 15	Hydrometallurgy or pyrometallurgy
1.8 to 3		10 to 25		15 to 35	Pyrometallurgy
0.25	0.01 to 0.02	5	0.2 to 1	35 to 45	Left in situ

Figure 31.3 Typical section through a laterite deposit. (Reprinted from ref. [31.3]. With permission.)

31.5.2
Nickel Deposits

Nickel deposits are widely spread over the world as is shown in Figure 31.4. Some comments are given below on the presence of ores in five important nickel countries.

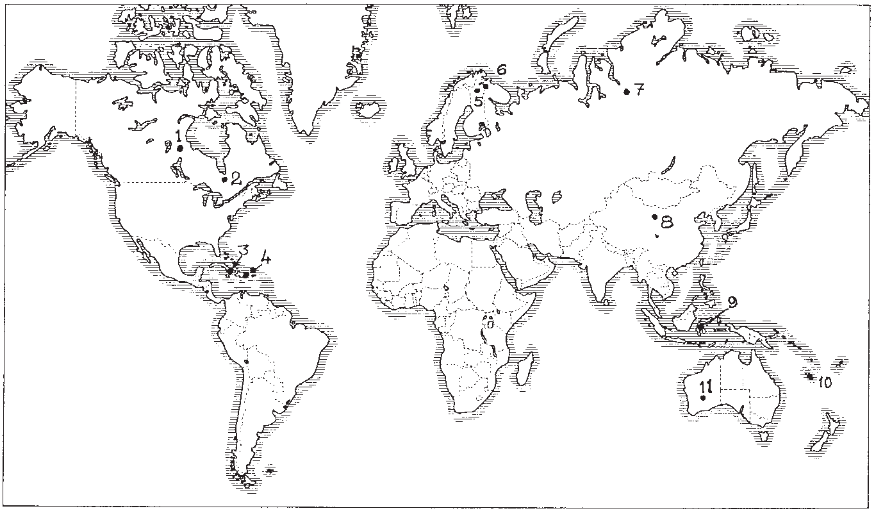


Figure 31.4 Important nickel deposits in the world. (Reprinted from SGU PM 1993:3. Theme Nickel, p. 38. Geological Survey of Sweden. With permission.)
1. Thompson, Manitoba; (the new, huge, deposit at Voisey's Bay in Labrador is not marked in the figure); 2. Sudbury, Ontario; 3. Cuba; 4. Dominican Republic; 5. Keivista, Sodankylä, Finland; 6. Pechenga-Monchegorsk, Kola Peninsula, Russia; 7. Norilsk, Siberia; 8. Jinchuan, China; 9. Indonesia; 10. New Caledonia; 11. Kambalda, Western Australia

31.5.2.1 **Russia**

The reserves in the Norilsk area, more than 900 million tonnes of ore, are situated in the Siberian tundra zone with permanent ground frost. The Norilsk–Nikel combine, the biggest nickel producer in the world, is also the owner of the mines in Pechenga-Monchegorsk on the Kola Peninsula.

31.5.2.2 **Canada**

The Sudbury region of Ontario, northwest of Lake Nipissing, has been the principal nickel-producing district in Canada since 1883. The Sudbury ore contains 1.5% Ni. Another large and established Canadian nickel deposit is that in Manitoba. Canadian geologists have continued to search for, and have even found, new areas of mineralization in their nickel-rich country. A huge nickel–copper–cobalt deposit has been discovered at Voisey's Bay in Labrador (not marked in Figure 31.4) and is now in development.

31.5.2.3 Australia

Australia is now third among the large nickel-producing countries in the world and is beginning to rival Canada. *Sulfide ores* have been mined for a long time in Western Australia, in Kambalda, Leinster and Mount Keith. Since 1998 several mines with laterite ores have been opened in the Kambalda Goldfields region.

31.5.2.4 New Caledonia

New Caledonia, an island east of Australia, was discovered by James Cook in 1774 and given its name after *Caledonia*, the old name for Scotland. It became a French colony in 1853. In 1863 the French geologist Jules Garnier discovered nickel oxide ores on the island and the mineral garnierite is named after him. After that New Caledonia became the world's main producer of nickel and is still very important, even if no longer the most important. Large deposits of garnierite and limonitic laterites are typical for this nickel producer. Politically the island is still a French territory, although with a certain degree of self-government.

31.5.2.5 Indonesia

Laterites are formed in humid tropical and subtropical regions. This is the case in the important nickel country of Indonesia. About 8% of the world production of nickel come from the three islands Sulawesi, Gag and Halmahera.

31.5.2.6 World Reserves

The world reserves of nickel are estimated at 60 million tonnes [30.2], of which Australia provides 35%. The reserve base, including known deposits, which can be mined at some future time, is 160 million tonnes with 15% each in Australia and Cuba and 10% each in Canada and New Caledonia.

31.5.3

Mining of Nickel

The quantities mined in the year 2000 are collected in Table 31.1.

Table 31.1 Mined nickel quantities in the year 2000 [31.2]

Country	Production in mines. Contained Nickel. Tonnes	Percentage of the total	Country	Production in mines. Contained Nickel. Tonnes	Percentage of the total
Russia	270 000	21.6	South Africa	36 600	2.9
Canada	191 000	15.3	Botswana	34 500	2.8
Australia	168 300	13.5	Philippines	23 500	1.9
New Caledonia	127 500	10.2	Greece	19 500	1.6
Indonesia	98 200	7.9	Zimbabwe	8 200	0.7
Cuba	68 300	5.5	Kazakhstan	3 000	0.2
Columbia	58 900	4.7	Finland	2 600	0.2
China	51 100	4.1	Norway	2 500	0.2
Brazil	45 300	3.6	Venezuela	2 500	0.2
Dominican Republic	39 900	3.2			
			Total (rounded)	1 250 000	100

31.6 Nickel in Nodules, in Meteorites and in the Earth's Core

The manganese nodules that occur in vast quantities on the deep ocean beds, at a depth of approximately 4000 m, contain 0.5–1.5% nickel. These deposits could possibly be a nickel resource in the future.

Most of the meteorites arriving at the earth's surface from space are stone meteorites. Some, however, are iron meteorites, consisting of iron–nickel alloys with a nickel content of 4–20%. These meteorites are regarded as residues of the matter from which our earth was formed 4.6 billion years ago. If this is so, very large quantities of nickel must be located in the earth's core, which is mainly an alloy of iron and nickel. The mass of the core is 32.5% of the total mass of the earth.

31.7
Manufacture of Nickel

in 2000 the total world plant production was 1120 thousand tonnes. Of this quantity nickel metal was 640, ferronickel 220, oxide and sinter 99, chemicals 18 while unspecified was 143 thousand tonnes (contained nickel) [31.2]. Nickel is obtained in many forms, including electrolytic cathode plates, carbonyl powder, hydrogen-reduced powder, nickel pellets and ferronickel.

31.7.1
Methods for Sulfide Ores – Matte Production

31.7.1.1 Primary Smelting

Sulfide ores are usually concentrated by mechanical upgrading and flotation processes at the mine. The nickel concentrate is then transported to the refinery for pyrometallurgical treatment. After a roasting, to drive off part of the sulfur as sulfur dioxide SO_2, the material is melted with a siliceous flux. This primary smelting forms two liquid phases, one a silicate slag and one a sulfide phase, a *low-grade matte,* containing nickel and copper but also some iron.

31.7.1.2 Converting

In the converting operation air or oxygen-enriched air is blown through the molten matte to form iron oxide and sulfur dioxide. Iron sulfide is removed from the matte by oxidation. A slag is formed containing the iron but also some valuable nickel and copper, so it is returned to the primary smelting. The end product of converting is a *high-grade matte*. It contains 20% S, some copper, less than 1% Fe and also those precious metals originally present in the ore concentrate.

31.7.1.3 New Technique – A Step Forward for the Environment

The nickel smelting industry has drawn public attention to emissions of sulfur dioxide, which are detrimental to the environment. The Finnish company Outokumpu has developed a *nickel flash smelting process,* totally without converters. There were several economic motives for this, but the main reasons were to reduce sulfur emissions and to improve the working conditions.

As has been said in Chapter 7 Copper, it is characteristic of flash smelting technology that powdered ore concentrate is suspended in an oxygen-enriched air and roasted and melted in a single process step. The reactions are strongly exothermic and the particles melt to form matte and slag [31.3].

The Direct Outokumpu Nickel (DON) process makes converting unnecessary, which is an important improvement environmentally. Now there is only one low, constant and highly concentrated flow of SO_2-rich gas from the flash smelting furnace, instead of the greatly fluctuating flow of converter gas of the conventional process.

The resulting matte, granulated directly from the furnace, has a low iron content, 2–4% Fe, but is high in nickel, 60–70% Ni. The nickel content of the slag is, howev-

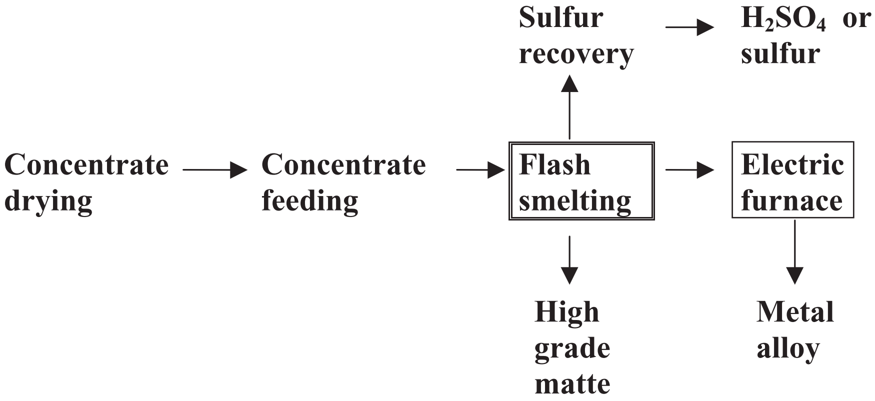


Figure 31.5 The flash smelting method for refining of nickel sulfide ores [31.4]

er, higher than in the previous process and more reduction is needed in an electric slag-cleaning furnace. Thus, the nickel smelter produces two separate granulated products: flash furnace matte and electric furnace metal alloy, see Figure 31.5.

Thus today the technology is available to produce sulfuric acid or elemental sulfur from oxides of sulfur, instead of discharging SO_2 into the atmosphere. This technique is being used more and more. But there is not always a market for large amounts of sulfuric acid produced by remotely situated smelters. For these industries a cost-effective alternative for reducing sulfur dioxide emissions is to remove as much as possible of the pentlandite-follower pyrrhotite (FeS to Fe_7S_8).

31.7.2
A Variety of Refining Processes

The high-grade matte from the converter process or the flash melting process contains sulfur and some amounts of copper, cobalt and iron and, in addition, traces of noble metals. Refined nickel is produced by a variety of methods and is delivered as nickel cathodes or nickel powder. The latter are produced partly by carbonyl processes, partly by hydrogen reduction in conjunction with pressure leaching processes. In the latter, matte is leached under pressure with acid or ammonia, and nickel is recovered as a powder by reduction with hydrogen under pressure.

A special refining process is the *carbonyl nickel process*, an old process, which was invented in 1902 in Wales and used as the *Langer–Mond process*. Originally the plant treated nickel–copper matte but the process today is highly modified. The principle is a treatment at 60°C with carbon monoxide at atmospheric pressure. Nickel carbonyl, $Ni(CO)_4$ is formed. This is a volatile liquid that melts at –19.3°C and boils at 42.5°C. In this process nickel (and some iron) is carried off while other metals remain. Heating the gas to 180°C decomposes it and pure nickel powder is obtained.

$$Ni(CO)_4 \rightarrow Ni + 4CO.$$

In a modern high-pressure variant the feed material is a special pretreated matte (with, for example, 77% Ni, 15% Cu, 4% (Co+Fe) and 4% S). Granules of this matte are treated with CO at temperatures up to 180°C and a pressure of 7 MPa. The nickel carbonyl vapor is decomposed, often on nickel pellets.

31.7.3
Methods for Laterite Ores

In the oxide–silicate ores nickel is so disseminated within the laterite that conventional ore-dressing methods do not work. The ore is often treated directly in pyrometallurgical processes, high-temperature reduction with carbon. This process yields *ferronickel*. Laterite ores are also leached with sulfuric acid in a high-temperature, high-pressure process. Nickel and cobalt are separated from purified solutions by solvent extraction.

31.8
Uses of Nickel

31.8.1
Alloys

31.8.1.1 Stainless Steels

The greatest field of application for nickel is *austenitic stainless steels*. This steel type and the influence of nickel are dealt with in Chapter 24 Chromium. Stainless-steel production accounted for more than 60% of the world nickel demand in the year 2000. The chemical industry is a very big consumer of nickel for a multitude of applications, mainly in stainless steels. In our everyday life we also meet nickel-containing, austenitic stainless steels in kitchen sinks, laundry equipment and cutlery, in railway cars and tank trailers. For the oil rigs offshore, with their exceptional corrosion problems, special stainless steels with high molybdenum contents, have been developed.

31.8.1.2 Superalloys

The invention of the *superalloys* in the 1930s made possible the manufacture of high-temperature components, turbine blades and discs, in engines for jet aircraft and rockets. This alloy family also has members with outstanding resistance to aggressive wet corrosion. Two typical examples are shown in Table 31.2. The nickel alloys contain ca. 15% chromium, which creates a passivity in the same way as is described for stainless steels (see Chapter 24 Chromium). For wet-corrosive environments, for example in the chemical industry, the alloys are alloyed with molybdenum, which increases their resistance against pitting. In high-temperature applications molybdenum would be detrimental

Table 31.2 Two typical examples of super alloys

	Alloy	Composition %			Used for
	Ni	**Cr**	**Fe**	**Mo**	
Inconel 600	76	16	8	–	High temperatures
Hastelloy C 276[1]	54	16	5	16	Aggressive wet-corrosive milieu

[1] Max 4 % W, 4 % V, 2,5 %Co

31.8.1.3 **Other Special Alloys**

Other important alloys are:

- *Monel metal*, a nickel alloy with 37% copper, very corrosion resistant in saltwater
- *Nikrothal*, an alloy with 80% Ni, 20% Cr, used as material for resistance wire in furnaces for temperatures up to 1200°C.
- *Invar*, an iron–nickel alloy with 36% Ni. Invar has a very low coefficient of thermal expansion and because of that is used in various precision instruments.

31.8.1.4 **Alloys for Coinage**

Nickel has traditionally been used for coinage, often with the composition 25% Ni and 75% Cu as a cladding layer and pure nickel in the core. Nickel in coins has been called into question, as some people are allergic to nickel. The European Union and the United States have been discussing a common approach to the issuing of new coinage. The authorities in the two regions have, however, adopted different positions with regard to nickel.

EMU, the European Monetary Union, decided to use eight denominations of coins, varying in size, color and thickness according to their values: 1, 2, 5, 10, 20 and 50 cent coins and 1 and 2 euro coins. (One *euro* is divided into 100 cents.) The 1-, 2- and 5-cent coins are minted from copper-covered steel, while the 10-, 20- and 50-cent ones are minted from an alloy called "Nordic Gold" (89% Cu, 5% Al, 5% Zn, 1% Sn). The one- and two-euro coins have inner and outer rings made of nickel-brass and copper alloys.

The US mint continues to use cupronickel cladding, that had been used earlier with few complaints of nickel dermatitis. The subject nickel in coins – past, present and future – has been reviewed by Bill Molloy at the Nickel Development Institute in Canada [31.5]

31.8.2
Nickel-based Batteries

Thomas Alva Edison invented the alkaline nickel–iron battery early in the 20th century. Iron is the negative pole of the battery, nickel oxide the positive. The cell has a terminal voltage of 1.15 V. In industrial applications and for local reserve power stations many cells are connected in series. The service lifetime for this battery type is restricted to 10 years. Introduction of the nickel–cadmium battery increased the lifetime to 25 years and NiCd-batteries are used extensively. Small batteries were involved in the explosive development of battery-driven equipment for video cameras, shavers, portable computers and mobile telephones during the 1980s. Cadmium is, however, such a huge problem for the environment that the demand for an alternative became more and more urgent. When a NiCd-battery is charged the nickel electrode is connected to the positive pole of the rectifier. Oxygen gas is evolved and nickel oxide is formed. At the cadmium electrode hydrogen is formed. This was a considerable drawback. In the search for an alternative to cadmium, the driving force was to find a material that would be acceptable for the environment and with a big capacity to store hydrogen. During the 1960s the unique ability of rare earth metals to store hydrogen became known. At the end of the decade it was discovered that the intermetallic compound $LaNi_5$ functioned very well as a negative electrode. This electrode was given the designation MH. The new ecofriendly NiMH battery started to replace NiCd at the beginning of the 1990s.

31.8.3
Nickel Plating

Electroplating of nickel can be performed on different substrate materials, among which the most usual are steel and copper alloys. For the nickel plating of steels in earlier years a layer of copper was first applied. At the present time the nickel coating is plated directly on the steel surface. A thin outer layer (0.3 μm) of chromium is applied over the nickel to keep the luster. Nickel is electrochemically nobler than steel in ordinary corrosion environment, e.g. salt water. Thus nickel does not give any cathodic protection at defects that penetrate the layer. For corrosion protection of steel the nickel layers therefore need to be free from defects.

Nickel plating of plastics, especially ABS and mixtures of ABS and polycarbonate, is also possible nowadays. Plating of nonconductive substrates starts with an electroless (autocatalytic) nickel plating.

The development of baths for nickel plating started in the middle of the 19th century. In 1916 O. P. Watts introduced the bath containing boric acid (for buffering purposes) that is still the most used and is also the basis for bright plating baths. *Brighteners of the first class (carriers)* work by refining the grain size of the structure and provide deposits with increased luster. Examples of agents with this effect, are sacharin (*o*-sulfobenzoic imide) and benzene sulfonamide. Carriers are used in concentrations of 1–25 g/l. *Brighteners of the second class (levelers)* are just levelers, and produce bright or brilliant nickel layers. Examples of agents, used at concentrations of 0.005–0.2 g/l, are thiourea and 1,4-butyne-2-diol.

Besides the Watts bath, the *sulfamate bath* is of great importance, especially for the plating of technically advanced components. It is based on the nickel salt of sulfaminic acid NH_2SO_3H. Motives for using this bath type are the possibility of using high current densities (rapid plating) and, in particular, that it produces deposits of low stress.

31.8.4
Catalysts

Nickel powder with very small grain size can adsorb up to 17 times of its own volume of hydrogen. This powder is used as a catalyst for many processes, e.g. hydrogenation of vegetable oils and cracking of ammonia to nitrogen and hydrogen.

31.9
Nickel in Life

31.9.1
Very Similar but Quite Different!

The elements Fe, Co and Ni, the triad in the middle of the periodic table, are similar from the chemical point of view but quite different in their influence on the environment and their significance for life. As described in Chapter 8 Iron, this element is tremendously important for human life, as its atom is essential in hemoglobin and is thus responsible for oxygen uptake in the lungs. Cobalt, present in the form of vitamin B_{12}, is necessary to prevent serious anemia. The role of nickel in mammals and humans is very limited and confined to its presence in one single enzyme, *urease*, which catalyzes the decomposition of urea to ammonia. Nickel was, however, very important in a very early epoch of life on earth.

The environment in which life began on our earth had an atmosphere of CH_4, H_2 and H_2S. The elementary functions of the archaebacteria in such an atmosphere needed nickel-based enzymes as catalysts. At the point in the earth's history when oxygen began to dominate, the environment was changed to an atmosphere characterized by O_2, N_2 and CO_2. This change drastically reduced the need for nickel as a catalyst and its role was taken over by the elements iron, copper and manganese.

Anaerobic bacteria are, however, still active in very special oxygen-free environments, anaerobic niches in the geochemical world. This hidden environment resembles the conditions in which life began on our planet. The bacteria derive their energy supply by metabolizing hydrogen H_2 and liberating methane CH_4, a reaction catalyzed by nickel.

31.9.2
Nickel Toxicology

Nickel is an essential element for some plants and toxic for others. On soils rich in nickel, especially those formed from the mineral serpentine, some nickel-tolerant vegetables have been developed by genetic adaptation. The vegetation in New Caledonia is well known, where plants with nickel contents of up to 1% of the dry weight can be found.

Observations of excess nasal and pulmonary cancers in people working with nickel oxide or high-temperature roasting of nickel–copper matte resulted in the suspicion that nickel might cause respiratory cancer. The International Committee on Nickel Carcinogenesis in Man has carefully studied the subject. This committee, ICNCM, updated existing studies and evaluated the collective results [31.6]. The following conclusion of the ICNCM work is cited from ref. [31.7]:

> More than one form of nickel gave rise to respiratory cancer in men employed at the refineries. The cancer risks were primarily related to exposure to soluble nickel at concentrations greater than 1 mg Ni/m^3 and to less soluble forms at concentrations greater than 10 mg Ni/m^3. The ICNCM found:
> - there was an absence of any form of hazard from metallic nickel
> - there was no substantial evidence that occupational exposure to nickel or any of its compounds was likely to produce cancer other than in the lung and nose
> - the few small excesses that were observed in cohorts with excess lung or nasal cancer could be attributed to misdiagnoses or to chance.

The group also considered that the risk to the general population from exposure to <1 μg/m^3 of nickel in the ambient air is minute or nonexistent.

To make the environment safe for workers in the nickel industry, Threshold Limit Values (TLV) for nickel have been specified. One example (1999) is 0.5 mg Ni/m^3 air. For soluble compounds TLV is 0.1 mg Ni/m^3 air and for nickel carbonyl it is 0.007 mg Ni/m^3 air.

Nickel contact dermatitis, nickel allergy, is well recognized and is more usual among women than men. Persistent eczema may occur after sensitization from such nickel-containing components as nickel-plated earrings. Recent studies have indicated that sensitization can be avoided by use of alloys resistant to corrosion by sweat.

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32
Platinum Group Metals

32.1 Ru
Facts about Ruthenium

32.1.1 Ru
The Element

Symbol:	Ru
Atomic number:	44
Atomic weight:	101.07
Ground state electron configuration:	[Kr]$4d^7 5s^1$
Crystal structure:	Hexagonal hcp with $a = 2.71$ Å, $c = 4.28$ Å

32.1.2 Ru
Discovery and Occurrence

Discovery: Priority for a sixth platinum group element was claimed in 1809 by the Pole Sniadecki and in 1828 by Osann from Estonia. None of these discoveries was approved. In 1844 Karl Karlovich Klaus, Estonia, discovered a new metal in Russian platinum and named the new element ruthenium after Russia.

Most important mineral: Ruthenium is a PGM (platinum group metal). It is mainly found alloyed with other platinum metals, from which it is recovered commercially. In the PGM deposits in the South African Merensky Reef the ruthenium content (relative to the total PGM quantity) is 8%, in the Canadian Sudbury and Russian Norilsk deposits 3% and 2% respectively.

Ranking in order of abundance in earth crust:	77–80
Mean content in earth crust:	0.001 ppm (g/tonne)
Mean content in oceans:	$7 \cdot 10^{-7}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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32.1.3 Ru

Chemical Characterization

Ruthenium is a hard, white metal. It does not tarnish at room temperature and is not attacked by acids, not even aqua regia. If potassium chlorate is added, however, the reaction is explosive. Ruthenium is used as an alloying element for platinum and palladium, making these metals harder by solution hardening. Such alloys have a high resistance to wear and are used in the manufacture of tips for fountain-pen nibs. A content of 0.1% Ru in titanium improves the corrosion resistance of this metal. Stable anodes for chlorine production are made of titanium, coated with ruthenium. A new technique for improved storage capacity on hard disks uses ruthenium.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ru^{III} as in RuF_3	$Ru(g) \rightarrow Ru^+(g) + e^-$	710	$Ru(g) + e^- \rightarrow Ru^-(g)$
Ru^{IV} as in RuO_2 and RuF_4	$Ru^+(g) \rightarrow Ru^{2+}(g) + e^-$	1620	–101
Ru^V as in RuF_5	$Ru^{2+}(g) \rightarrow Ru^{3+}(g) + e^-$	2747	
Ru^{VI} as in RuF_6			
Ru^{VII} as in RuO_4^-			
Ru^{VIII} as in RuO_4			

Standard reduction potential:	$RuO_2(s) + 4H^+ + 4e^- \rightarrow Ru(s) + 2H_2O(l)$	$E^0 = +0.68$ V
	$Ru^{3+}(aq) + e^- \rightarrow Ru^{2+}(aq)$	$E^0 = +0.249$ V
	$Ru^{2+}(aq) + 2e^- \rightarrow Ru(s)$	$E^0 = +0.455$ V

Electronegativity (Pauling): 2.2

Radii of atoms and ions:	Atomic:	130 pm
(WebElements™)	Covalent:	126 pm
	Ru^{3+} (6-coordinate, octahedral):	82 pm
	Ru^{4+} (6-coordinate, octahedral):	76 pm
	Ru^{5+} (6-coordinate, octahedral):	70.5 pm
	Ru^{7+} (4-coordinate, tetrahedral)	52 pm
	Ru^{8+} (4-coordinate, tetrahedral)	50 pm

32.1.4 Ru
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
12 370 kg m^{-3} 12.37 g cm^{-3}	8.17 cm^3	2583 K 2310 °C	4175 K 3902 °C	238 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
123	117	115	108	98

Coefficient of linear expansion K^{-1}

100 K	298 K	500 K	800 K
–	$6.4 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
13.4	71	100	156	278	444

Mass magnetic susceptibility χ_{mass} at 293 K	$+5.37 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
447 GPa	172 GPa	371 GPa	0.30

32.1.5 Ru
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	25.5 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	568 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	643 $kJmol^{-1}$
Entropy S^0 at 298 K	28.2 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	13.5	24.06	25.7	28.2	31.4	31.4

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Ru + O_2 \rightarrow RuO_2$	–170	–	–	–	–

32.1.6 Ru
Nuclear Properties and X-ray

Isotope range, natural and artificial	90–115

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{96}Ru	Stable	5.52	+0	–
^{98}Ru	Stable	1.88	+0	–
^{99}Ru	Stable	12.7	+5/2	–0.6413
^{100}Ru	Stable	12.6	+0	–
^{101}Ru	Stable	17.0	+5/2	–0.7189
^{102}Ru	Stable	31.6	+0	–
^{104}Ru	Stable	18.7	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{99}Ru	^{101}Ru
Reference compound	$K_4Ru(CN)_6/D_2O$	
Frequency MHz (^1H = 100 MHz)	4.605	5.161
Receptivity D^P relative to ^1H = 1.00	$1.44 \cdot 10^{-4}$	$2.71 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	0.821	1.55
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-1.229 \cdot 10^7$	$-1.377 \cdot 10^7$
Nuclear quadropole moment, barn	0.079	0.46

Ru

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
43	Tc	18.251
44	Ru	19.150
45	Rh	20.073

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	177
17.37 keV (MoKα_2)	21.9

Ru

Neutron absorption	Thermal neutron capture cross section	2.6 barns

32.1 Rh
Facts about Rhodium

Rh

32.1.1 Rh
The Element

Symbol: Rh
Atomic number: 45
Atomic weight: 102.91
Ground state electron configuration: [Kr]$4d^8 5s^1$
Crystal structure: Cubic fcc with $a = 3.80$ Å

32.1.2 Rh
Discovery and Occurrence

Discovery: In 1803, W. H. Wollaston in England investigated the aqua regia solution of platinum. After removal of platinum and palladium he found a new metal, which he named *rhodium* because of the rose colors of its salts. The metal itself was prepared by hydrogen reduction.

Most important mineral: Rhodium is a PGM (platinum group metal). It is mainly found alloyed with other platinum metals, from which it is recovered commercially. In the South African Merensky Reef and the Canadian Sudbury and Russian Norilsk deposits the rhodium content (relative to the total PGM quantity) is about 3%.

Ranking in order of abundance in earth crust: 77–80
Mean content in earth crust: 0.001 ppm (g/tonne)
Mean content in oceans: –
Residence time in oceans: –
Mean content in an adult human body: –
Content in a man’s body (weight 70 kg): –

Rh

32.1.3 Rh
Chemical Characterization

Rhodium is silvery white with a high reflectance. Aqueous solutions of many of its salts are rose colored, giving rise to its name (from Greek *rhodon*, “rose”). Platinum alloys with rhodium have an important use in thermocouples for the determination of high temperatures in furnaces and laboratory equipment. Organic rhodium compounds have been found to be effective catalysts (homogenous) in pharmaceutical production of, for instance, the drug L-Dopa for the treatment of Parkinson’s disease.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Rh^{III} as in Rh_2O_3 and RhF_3	$Rh(g) \rightarrow Rh^+(g) + e^-$	720	$Rh(g) + e^- \rightarrow Rh^-(g)$
Rh^{IV} as in RhO_2, RhF_4, and K_2RhF_6	$Rh^+(g) \rightarrow Rh^{2+}(g) + e^-$	1740	–110
Rh^{VI} as in RhF_6	$Rh^{2+}(g) \rightarrow Rh^{3+}(g) + e^-$	2997	

Standard reduction potential: $Rh^{3\pm}(aq) + 3e^- \rightarrow Rh(s)$ $E^0 = +0.76$ V

Electronegativity (Pauling): 2.28

Radii of atoms and ions: (WebElements™)		
	Atomic:	135 pm
	Covalent:	135 pm
	Rh^{3+} (6-coordinate, octahedral):	80.5 pm
	Rh^{4+} (6-coordinate, octahedral):	74 pm
	Rh^{5+} (6-coordinate, octahedral):	69 pm

32.1.4 Rh

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
12 410 kg m^{-3} 12.41 g/cm^3	8.29 cm^3	2239 K 1966 °C	4000 K 3727 °C	243 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$				
173 K	**273 K**	**373 K**	**573 K**	**973 K**
156	151	147	137	–

Coefficient of linear expansion K^{-1}			
100 K	**293 K**	**500 K**	**800 K**
$5 \cdot 10^{-6}$	$8.2 \cdot 10^{-6}$	$9.3 \cdot 10^{-6}$	$10.8 \cdot 10^{-6}$

Resistivity nΩm					
78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
4.6	43	62	102	200	330

Mass magnetic susceptibility χ_{mass} at 293 K	$13.6 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties			
Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
377 GPa	150 GPa	258 GPa	0.26

32.1.5 Rh
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	21.7 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	495 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	556 $kJmol^{-1}$
Entropy S^0 at 298 K	31.51 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	15.1	24.98	28.2	31.6	40.2	41.8

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Rh + O_2 \rightarrow RhO_2$	–183	–179	–168	–158	–148

32.1.6 Rh
Nuclear Properties and X-ray

Isotope range, natural and artificial 94–117

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{103}Rh	Stable	100	–1/2	–0.0884

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{103}Rh
Reference compound	mer-$[RhCl_3(SMe_2)_3]$
Frequency MHz (^1H = 100 MHz)	3.172
Receptivity D^P relative to ^1H = 1.00	$3.17 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.181
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-0.847 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
44	Ru	19.150
45	Rh	20.073
46	Pd	21.021

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	190
17.37 keV (MoKα_2)	23.6

Neutron absorption	**Thermal neutron capture cross section**	145 barns

32.1 Pd
Facts about Palladium

32.1.1 Pd
The Element

Symbol:	Pd
Atomic number:	46
Atomic weight:	106.42
Ground state electron configuration:	[Kr]4d^{10}
Crystal structure:	Cubic fcc with a = 3.89 Å

32.1.2 Pd
Discovery and Occurrence

Discovery: W. H. Wollaston in England dissolved natural platinum in aqua regia, removed the black residue by filtering and added mercury cyanide. A yellow precipitate was formed. When this was calcinated a metal, not platinum, was obtained. He named the new element *palladium* after the asteroid *Pallas*, discovered in 1802. The discovery year for palladium was 1803.

Most important mineral: Palladium is a PGM (platinum group metal). It is mainly found alloyed with other platinum metals in South Africa. Russia, the United States and Canada. In the Canadian Sudbury and the Russian Norilsk deposits the palladium contents are higher than that of platinum.

Ranking in order of abundance in earth crust:	70
Mean content in earth crust:	0.015 ppm (g/tonne)
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

32.1.3 Pd
Chemical Characterization

Palladium is a silvery white metal, ductile and chemically resistant. Finely divided it is an excellent adsorbent for gases, taking up 900 times its own volume of hydrogen at room temperature. The largest and fastest growing application of palladium is in the production of automobile catalytic converters, which reduce harmful emissions from the engine. In a modern converter three reactions occur: Oxidation of unburned hydrocarbons, oxidation of carbon monoxide and reduction of nitrogen oxides NOX. In jewelry palladium is used, alloyed with gold, in one of the types of white gold (see Chapter 5 Gold).

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
Pd^{II} as in PdO, PdF_2 and $[PdCl_4]^{2-}$	$Pd(g) \rightarrow Pd^+(g) + e^-$	804	$Pd(g) + e^- \rightarrow Pd^-(g)$
Pd^{III} as in the complex $[PdL_2]^{3+}$;	$Pd^+(g) \rightarrow Pdt^{2+}(g) + e^-$	1870	–53.7
L=1,4,7-trithiacyclononane	$Pd^{2+}(g) \rightarrow Pdt^{3+}(g) + e^-$	3177	
Pd^{IV} as in PdF_4			

Standard reduction potential: $Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$ $E^0 = +0.915$ V

Electronegativity (Pauling): 2.20

Radii of atoms and ions:	Atomic:	140 pm
(WebElements™)	Covalent:	131 pm
	Van der Waals	163 pm
	Pd^{2+} (6-coordinate, octahedral):	100 pm
	Pd^{2+} (4-coordinate, square-planar):	78 pm
	Pd^{3+} (6-coordinate, octahedral):	90 pm
	Pd^{4+} (6-coordinate, octahedral):	75.5 pm

32.1.4 Pd

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
12 023 kg m^{-3} 12.02 g/cm^3	8.85 cm^3	1825 K 1552 °C	3236 K 2963 °C	244 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
72	72	73	79	93

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$8 \cdot 10^{-6}$	$11.8 \cdot 10^{-6}$	$13.2 \cdot 10^{-6}$	$14.5 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
17.3	100	138	210	330	420

Mass magnetic susceptibility χ_{mass} at 293 K	$+67.0 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
122 GPa	44 GPa	180 GPa	0.39

32.1.5 Pd
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	16.7 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	390 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	378 $kJmol^{-1}$
Entropy S^0 at 298 K	37.57 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	17.9	25.98	27.7	30.0	34.7	34.7

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$2Pd + O_2 \rightarrow 2PdO$	–130	–100	–25	–	–

32.1.6 Pd
Nuclear Properties and X-ray

Isotope range, natural and artificial 94–120

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{102}Pd	Stable	1.02	+0	–
^{104}Pd	Stable	11.14	+0	–
^{105}Pd	Stable	22.33	+5/2	–0.642
^{106}Pd	Stable	27.33	+0	–
^{108}Pd	Stable	26.46	+0	–
^{110}Pd	Stable	11.72	+0	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{105}Pd
Reference compound	K_2PdCl_6/D_2O
Frequency MHz (^1H = 100 MHz)	4.576
Receptivity D^P relative to ^1H = 1.00	$2.53 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	1.45
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-1.23 \cdot 10^7$
Nuclear quadropole moment, barn	0.66

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
45	Rh	20.073
46	Pd	21.021
47	Ag	21.991

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	200
17.37 keV ($MoK\alpha_2$)	24.9

Neutron absorption **Thermal neutron capture cross section** 6.0 barns

32.1 Os
Facts about Osmium

32.1.1 Os
The Element

Symbol:	Os
Atomic number:	76
Atomic weight:	190.23
Ground state electron configuration:	$[Xe]4f^{14}5d^6 6s^2$
Crystal structure:	Hexagonal hcp with $a = 2.73$ Å, $c = 4.32$ Å

32.1.2 Os
Discovery and Occurrence

Discovery: In 1803, S. Tennant in England discovered a new metal in the black residue remaining after dissolution of natural platinum in aqua regia. The oxide of the new element had a characteristic bad odor. Tennant took this as a reason to name the new element *osmium* after the Greek word for *smell*.

Most important mineral: Osmium is a PGM (platinum group metal). It is mainly found alloyed with other platinum metals, from which it is recovered commercially. In the South African Merensky Reef and the Canadian Sudbury and Russian Norilsk deposits, the osmium content (relative to the total PGM quantity) is about 1%. A special naturally occurring alloy is osmiridium containing, for example, 50% iridium, 25% osmium, with other PGMs making up the total.

Ranking in order of abundance in earth crust:	76
Mean content in earth crust:	0.0015 ppm (g/tonne)
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

32.1.3 Os

Chemical Characterization

Osmium is a bluish-white metal that is not attacked by ordinary acids, but dissolves slowly in aqua regia. It has the highest melting point and lowest vapor pressure of the PGM metals. For this reason, Karl Auer von Welsbach used osmium for the first metal filament lamp. The tetroxide is highly toxic. Concentrations in air as low as 10^{-7} g m^{-3} can cause lung congestion and eye damage. On the other hand a type of osmium-containing sensor is implanted in diabetes patients for continuously monitoring the blood glucose levels.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Os^{IV} as in OsO_2 and OsF_4	$Os(g) \rightarrow Os^+(g) + e^-$	840	$Os(g) + e^- \rightarrow Os^-(g)$
Os^{V} as in OsF_5	$Os^+(g) \rightarrow Os^{2+}(g) + e^-$	1600	–108
Os^{VI} as in OsF_6			
Os^{VII} as in $[OsO_4]^-$			
Os^{VIII} as in OsO_4			

Standard reduction potential:

$OsO_4(s) + 4H^+(aq) + 4e^- \rightarrow OsO_2(s) + 2H_2O(l)$ $E^0 = +1.01$ V

$OsO_2(s) + 4H^+(aq) + 4e^- \rightarrow Os(s) + 2H_2O(l)$ $E^0 = +0.687$ V

Electronegativity (Pauling): 2.2

Radii of atoms and ions:
(WebElements™)

Atomic:	130 pm
Covalent:	128 pm
Os^{4+} (6-coordinate, octahedral):	77 pm
Os^{5+} (6-coordinate, octahedral):	71.5 pm
Os^{6+} (6-coordinate, octahedral):	68.5 pm
Os^{7+} (6-coordinate, octahedral):	66.5 pm
Os^{8+} (4-coordinate, tetrahedral):	53 pm

32.1.4 Os

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
22 600 kg m^{-3} 22.60 g/cm^3	8.42 cm^3	3323 K 3050 °C	5300 K 5027 °C	130 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 173 K	273 K	373 K	573 K	973 K
93	88	87	87	–

Coefficient of linear expansion K^{-1} 100 K	298 K	500 K	800 K
–	$5.1 \cdot 10^{-6}$	–	–

Resistivity nΩm 78 K	273 K	373 K	573 K	973 K	1473 K
–	81	114	178	304	460

Mass magnetic susceptibility χ_{mass} at 293 K $+0.65 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Paramagnetic (as susceptibility is positive)

Elastic properties Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	–	0.25

32.1.5 Os
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	29.3 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	628 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	791 kJmol^{-1}
Entropy S^0 at 298 K	32.6 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	–	24.7	26.0	27.5	31.2	33.0

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Os + O_2 \rightarrow OsO_2$	–233	–199	–113	–26	–

32.1.6 Os
Nuclear Properties and X-ray

Isotope range, natural and artificial 162–196

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{187}Os	Stable	1.6	–1/2	0.0647	–	–	–
^{188}Os	Stable	13.3	+0	–	–	–	–
^{189}Os	Stable	16.1	–3/2	0.6599	–	–	–
^{190}Os	Stable	26.4	+0	–	–	–	–
^{192}Os	Stable	41.0	+0	–	–	–	–
^{184}Os	Active	0.02	+0	–	$5.6 \cdot 10^{13}$ y	–	–
^{186}Os	Active	1.58	+0	–	$2 \cdot 10^{15}$ y	α	2.822 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{187}Os	^{189}Os
Reference compound	OsO_4/CCl_4	
Frequency MHz (^1H = 100 MHz)	2.282	7.765
Receptivity D^P relative to ^1H = 1.00	$1.99 \cdot 10^{-7}$	$3.93 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	$1.13 \cdot 10^{-3}$	2.25
Magnetogyric ratio, radT^{-1}s^{-1}	$0.619 \cdot 10^7$	$2.107 \cdot 10^7$
Nuclear quadropole moment, barn	–	0.86

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
75	Re	59.718
76	Os	61.487
77	Ir	63.287

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	182
17.37 keV (MoKα_2)	101

Neutron absorption **Thermal neutron capture cross section** 15 barns

32.1 Ir
Facts about Iridium

32.1.1 Ir
The Element

Symbol: Ir
Atomic number: 77
Atomic weight: 192.22
Ground state electron configuration: [Xe]$4f^{14}5d^76s^2$
Crystal structure: Cubic fcc with a = 3.84 Å

32.1.2 Ir
Discovery and Occurrence

Discovery: In connection with the discovery of osmium, S. Tennant in England found an additional metal. When its salts were dissolved in acid different colors were observed. Because of that the new element was given the name *iridium* after *iris*, rainbow. The discovery year was 1803.

Most important mineral: Iridium is a PGM metal (platinum group metal). It is mainly found alloyed with other platinum metals, from which it is recovered commercially. In the South African Merensky Reef and the Canadian Sudbury and Russian Norilsk deposits, the rhodium content (relative to the total PGM quantity) is 1–2%. A special naturally occurring alloy is osmiridium containing, for example, 50% iridium, 25% osmium, with other PGMs making up the total.

Ranking in order of abundance in earth crust: 77–80
Mean content in earth crust: 0.001 ppm (g/tonne)
Mean content in oceans: –
Residence time in oceans: –
Mean content in an adult human body: –
Content in a man's body (weight 70 kg): –

32.1.3 Ir

Chemical Characterization

Iridium is a white, brittle and hard metal. Its density of 22.56 g/cm^3 is the highest of all elements. It is chemically very inert and resists even the action of aqua regia. However, the metal is attacked by molten salts, such as NaCl and NaCN. Iridium is the most corrosion-resistant metal known, and was used in making the standard meter bar of Paris, an alloy of 90% platinum and 10% iridium. This is now obsolete as is also the old Pt–Ir kilogram block. Length and weight definitions are now based on fundamental physical constants. The resistance to high temperature in severe environments is the background to the use of iridium as an electrode material in spark plugs. In this application it is more resistant than platinum. As a consequence the electrode can be reduced in size, leaving more room for the spark in the chamber.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ir^{III} as in Ir_2O_3 and IrF_3	$Ir(g) \rightarrow Ir^+(g) + e^-$	880	$Ir(g) + e^- \rightarrow Ir^-(g)$
Ir^{IV} as in IrO_2	$Ir^+(g) \rightarrow Ir^{2+}(g) + e^-$	1600	–151
Ir^{V} as in IrF_5			
Ir^{VI} as in IrF_6			

Standard reduction potential: $Ir^{3+}(aq) + 3e^- \rightarrow Ir(s)$ $E^0 = +1.156$ V

Electronegativity (Pauling): 2.20

Radii of atoms and ions: (WebElements™)		
	Atomic:	135 pm
	Covalent:	137 pm
	Ir^{3+} (6-coordinate, octahedral):	82 pm
	Ir^{4+} (6-coordinate, octahedral):	76.5 pm
	Ir^{5+} (6-coordinate, octahedral):	71 pm

32.1.4 Ir

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
22 560 kg m^{-3} 22.56 g/cm^3	8.52 cm^3	2719 K 2446 °C	4701 K 4428 °C	131 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
156	147	145	139	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$4.4 \cdot 10^{-6}$	$6.4 \cdot 10^{-6}$	$7.2 \cdot 10^{-6}$	$8.1 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
9	47	68	108	220	335

Mass magnetic susceptibility χ_{mass} at 293 K	$+1.67 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
528 GPa	210 GPa	320 GPa	0.26

32.1.5 Ir
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	26.4 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	564 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	665 kJmol^{-1}
Entropy S^0 at 298 K	35.48 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	17.3	25.10	26.8	29.2	35.1	38.1

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Ir + O_2 \rightarrow IrO_2$	–161	–128	–54	–	–

32.1.6 Ir
Nuclear Properties and X-ray

Isotope range, natural and artificial 165–198

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{191}Ir	Stable	37.3	+3/2	0.1462
^{193}Ir	Stable	62.7	+3/2	0.1592

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{191}Ir	^{193}Ir
Reference compound	–	–
Frequency MHz (^1H = 100 MHz)	1.719	1.872
Receptivity D^P relative to ^1H = 1.00	$1.09 \cdot 10^{-5}$	$2.34 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.0620	0.134
Magnetogyric ratio, radT^{-1}s^{-1}	$0.481 \cdot 10^7$	$0.523 \cdot 10^7$
Nuclear quadropole moment, barn	0.82	0.75

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
76	Os	61.487
77	Ir	63.287
78	Pt	65.123

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	190
17.37 keV ($MoK\alpha_2$)	105

Neutron absorption	**Thermal neutron capture cross section**	425 barns

32.1 Pt
Facts about Platinum

32.1.1 Pt
The Element

Symbol:	Pt
Atomic number:	78
Atomic weight:	195.08
Ground state electron configuration:	$[Xe]4f^{14}5d^96s^1$
Crystal structure:	Cubic fcc with *a* = 3.92 Å

32.1.2 Pt
Discovery and Occurrence

Discovery: Natural platinum has been known since antiquity and became well known in New Granada in South America in the 18th century. It was, however, an alloy of different platinum group metals, PGMs. Pure and malleable platinum was prepared by W. H. Wollaston in the first decade of the 19th century.

Most important mineral: *Cooperite* PtS and *sperrylite* $PtAs_2$ are platinum minerals. The element is, however, mainly found as native metal and as alloys with the other platinum metals or with gold. The ores in which platinum is found are magmatic as in the Bushveld complex.(Figure M46) or alluvial as in Witwaterstrand, both in South Africa. Russia, the United States and Canada are also big platinum producers.

Ranking in order of abundance in earth crust:	73–74
Mean content in earth crust:	0.005 ppm (g/tonne)
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

32.1.3 Pt
Chemical Characterization

Platinum, which has given the name to the platinum group metals, is a grayish-white metal. Its excellent chemical and thermal resistance are used in many applications. In chemical laboratories all over the world platinum is the crucible material of choice. The metal is used for contacts in the electronic industry as well as for catalytic purposes in the chemicals industry. A considerable amount of the platinum used goes into jewelry, in which it is often alloyed with gold. It is also used for dental fillings. Within medicine platinum has an important use in the anti-tumor drug cisplatin.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Pt^{II} as in PtO	$Pt(g) \rightarrow Pt^+(g) + e^-$	870	$Pt(g) + e^- \rightarrow Pt^-(g)$
Pt^{IV} as in PtF_4 and $(NH_4)_2PtCl_6$	$Pt^+(g) \rightarrow Pt^{2+}(g) + e^-$	1791	–205
Pt^V as in PtF_5			
Pt^{VI} as in PtF_6			

Standard reduction potential:		
	$[PtCl_6]^{2-}(aq) + 2e^- \rightarrow [PtCl_4]^{2-}(aq) + 2Cl^-(aq)$	$E^0 = +0.726$ V
	$[PtCl_4]^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4Cl^-$	$E^0 = +0.758$ V
	$Pt^{2\pm}(aq) + 2e^- \rightarrow Pt(s)$	$E^0 = +1.188$ V

Electronegativity (Pauling): 2.28

Radii of atoms and ions: (WebElements™)		
	Atomic:	137 pm
	Covalent:	128 pm
	Van der Waals	175 pm
	Pt^{2+} (6-coordinate, octahedral):	94 pm
	Pt^{2+} (4-coordinate, square-planar):	74 pm
	Pt^{4+} (6-coordinate, octahedral):	76.5 pm
	Pt^{5+} (6-coordinate, octahedral):	71 pm

32.1.4 Pt

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
21 450 kg m^{-3} 21.45 g/cm^3	9.09 cm^3	2045 K 1772 °C	4098 K 3825 °C	133 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
73	72	72	73	78

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$6.6 \cdot 10^{-6}$	$8.8 \cdot 10^{-6}$	$9.6 \cdot 10^{-6}$	$10.3 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
19.6	98.1 (106 at 298 K)	136	210	343	483

Mass magnetic susceptibility χ_{mass} at 293 K	$+13.0 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
168 GPa	61 GPa	228 GPa	0.38

32.1.5 Pt
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	19.7 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	500 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	565 $kJmol^{-1}$
Entropy S^0 at 298 K	41.63 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	19.6	25.86	27.5	29.7	34.5	34.7

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Pt + O_2 \rightarrow PtO_2$	–168	–162	–160	–158	–157

32.1.6 Pt
Nuclear Properties and X-ray

Isotope range, natural and artificial	168–202

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{192}Pt	Stable	0.79	+0	–	–	–	–
^{194}Pt	Stable	32.9	+0	–	–	–	–
^{195}Pt	Stable	33.8	–1/2	0.6022	–	–	–
^{196}Pt	Stable	25.3	+0	–	–	–	–
^{198}Pt	Stable	7.2	+0	–	–	–	–
^{190}Pt	Active	0.01	+0	–	$6.5 \cdot 10^{11}$ y	α	3.249 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{195}Pt
Reference compound	$[Pt(CN)_6]^{2-}$
Frequency MHz (^1H = 100 MHz)	21.414
Receptivity D^P relative to ^1H = 1.00	$3.51 \cdot 10^{-3}$
Receptivity D^C relative to ^{13}C = 1.00	20.1
Magnetogyric ratio, $radT^{-1}s^{-1}$	$5.839 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV
77	Ir	63.287
78	Pt	65.123
79	Au	66.990

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	197
17.37 keV ($MoK\alpha_2$)	108

Neutron absorption	**Thermal neutron capture cross section**	10 barns

32.2
The Platinum Group Metals – PGMs – An Overview

The platinum metals are situated in groups 8–10 and periods 5 and 6 in the periodic system. As shown in Table 32.1 the melting points of the metals decrease to the right in every period (Ru → Pd and Os → Pt) and increases upwards in each group. Osmium has the highest melting point of all metals after tungsten and rhenium. The hardness of the metals varies in the same way but still more markedly. Platinum and palladium are soft and ductile. All the platinum metals are noble and as bulk metals they are not attacked at all by air and water. Osmium is grayish blue, platinum grayish-white, the others are silver-white. At high temperatures the metals ruthenium and osmium form volatile oxides RuO_4 and OsO_4 while platinum compounds of the type ammonium hexachloroplatinate $(NH_4)_2PtCl_6$ do not form an oxide on calcination but a very finely powdered metal, platinum sponge. This has a very large specific surface and is used as a catalyst.

Table 32.1 The platinum metals and their properties – an overview

Metal	**Period 5**			**Period 6**		
	Ruthenium Ru	**Rhodium Rh**	**Palladium Pd**	**Osmium Os**	**Iridium Ir**	**Platinum Pt**
Atomic Number	44	45	46	76	77	78
Atomic Weight	101.07	102.91	106.42	190.23	192.22	195.08
Melting point, °C	2310	1966	1552	3050	2446	1772
Hardness Vickers[a)]	240	120	41	350	220	41
Density, g/cm^3	12.37	12.41	12.02	22.60	22.56	21.45
Group No.	8	9	10	8	9	10

a) Vickers values HV according to ref. [32.10]

32.3
Discovery of Natural Platinum

32.3.1
A Stranger Among the Hieroglyphs

A scene in the Louvre in 1900: A box of great value, an article from Egyptian Thebes, was being examined. It dated back to the 8th century BC, and was decorated with hieroglyphs on thin strips of silver on one side and of gold on the other. The experts of the museum wanted to know more about the metals. They contacted the well-known scientist Berthelot[1], who was allowed to take small samples out of the valuable decorations. He reported that samples with the appearance of gold dissolved in aqua regia and were undoubtedly of gold. Equally, samples that looked like silver and that dissolved in nitric acid were made of silver.

However, Berthelot also made a confusing observation. One of the small silver strips with hieroglyphs did not dissolve in nitric acid, but it was also difficult to dissolve it in aqua regia. Thus it was neither silver nor gold. The confusing metal was not pure platinum. Berthelot concluded that the material was a complex alloy of different platinum metals. At this time platinum and platinum metals were known but their history was not. Could it be that platinum and alloys of platinum metals were known in Ancient Egypt? Berthelot thought not. Most likely the alloy with its silvery appearance was used by chance and hammered at the same time as the silver strips. It is easy to imagine the astonishment of the Egyptian silversmith. Such a curious silver! So hard and difficult to work by comparison with the common silver.

During the 20th century several platinum ornaments, settings in gold pieces, were found in museum. Often the complex alloys contained osmium, iridium, ruthenium and platinum.

32.3.2
Platinum in the Old World

Silver and gold played an important role in ancient Greece and Rome and also in medieval Europe. Platinum did not, even if it was known as a curiosity. In his *Natural History* Pliny the Elder depicted *plumbum album*, literally white lead, found in the sands of Portugal and Galicia (Spain). This has been construed as tin, but it was said to have *the same weight as gold*. Pliny also describes a metal *adamas*: “It has sometimes been found in mines and then together with gold. Its hardness is indescribable and so is also its ability to withstand fire.”

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[1] Pierre E. M. Berthelot (1827–1907) was a distinguished French chemist, who had made many notable achievements in organic chemistry and within education. In 1889 he succeeded Louis Pasteur as the permanent secretary of the French Academy of Sciences. In the period 1895–96 he also was the French Foreign Minister.

Were *plumbum album* and *adamas* perhaps platinum?

Rumors of occasional finds of a remarkable metal in the Central European mountains were spread. Agricola, who summarized the situation for chemistry, mineralogy and metallurgy in the middle of the 16th century, mentions nothing that can be related to platinum. Thus, at that time the metal was of no practical importance. In 1679, a Bohemian priest and historian, *Bohuslav Babinus*, published in Prague a large work *Miscellanea Historica Regni Bohemia*, in which he described a substance, which in all probability is platinum: “White gold (which one would swear to be silver except that its weight and a certain yellowish tinge pervading the metal persuaded otherwise), white gold, I say, which is dug out of the mountains. I have seen more than once.” [32.1].

32.3.3
Platinum in South America

32.3.3.1 Before the Spanish Conquest

The people in the province of Esmeralda in present-day Ecuador worked gold from the streams running down the Andes. The yellow metal was sometimes contaminated with a white one, which had to be removed by hand. This was platinum, which was thus known long before it began to be investigated in Europe in the 18th century AD. W. C. Farabee, an anthropologist from the University of Pennsylvania wrote [32.2]:

> The native Indian workers of Esmeralda were metallurgists of marked ability; they were the only people who manufactured platinum jewelry. In our collection [in the University Museum] will be seen objects of pure platinum, objects with a platinum background set with tiny balls of gold used to form a border, and objects with one side platinum and the other gold.

It is impressive to have objects manufactured in platinum, but how was it possible as its melting point is as high as 1772°C? Objects found on the small island of la Tolita off the coast of Esmeralda and dated to 100–400 AD were carefully studied by K. Bergsöe in the 1930s [32.3]. He paid particular attention to the technique used for their manufacture. The Indians had mixed small platinum grains with a small amount of gold dust. The mixture was placed on charcoal and heated with a blowpipe. The heat obtained is not sufficient to melt platinum, but gold melts and flows out as a binding phase and solders the platinum grains together. At the same time the two metals penetrate each other to some extent, creating tiny alloy layers. Soldering and superficial alloy formation lead to pore closure. Solid and forgeable platinum components are obtained. This advanced powder metallurgy is in fact an important technique nowadays. It is described for cemented carbide in Chapter 26 Tungsten.

32.3.3.2 The New Granada

Once Columbus had discovered America, Spaniards and Portuguese competed for the regions that constitute South and Central America. After some disputes the fields of interest were defined for the two European countries. In 1494, the Borgia Pope Alexander VI draw a line, running south from the mouth of the River Amazon to southern Brazil. Regions west of this line were Spanish, the region east of it was a Portuguese possession.

The huge Spanish territory was divided into two vice-royalties: New Spain north of Panama with Mexico as capital and Peru to the south with Lima as its capital. Later, in 1718, one part of Peru was detached and reorganized to a separate vice-royalty, New Granada, with the old native city of Santa Fé de Bogotá as capital. What noble metals did the Spaniards find in their large empire? Gold and silver in many places. It was, however, in New Granada that white gold was rediscovered and given its name, platinum.

32.3.3.3 **Chocó – The Platinum Country**

Chocó was a region in New Granada, a long narrow strip of land between the Andes and the Pacific. The interior of the region was a dense jungle with meandering rivers, a dangerous place for the Spaniards, who had early captured the safer coastal area. In the middle of the 16th century small expeditions were sent into the jungle. On their return they told of hostile natives, which further reduced the interest in seizing this part of Chocó. But they also spoke of rich findings of gold, real gold and white gold. Young and brave people became anxious to be rich even if they had to stand up to risks and hardships. Not until the end of the 17th century was the whole Chocó pacified and settled, and during the two decades around the turn of the century exploitation of the metal and mineral resources was organized. Spanish immigration increased markedly and perhaps the development contributed to the founding of New Granada in 1718. The import of Negro slaves from West Africa for work in the deposits is connected with a streak of anguish.

The sources of gold in Chocó were among the richest in the world at that time but miners, eagerly working in the fields, soon observed a drawback with the Chocó deposits. Small grains of a white metal appeared with gold in washing and they had to be removed by laborious sorting by hand. This *oro blanco*, white gold, looked like silver but was something else. At this time the metal got its Spanish name, Platina, a disparaging designation for *Plata*, the word for silver. The first reference to *platina* or *Platina del Pinto* is from 1707 (Pinto was a small river, no longer known by that name). A first, not very creditable, use of platinum was to adulterate gold. This behavior was forbidden but the practice continued for many years. During almost the whole century, platinum itself was regarded as worthless. It was regarded by some people as a sort of gold that was not yet ripe. They thought that by being thrown back into the rivers it might get time to mature and turn yellow.

> The old knowledge among the native peoples was, however, not forgotten. The Incas, who had overrun Esmeralda well before the Spanish conquest, adopted both the appreciation of platinum and the technique of manufacturing ornaments from it. Spanish craftsmen learned from them and some of the articles they fabricated have been known in history. In 1730 “a rapier guard and a set of buckles in platinum” was manufactured as a gift to the Viceroy of New Granada. It was said of the metal used that it was heavier than gold, brittle and with bad coherence. It had been obtained as dross in the district of Chocó.

The negative view of platinum is in accordance with a description given by a Frenchman, *Jean Baptiste Leblond* (1747–1815). He had spent some years in South America and had brought home to Paris as much as 100 kg of platinum, certainly illegally. He said that

> *...gold and platinum were recovered together by washing and were then separated grain by grain. Also amalgamation with mercury was used. The platinum had to be thrown into the river. In addition all export of platinum was forbidden in order to prevent fraud arising from melting it with gold. The gold from Chocó was sent to Mints in Santa Fé de Bogotá and in Popayan, where a final separation was made of platinum present.*

He read a paper in 1785 to the Academy of Sciences in Paris about platinum and the deposits in the provinces of Novita and Citara in the district of Chocó.

What Leblond does not mention is that the Viceroy of New Granada was ordered in 1759 to collect a large quantity of platinum from the dumps around the Mints at Bogotá and Popoyan and send it to Spain. From this shipment, platinum was forwarded to chemists and scientific institutions in Europe. This was of great importance in the development of knowledge about platinum over the following three decades.

32.3.3.4 **Platinum Without Gold**

Colombia gained independence from the Spanish Crown at the beginning of the 19th century. The independent Republic of Columbia was founded and *Simón Bolivar* was leader in the struggle for liberation. He contacted the "traveling scientist" *Alexander von Humboldt*[2] in order to get his help with the recruitment of a geologist and chemist, who could develop mineral prospecting and metal production in the new country.

On von Humboldt's recommendation the Frenchman *Jean Baptiste Boussingault* was engaged in 1822. He had many duties involving geology, metallurgy and agriculture. He asked a very important question: In Chocó we find platinum and gold grains mixed. Weathering of rocks has formed them far up in the mountains. Are gold and platinum mixed even there, or do they have different origins in special gold and platinum deposits? In 1826 he arranged an expedition to a high plateau, 2700 m (9000 feet) above sea level, to the village of Santa Rosa de Osos near Medillin. There he found – for the first time – a deposit of platinum grains mixed with oxides of iron but free from gold. The grains were of the same form and appearance as those found – together with gold – in the valleys of the Chocó. Von Humboldt was immediately informed and he published the discovery, in the name of Boussingault, in *Annale de Chimie et de Physique*, 1826, 32, 204–212.

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[2] Alexander von Humboldt had studied at the Bergakademie Freiberg in Germany together with André Manuel del Rio (see Chapter 21 Vanadium), with whom he had continued contacts when del Rio was put in charge of the *Real Seminario de Mineira* in Mexico, a position he retained even after Mexico's liberation from Spain.

32.3.4
Platinum and the Form of the Earth

The first person to make Europe familiar with the Spanish word *platina* was a young naval officer Antonio de Ulloa. In the 1730s physicists and astronomers were discussing whether the earth was sharpened at the poles (like an egg) or flattened (like an oblate spheroid) as Newton had maintained. The French Academy of Sciences decided to search for the truth. They needed to compare the length of a degree of longitude near the pole and near the equator. One expedition was sent to Lapland, far north in Sweden, and the French king Louis XV applied for permission from his uncle, the Spanish king Philip V, that another should be allowed to make the same measurement at Quito near the equator in New Granada. The answer was yes but on one condition: two Spanish officers, educated in science, should be allowed to participate. One of them was Don Antonio de Ulloa, then 19 years of age. In 1735 the expedition left Europe and in the next year its astronomical and physical observations were made. After that de Ulloa had time to explore the territory and pick up information about gold and platinum deposits. On the way back their ship sailed round Cape Horn but was captured by a British warship. De Ulloa was imprisoned and sent to London. There he got to know William Watson of the Royal Society and told him about platinum in New Granada. The young Spaniard was released and allowed to return to Spain. In 1748 he compiled a book about the South American journey, in which he also described the gold and platinum district of Chocó. In the book he also mentions that several gold mines had been abandoned due to their disturbing content of platinum. Watson read a translation of the platinum section to the Royal Society in 1750.

The result of the expeditions? Newton had been right. The earth is an oblate spheroid.

32.3.5
Platinum in Europe

The new metal, platinum, occurred in South America. The chemical knowledge existed in Europe. In the middle of the 18th century samples of platinum found their way over the Atlantic and reached laboratories in England, Germany, France and Sweden.

32.3.5.1 A Start in England and Germany

A first sample of platinum for scientific examination reached Europe in 1741. The Englishman *Charles Wood* had settled on Jamaica after difficulties in his father's iron industry in England. He worked for the government of Jamaica as an assayer of gold and silver. He bought a quantity of platinum from a smuggler. He made his own examination and noted that the metal occurred as grains the size of shot in magnetic sand (magnetite). He found that it was impossible to melt the metal without the addition of copper, silver or tin. After his return to England he handed the platinum sample over to Dr William Brownrigg, a general practitioner. He made some simple experiments regarding the metal's solubility in acids but soon passed the material on to *William Watson* of the Royal Society for a more careful investigation. In 1751 Watson wrote to his friend professor G. M. Bose at the University of Wittenberg in Germany. In particular, he mentioned that platinum takes a high polish on grinding and recommended the metal for telescope mirrors. Professor Bose published this information in the first number of a journal on popular science, *Physical Curiosities* in Germany.

Watson's achievements aroused curiosity about platinum in Europe. The French chemist A. F. de Fourcroy wrote at the end of the century:

> These first attempts, which announced very extraordinary properties for the new metal, made a great commotion in Europe at a time when the discovery of a metal, as singular as this, appeared to be a quite unexpected phenomenon. Then the great chemists of Europe set to work on platinum and its distinctive properties.

In London William Lewis continued the work with platinum that William Watson had begun. In 1754 he presented a paper to the Royal Society with the title *Experimental Examination of a white metallic Substance said to be found in the Gold Mines of the Spanish West Indies, and there known as by the Appellations of Platina, Platina di Pinto, Juan Blanca*. In five papers he described his findings about the new metal:

- Pure platina is a white metallic substance, to some small degree malleable
- It is not brought into fusion by the greatest degree of fire but is permanent in the fire
- Nearly as ponderous as gold
- Indestructible by nitre; unaffected by sulphur
- The spirits of sal-ammoniac added to solutions of platina (in aqua regia) diluted with distilled water, precipitated a fine red sparkling powder; which exsiccated and exposed to the fire in an iron ladle became blackish; without at all fulminating, which calces of gold, prepared in the same manner, do violently.

Lewis made many attempts to melt platinum by alloying with other metals and he tried, in the same way, to make platinum more malleable. He succeeded in melting the alloys but he made little progress regarding ductility. When platinum was melted together with an equal part of gold a brittle alloy was obtained.

In Berlin, Andreas Sigismund Marggraf (see Chapter 14 Magnesium and Calcium), director of the chemical laboratory at the Berlin Academy of Sciences 1754–1760, made many experiments with platinum. He observed traces of mercury in the native platinum and concluded that it was a residue from an amalgamation process. He repeated Lewis's experiments with sal ammoniac and obtained the same result.

32.3.5.2 Early Swedish Platinum Efforts

In the middle of the 18th century, the Laboratorium Chymicum in Stockholm (see Chapter 30 Cobalt) was an institution with a worldwide reputation. When the platinum question came up in Europe it was natural that the eyes of European chemists were directed towards Stockholm. It was *Henrik Scheffer* who was assigned to examine the new metal.

> Henrik Scheffer (1710–1759) studied mathematics in Uppsala with Anders Celsius and chemistry under Georg Brandt at the Laboratorium Chymicum. In 1739 he became manager of a gold mine and factory in Ädelfors but returned about 1750 to Stockholm and the Laboratorium Chymicum. In 1775 professor Torbern Bergman in Uppsala published Scheffer's Collected Lectures in Chemistry.

In November 1751 he presented a paper to the Royal Swedish Academy of Sciences in Stockholm, a report with the title *White Gold, or the seventh Metal*. Scheffer began with the statement: "In 1750, in June I got from Herr Assessor Rudensköld[3] a dark sand, which the Assessor had got in Spain with the information that it comes from West India."

And he continued:

> This sample consists of dark grains of sand, grains of iron ore, attracted by the magnet, some genuine grains of gold and finally flat triangles, white as silver, which were not all attracted by the magnet. These triangular metal grains seemed to be iron, which for some reason had been white on the outside; strangely enough they are not drawn by the magnet although the are as malleable as any iron may be.

Scheffer managed to separate 40 grains of the unknown metal and used them for investigation. The metal was not soluble in sulfuric nor in nitric acid. Aqua regia dissolved it easily. The metal could not be melted at the highest temperature obtained but addition of copper made fusion possible. Scheffer made the important finding that platinum could be melted at a rather low temperature when mixed with arsenic. Modern physical research confirms this. Pure platinum melts at 1772°C and that temperature was impossible to reach in the middle of the 18th century. At an arsenic content of 5% the melting starts at about 600°C and is complete at 1450°C. The eutectic alloy (with the lowest melting point) has an arsenic content of 13% and melts at 600°C.

Scheffer states that the new element is not one of the six metals hitherto known in all countries. It is not gold or silver and does not contain copper, tin, lead or iron. It is a seventh metal, a new noble metal, as resistant as gold and silver. It is hard but also malleable. He observed – like Lewis and Marggraf – that when ammonium chloride was added to a platinum solution in aqua regia a red precipitate was formed. This

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[3] Ulrik Rudenschöld was in 1740–44 secretary at the Swedish embassy in Madrid. No doubt he had heard the rumors about a new metal from South America. Obviously he had also got samples of the metal, which he handed over to the Laboratorium Chymicum in Stockholm.

note became important in subsequent research work (Wollaston and Tennant section 32.4.1 in this chapter), which led to the discovery of osmium and iridium.

Scheffer also gave a recommendation for a practical use of the new metal. No other metal, he says, is so well suited for manufacturing telescope mirrors. It is as resistant as gold to attack from air and moisture. The fact that it is colorless is a benefit when compared to gold. He would like to see an alloying addition that makes both melting and polishing possible. He was obviously not satisfied with his own alloying element arsenic. Perhaps the quality of the polished surface was impaired.

32.3.5.3 **Spanish–Swedish Contacts**

In 1751, the Spanish king Ferdinand VI sent Don Antonio de Ulloa out for a scientific European tour. In the fall de Ulloa spent some weeks in Stockholm and met Swedish scientists. Certainly he met Henrik Scheffer, who at that time was in the final phase of his platinum investigation. De Ulloa was also elected as a member of the Swedish Academy of Sciences at its meeting on 12 October. The secretary of the Academy at that time was Pehr Wilhelm Wargentin, astronomer and mathematician. Probably he exchanged thoughts with his Spanish guest about the flattening of the earth at its poles.

32.3.5.4 **A French Platinum Bomb**

The French count and scientist G. L. Leclerc de Buffon (1707–88) dropped a bombshell in July 1773. At a conference in Dijon Academie des Sciences he tried to destroy the belief that platinum is a specific metal in the way that gold, silver, copper and iron are. He thus objected to what Scheffer had asserted and with him other scientists such as Watson, Lewis and Marggraf. De Buffon declared:

> It is improper that chemists have regarded platinum as a new metal, perfect, individual, and different from all the others. It is not believable that one may include in the class of metals a substance that is neither ductile nor fusible. It is not at all a new metal but a mixture, an alloy of iron and gold, formed by nature.

De Buffon was far from being a nobody. He contributed greatly to the strong position of French science from the middle of the 18th century. He edited a monumental work in 44 volumes, *Histoire naturelle, générale et particulière* (together with L. Daubenton and B. G. E. de Lacépède). He had a good reputation, although he was inclined to make hasty generalizations.

In connection with his speech in Dijon he presented a sample of platinum to Guyton de Morveau, asking him to verify that it was possible to divide the metal into two parts, one magnetic (iron) and one nonmagnetic (gold).

Several chemists in France were skeptical of de Buffon's cocksure assertions. P. J Macquer and A. Baumé in fact regarded platinum as a genuine metal. Torbern Bergman in Uppsala finally refuted the iron–gold theory.

In 1760 Berman had obtained a piece of platinum from Claes Alströmer, who had visited Spain in order to study sheep breeding. For some reason (compare section 32.3.3.3 and the Spanish intention to distribute platinum for scientific examinations) he then obtained a sample of the new metal and handed it over to his friend Torbern Bergman.

In 1777 professor Bergman presented a report to the Swedish Academy of Sciences. It was published in Latin (1779), in French (1780) and in English (1784). In the conclusion he wrote:

> Since platina surpasses all metals except gold in weight[4], and is always found to be contaminated by iron, some scientists have believed that it could not be freed from this, that platina is nothing but a mixture of gold and iron. However, Dr. Lewis has, for several reasons, rejected this opinion. By melting together gold and iron, in whatever proportion, no such alloy is obtained which in specific gravity or other properties resembles platina in the least. Furthermore the amount of iron in the natural platina can be so reduced that it becomes hardly detectable...

32.3.5.5 **An Alchemical Note on Platinum in the Memoirs of Casanova**

The story of the discovery of the elements is illustrated in the most unexpected sources, in this case Casanova's memoirs. In 1757 a wealthy woman in Paris, the Marquise d'Urfé, had expressed a wish to meet Casanova in her home. On his arrival he was somewhat astonished to find that she liked to discuss and demonstrate chemistry. Alchemy and occultism were her special interests, and she showed her complete alchemical laboratory – among other things a vessel containing platina del Pinto, which she intended to convert into gold. "C'etait M. Vood en personne qui lui en avait fait présent l'anné 1742" (about Charles Wood see section 32.3.5.1). The amazed womanizer had to accept a detailed lesson on platinum. She showed how platinum resists attack from hydrochloric, sulfuric and nitric acids, but yields to aqua regia. From its aqua regia solution platinum could be precipitated by sal ammoniac, "which never was possible with gold". Further she demonstrated that platinum is more difficult to fuse than gold. She could, however, melt platinum by means of a burning mirror! How was she able to do this? Perhaps she used Henrik Scheffer's recipe and added arsenic, truly a proper ingredient for an alchemist.

32.4
The Discovery of Platinum Metals in Platinum

32.4.1
Tennant and Wollaston

William Hyde Wollaston (Figure 32.1) was more significant than anybody else in platinum research, and even for the technology of the platinum metals. He and his colleague *Smithson Tennant* showed that naturally occurring platinum is an alloy, con-

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[4] In fact the density of platinum is higher than that of gold. Bergman had examined natural platinum, which also contains the lighter palladium, not discovered when Bergman made his investigation.

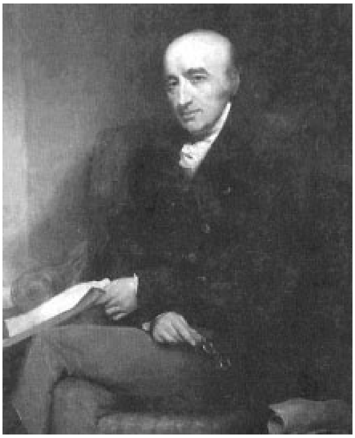

Figure 32.1 William Hyde Wollaston (1766–1828). (Reprinted from ref. [32.1] and reproduced with permission from the Royal Society of London.)

taining several metals. One of Wollaston's important achievements was his manufacturing of pure, malleable platinum, even on a commercial scale, and he developed the industrial use of the metal.

Wollaston was born in 1766 and studied science and medicine in Cambridge. At first he worked as a doctor but he gave up medicine in order to carry out physical and chemical research. He gradually attained a great reputation. Berzelius, who met him in London in 1812, expressed his admiration for his knowledge and personal integrity. "I have got more from an hour's conversation with him than from reading heavy printed writings." In his travel diary Berzelius writes that there is a saying that "whoever argues against Wollaston is wrong".

Smithson Tennant, born in 1761, started to study chemistry at the university in Edinburgh in 1781 and continued in Cambridge in 1782. In the summer of 1784 he made a tour in Sweden and met Carl Wilhelm Scheele and Johan Gottlieb Gahn. Several mines and factories were visited. On the return journey he passed through Helmstädt in Germany, where he met Lorenz Crell. The following year he visited Lavoisier in Paris and Guyton de Morveau in Dijon. In Cambridge, Tennant and Wollaston became good friends and a lengthy co-operation began. They agreed to carry out joint research work on platinum. Wollaston was particularly interested in developing a method for the production of malleable platinum, and he wanted the technique to be applicable on an industrial scale. The work research produced unexpected results – the discovery of four new metals, hidden in natural platinum.

At the start of the 19th century it was known that platinum is soluble in aqua regia. Likewise known was the fact that ammonium chloride precipitates the platinum from the aqua regia solution. In modern chemical terms the precipitate is ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$.

Two further important observations had been made. Firstly, when natural platinum is treated with aqua regia a small black residue, difficult to dissolve, is obtained. It was thought to be some contamination or graphite. The other observation concerned the color of the chloroplatinate precipitate, which could vary from light yellow to dark red. The variation seemed to be connected with the black, undissolved residue. If the treatment with aqua regia had been very careful, the black residue was large and the precipitate light yellow. On the other hand, after a vigorous acid treatment the residue was partly dissolved and the precipitate was dark red. Henrik Scheffer had described his platinum precipitate as definitely red.

On Christmas Eve 1800, Wollaston and Tennant bought about 170 kg platinum for £795 from a London merchant, probably smuggled goods. It had come from Jamaica and originally from Cartagena in New Granada. With this material they began an extensive investigation. They agreed on a distribution of the work, implying that Tennant would examine the black residue, while Wollaston would investigate the solution after the aqua regia treatment.

32.4.2
Osmium and Iridium

Tennant's curiosity was aroused and he set to work eagerly. In 1803 he wrote to Joseph Banks, president of the Royal Society, that the black residue was not graphite as many investigators had thought. Instead it contained metals, which up to now were unknown. It was an important letter. Through it he secured priority in the coming discoveries. Investigations had also been started in France. In 1803 the mining engineer *H. V. Collet-Discotils* had published results from such investigations [32.4]. A. F. de Fourcroy and N. L Vauquelin, known from the discovery of chromium, were also on the same trail [32.5]. They had found that the black residue was attacked by molten potassium hydroxide. On treatment of the melt with water a green solution and a green flocculent residue were obtained. They thought that the solution contained chromium, which Vauquelin had discovered in 1797 and that the precipitate contained an unknown metal.

Tennant continued tirelessly in 1803. He also treated the black residue with fused potassium hydroxide and leached the product with water. He showed that the solution did not contain chromium. When he neutralized with acid he could isolate the hydroxide of an unknown metal. Tennant was astonished when he attempted to transform the hydroxide to oxide by calcination. The oxide was volatile and disappeared from his crucible. He repeated the experiment and saved the oxide by distillation. The colorless oxide was condensed to an oily liquid, which at room temperature changed to a semi-transparent, pale yellow substance. In all stages of the process the new oxide had a characteristic unpleasant smell. Tennant took this as a reason to name the new element *osmium* after the Greek word for *smell*.

In the green precipitate from the water treatment of the alkali melt, Tennant found an additional metal. When it was dissolved in acid several colors were observed. For this reason the new element was given the name *iridium* after *iris*, rainbow. The French scientists Fourcroy and Vauquelin did accept Tennant's priority.

32.4.3
Palladium and Rhodium

Wollaston worked on his assignment in accordance with the mutual agreement. He dissolved natural platinum in aqua regia, removed the black residue by filtering and examined the filtrate. The excess of aqua regia was evaporated. When he added mercury cyanide, drop by drop, a yellow precipitate was formed. On calcination a metal was obtained that was not platinum. He named the new element *palladium* after the asteroid *Pallas*, discovered in 1802. The discovery year for palladium was 1803. Today we know that it was the almost insoluble palladium cyanide $Pd(CN)_2$ that Wollaston precipitated with mercury cyanide.

> Wollaston intended to do more experiments in order to reassure himself about the results. On the other hand he wanted to make his discovery public as soon as possible as he was afraid that the Frenchmen were on the same track. Now he used a very unconventional and obscure method of publication. He wrote a small handbill to members of London's scientific community, informing them anonymously about a new noble metal, *Palladium* or *New Silver*. It was announced that the metal could be obtained only in the shop of a well-known collector and dealer in minerals, situated in London's Soho. A young Irish chemist and member of the Royal Society, *Richard Chenevix*, bought the whole quantity and examined the metal. He then submitted a presentation to Royal Society and asserted that the metal was not new at all but an alloy of platinum and mercury in the proportion of 2 to 1. Mr. Chenevix broadcast his results all over Europe. Well-known chemists such as V. Rose and M. H. Klaproth in Berlin also examined the same palladium sample but could not detect any mercury in it. Vauquelin in Paris checked the properties claimed in the handbill, and found them to be correct. Not until 1805 did Wollaston put an end to the mystery and reveal himself as the discoverer of palladium. This was an unpleasant surprise to Chenevix after his arguments against the existence of this new element. He remained, however, good friend with Wollaston and his family. He himself abandoned science and turned to writing novels and plays. Desmond Reilly has told the sad story of Richard Chenevix and his palladium adventure [32.6]

Wollaston continued his investigation of the aqua regia solution of platinum in 1803. He then discovered an additional metal in the following way. An aqua regia solution was partially neutralized with sodium hydroxide. Platinum was precipitated with ammonium chloride in the usual way and palladium with mercury cyanide. The common precipitates of chloroplatinate and palladium cyanide were removed by filtering. Hydrochloric acid was added to the filtrate and the solution was evaporated to dryness. Wollaston tried to dissolve the residue in alcohol but a beautiful dark-red powder remained undissolved. It proved to be a double chloride of sodium and a new element. Wollaston called the new metal *rhodium* because of the rose colors of its salts. The metal itself was prepared by hydrogen reduction and washing away the sodium chloride with water.

The result indicates that Wollaston's aqua regia attack had been very powerful since rhodium had been dissolved. The modern acid treatment for separation of platinum metals is carried out in a careful and well-balanced process. Then rhodium stays undissolved.

32.4.4
Ruthenium

At the beginning of the 19th century, Vauquelin in Paris wrote, "It is rumored that platinum has been discovered in Russia." In 1820 it was officially confirmed that platinum in fact had been found near Yekaterinburg on the slopes to the east of the Ural Mountains. At the mining laboratory in St Petersburg an analysis in 1824 showed that in reality it was so-called *osmiridium* with 60% iridium, 30% osmium, 2% platinum, 0.7% gold and 5% iron. Later in the same year other samples were analyzed showing a platinum content of 97%. The Russian authorities rapidly decided that the deposits of platinum metals should constitute a state-owned monopoly. Samples from the Russian platinum deposits were sent for examination to different institutes and universities in the Russian Empire. This resulted in great attention to and interest in platinum among scientists in Poland and in the Baltic States. In fact the Pole *Jedrzej Sniadecki*, professor at the University of Vilnius, started a platinum research long before the official Russian interest in this field had been awakened. He was well aware of Wollaston and Tennant and their investigations and repeated them with platinum from South America. He said he had found a further element in natural platinum, a metal that he named *vestium*, after the asteroid *Vesta*. He published his results in Poland in 1808 and in Russia in 1809. A commission in Paris, of which Fourcroy and Vauquelin were members, could not verify the new discovery.

In 1828 G. W. Osann, professor in Dorpat, also found a sixth platinum metal. This time it was Berzelius, who checked and found that the samples from the discoverer contained no elements other than palladium, rhodium, osmium and iridium.

One further scientist was encouraged to investigate the Russian platinum finds. He was *Karl Karlovich Klaus*, born in Dorpat, Estonia, in 1796. Karl grew up under poor circumstances and was orphaned early. Yet he gained an education in a pharmacy in St Petersburg. After that he obtained a position in 1831 as an assistant in the university of his hometown. Seven years later he was appointed to be a professor of chemistry at the University of Kazan (east of the Volga) and there he began to do some research into platinum metals. He repeated the well-known experiments with dissolution in aqua regia and observed the black residue containing osmium and iridium. He treated such a residue with potassium hydroxide and potassium nitrate in a silver crucible. The melt was leached in a large volume of water, which was allowed to act in darkness for four days. The solution was filtered and neutralized with nitric acid and a precipitate of osmium hydroxide was formed. The oxide was distilled off using Tennant's method. What Klaus saw, but which escaped Tennant, was a residue after the distillation, a chloride of a previously unknown element. The discovery was made in 1844 and he named the new element *ruthenium* after Russia. A sample was sent to Berzelius for confirmation. At first Berzelius was doubtful, but Klaus sent more samples and descriptions and eventually Berzelius was convinced and announced the discovery in Europe.

In 1852 Klaus returned to Dorpat and a professorship in chemistry at the university there. He continued his platinum metal research until his death in 1864.

32.4.5
Malleable Platinum

The original goal set by Wollaston for his platinum research was not to find new elements. Instead it was to find a method for refining platinum in order to make it malleable, a method that could be used in large-scale production. Obviously he succeeded but it would seem that he kept the manufacturing process secret. Not until the last weeks of 1828 – when he knew he was close to death – did Wollaston agree to reveal the details of his process. He did this by dictating a letter to the Royal Society. An important point in his process was that the aqua regia used for dissolution was not too strong. The acid had to be prepared from hydrochloric acid and nitric acid diluted with water. This slowed down the process but as compensation the dissolution would continue for several days with natural metal always present. By this means the dissolution of iridium from the natural platinum was obstructed. When the chloroplatinate had been precipitated it had to be transformed to platinum by careful heating. Grinding of the small platinum particles could not be done mechanically with hard tools but by hand with wooden tools. It was important that the surfaces of the small platinum particles were clean and active in the following powder metallurgical forming and sintering.

32.5
Occurrence of the Platinum Group Metals

32.5.1
The Geology

Platinum has a certain tendency to form sulfides and arsenides, as for instance in the minerals *cooperite* PtS and *sperrylite* $PtAs_2$. The inclination of platinum to form sulfides has the consequence that platinum often occurs with copper and nickel ores, especially pentlandite. The metals are, however, mainly found as metallic phases, alloys with each other, with gold and with iron. The important alloy osmiridium with high contents of osmium and iridium also occurs in nature.

Primary platinum ores have a magmatic origin. The largest known deposit of this type is the South African Bushveld complex. At the bottom of this the minerals sperrylite and cooperite have separated along with chromite and pyrites of nickel, copper and iron. The platinum content of the mined ore is 3–20 g/tonne. Figure M46 shows platinum group element minerals and gold Au in coarse *pyroxene-anorthosite*. The picture covers a 30-mm width of the specimen, taken from a drill core from the Merensky Reef in the Brakspruit Deposit at the western limits of the Bushveld Complex, near Marikana Town, South Africa.

> Rumors of platinum in South Africa began to circulate in 1923 and many prospectors tried to find the mineral sources. In June 1924 the consulting geologist Dr. Hans Merensky in Johannesburg received by post a small bottle with a grayish-white concentrate. It had been found by a farmer, Andries Lombard in Maandagshoek to the north of Lydenburg in the Transvaal. Analysis of the sample confirmed the presence of platinum, rhodium and iridium. Merensky immediately went to investigate the area. He located the basic mineral in a reef, still known as *The Merensky Reef*.

The Stillwater deposit in Montana is similar to the Bushveld deposit. Unlike Bushveld the material is richer in palladium than in platinum. The nickel sulfide deposits in Sudbury, Canada, and Norilsk in Russia are important sources of palladium and platinum.

Weathering, washing and transport of primary deposits formed alluvial deposits of platinum group metals. Platinum and other heavy metals and minerals were concentrated in clay and sand. Secondary deposits occur in the Urals and Colombia. Osmiridium, originally found in Russia, is nowadays mainly obtained along with secondary deposits of gold in Alaska and in Witwatersrand in South Africa.

The content of platinum metals is low in the earth's crust. Approximate contents are given in parentheses (ppm): Ru (0.001), Rh (0.001), Pd (0.015), Os (0.0015), Ir (0.001), Pt (0.005).

32.5.2
Platinum Group Metals – Reserves

In the early stages of platinum's discovery South America and especially today's Colombia and Equador had the world's largest known platinum reserves, but this is not the situation today. Active prospecting has revealed new deposits that have deprived South America of its leading position. This has now been taken over by South Africa, where platinum was discovered in 1924 and which nowadays controls more than 85% of the world's platinum reserves. An estimate of the reserves in different countries is given in Table 32.2.

Table 32.2 Reserves of platinum group metals

Country	Reserves Tonnes	Reserve base Tonnes
South Africa	63 000	63 000
Russia	6 200	6 600
United States	1 700	2 200
Canada	310	390
Other countries	700	850
World total (rounded)	72 000	73 000

Figures taken from ref. [32.7].

Russia entered the platinum story late, but today is a big producer. However, it is not the deposits in the Urals that are worked. Three important deposits are linked with nickel and copper ores, one in Norilsk, east of the river Jenisej in Siberia and two on the Kola peninsula, Petschenga (Petsamo) and Monchegorsk. Canada has important deposits of a similar type in the Sudbury region.

The biggest mining of platinum-group metals occurs in South Africa. In the so-called Bushveld complex in Transvaal the metals are concentrated in big "reefs", the Merensky Reef, Platreef and UG2. In Table 32.3 the metal content and metal type in the Merensky Reef are compared with data from the Canadian Sudbury and the Russian Norilsk deposits.

Table 32.3 Platinum group metals in three deposits

	Norilsk	**Sudbury**	**Merensky**
Metal content g/tonne	**4**	**0.7–0.9**	**8.1**
Metal composition:			
% Pt	25	38	59
% Pd	67	40	25
% Ru	2	2,9	8
% Rh	3	3,3	3
% Ir	2	1,2	1
% Os	1	1,2	0,8
% Au			3,2

The Stillwater mine in Montana is the only primary palladium–platinum producer in the United States. Its ore is rich with a content of 19.9 g/tonne of Pd+Pt in the proportion 3:1

32.6
Production of Platinum-group Metals (PGMs)

The two metals platinum and palladium are of the greatest economic importance among the PGMs. The other four – rhodium, ruthenium, iridium and osmium – are obtained as by-products.

32.6.1
Mining

There are fewer than ten significant mining companies in the world producing platinum metal ores. Table 32.4 shows the most important ones.

Table 32.4 Data on important deposits

Country	Region	Start date	Major product	By-products
South Africa	Bushveld Complex	1925	Pt	Pd, Rh
Russia	Norilsk, Siberia	1935	Cu, Ni	Pd, Pt
USA	Stillwater, Montana	1987	Pd	Pt, Ni
Canada	Sudbury, Ontario	Abt.1890	Ni	Cu, Pd
Zimbabwe	Great Dyke	1996	Pt	Pd, Ni

Cited from Johnson Matthey: http://www.platinum.matthey.com/production/production.html

32.6.2
Enrichment of the PGMs

The ores in South Africa and in the United States are primarily worked for their contents of PGMs while the metals from the Russian and Canadian deposits are obtained as by-products from the working of nickel and copper ores. After mining both ore types are finely ground and enriched by flotation. Gravitational techniques may also be used.

From the copper and nickel ore concentrates platinum metals are collected in the anode slime from the copper electrolysis or in a residue after the nickel matte treatment with CO in the MOND process. This residue and the anode slime are worked up in a noble metal refinery.

32.6.3
Separating Platinum, Palladium, Iridium, Osmium, Rhodium and Ruthenium

Methods for separating the different platinum metals are complicated and are partly kept secret. The traditional method with dissolution in aqua regia is still used, in which platinum, palladium and gold are dissolved while the other platinum metals stay undissolved. Gold is obtained from the solution by reduction, platinum is precipitated as ammonium hexachloroplatinate and palladium as a dichlorodiammine compound. The residue after the first aqua regia treatment contains iridium, rhodium, osmium and ruthenium. They are separated in several complicated steps.

The liquid–liquid extraction technique is increasingly used for separation. A solution containing the PGMs passes an organic solution in a counter-flow process. For each metal a specific extractant complexes the ions and transfers them into the organic phase. This phase is then “stripped” and the metal in question is obtained. Additional distillations are used for osmium and ruthenium as well as a final ion-exchange procedure for rhodium.

32.6.4
Quantities of Platinum, Palladium and other PGMs Produced

World production in 2000 of PGMs, by country, is shown in Table 32.5.

Table 32.5 Quantities of metals produced in the year 2000

Country	Platinum kg	Palladium kg	Other PGMs Rh,Ir,Os,Ru kg
South Africa	114 500	55 800	36 500
Russia	35 000	84 000	14 100
United States	3100	10 300	–
Canada	6300	10 000	700
Japan[a)]	800	4700	–
Zimbabwe	500	400	40
Other countries	500	600	–
World total (rounded)	161 000	166 000	51 300

Figures taken from ref. [32.7].

a) Production derived entirely from imported ores.

32.7
Uses of the Platinum Group Metals

32.7.1
An Overview

The two main metals in the platinum group, platinum and palladium, are soft, ductile and easy to form. They are resistant to corrosion and high-temperature oxidation. Rhodium and iridium are difficult to work and so are ruthenium and osmium, the last two being almost unworkable in the metallic state. The heavy platinum metals, osmium, iridium and platinum, are very dense. One cubic centimeter of platinum weighs about twice as much as silver or lead. Palladium has about the same density as silver.

The platinum group metals all have strong catalytic activity in *heterogenous catalysis*. In this case the catalyst is present in a different phase from the reactants and products. Reactants from a gaseous or solution phase are adsorbed on the surface of the catalyst. The reaction occurs on *active sites* and the new product is formed. It is then desorbed and the reaction continues. In this field platinum and palladium are much more important than the other PGMs. For optimum catalytic action two or more metals are often combined. The petroleum industry has had the largest demand for platinum metal catalysts, especially in hydrogenation and dehydrogenation processes. Since 1979 the automotive industry has developed as the principal consumer of PGMs. Platinum, palladium and rhodium are used as catalysts for treating automobile exhaust emissions. In homogenous catalysis, reactants, products and catalysts are all present within the solution. This will be exemplified below in connection with the uses of rhodium.

In electronics, platinum, palladium and ruthenium are used for computer hard disks and for multilayer ceramic capacitors. Platinum and rhodium are used in sensor applications, for instance in equipment for measuring temperature. Palladium and platinum are used for dental purposes. As platinum and iridium are very resistant to chemical and high-temperature attack they are widely used for equipment in chemical industry and in laboratories. Compounds of platinum and osmium have been used in medicine for anti-cancer drugs and implanted sensors. Platinum and to some extent also palladium are used as jewelry and for investment items, such as coins and bars.

32.7.2
Platinum

32.7.2.1 Platinum – A Catalyst Before Catalysis

Humphry Davy discovered the catalytic action of platinum in1817. After serious explosions in the coal mines in England he worked on the development of a safety lamp for miners. He observed that gas containing coal particles burned without flame if it passed a platinum wire. Somewhat later J. W. Döbereiner in Leipzig found that hydrogen mixed with air was oxidized to water even at room temperature when the gas mixture was led over finely dispersed platinum. The word *catalysis* did not exist when Davy and Döbereiner made their epoch-making discoveries. It was Berzelius, who introduced the concept *catalysis* and *catalytic power* for the phenomena that Davy and Döbereiner had discovered. He used it in his report for the year 1836 to the Swedish Academy of Sciences. The catalytic discoveries continued. The Frenchman C. F. Kuhlman made an important discovery, which he also patented in 1838. When air and ammonia were allowed to pass over platinum sponge at 300°C in a glass tube, nitrogen oxides were formed, which gave nitric acid with water. The same day as his patent was granted he applied for a new patent, this time for oxidation of sulfur dioxide with air at high temperature and in the presence of platinum. The intention was in this case to make sulfuric acid. That process was in fact not new. In 1831 a young Englishman, P. Philips, had described it. In any case, decades passed before any of the pending or granted patents became used commercially for production of nitric and sulfuric acids. But used they became – on a large industrial scale! However, when the time came the original patents were old and no longer valid. The modern processes are described in Chapter 44 Nitrogen and Chapter 48 Sulfur, respectively.

32.7.2.2 Modern Applications of Platinum – Some Examples

Platinum black, finely divided metal, is a well-established catalyst for hydrogenation and dehydrogenation reactions. Platinum–rhodium gauzes are used as catalysts for the large-scale oxidation of ammonia to nitric oxide.

Platinum is also widely in low-voltage and low-energy contacts in the electronics industry. In chemistry laboratories all over the world platinum is used as for crucibles. Calcination and weighing for gravimetric analysis are carried out in platinum crucibles. In platinum crucibles mineral samples are melted with soda or other chemicals in order to facilitate dissolution. They are also indispensable for treatments with hydrofluoric acid, which is too aggressive for glass beakers, so the excellent chemical and thermal resistance of platinum is used. It is, however, important to remember what Casanova learned. Platinum is attacked by aqua regia, which destroys the valuable platinum crucible.

Platinum has an important use in medicine. The drug *cisplatin* is built of a central platinum atom and two ammonia molecules and two chlorine atoms see Figure 32.2. Cisplatin prevents the duplication of DNA during cell division and rapidly affects the division of cancer cells. It is therefore used in chemotherapy as an anti-tumor drug.

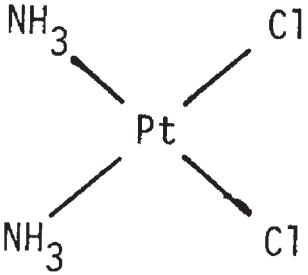

Figure 32.2 The structure of cisplatin, *cis*-diamminedichloroplatinum(II).

Platinum's use in catalytic converters for automobile exhaust emissions is mentioned in the palladium section and its use in thermocouples in the rhodium section.

32.7.3
Palladium

32.7.3.1 The Automobile Catalytic Converter

The largest and fastest growing application of palladium is in the production of automobile catalytic converters, which reduce harmful emissions from the engine. In a modern converter three reactions occur:

Oxidation of unburned hydrocarbons
e.g. $C_8H_{10} + 10.5O_2 \rightarrow 8CO_2 + 5H_2O$

Oxidation of carbon monoxide
$CO + 0.5O_2 \rightarrow CO_2$ or
$CO + H_2O \rightarrow CO_2 + H_2$

Reduction of nitrogen oxides NOX
$NO + CO \rightarrow 0.5N_2 + CO_2$

One further cleaning effect is that lead is avoided in the exhaust, as the converter requires unleaded gasoline to function. Normal petrol previously had 0.15 g lead per liter. The unleaded gasoline is not quite free from lead but its content is as low as 0.01 g/l.

A catalytic converter, Figure 32.3, contains an active catalyst on a carrier. The carrier is encapsulated in stainless steel and placed in the exhaust system between the intake/exhaust manifold and the muffler.

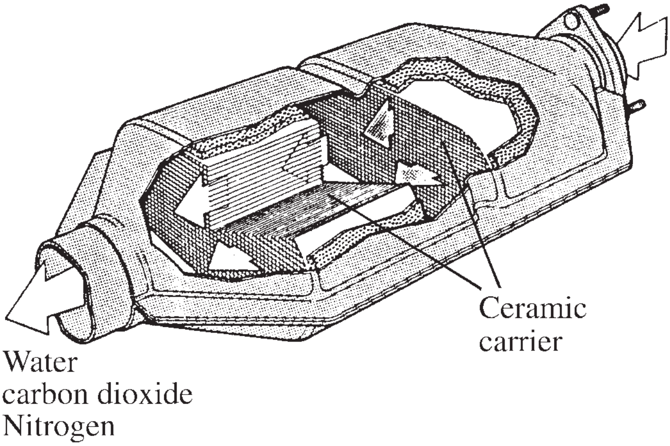

Figure 32.3 An automobile catalytic converter. (Reprinted from the booklet *Petrol Engine Volvo Components*. With permission.)

The carrier is a monolith with a shape similar to a honeycomb. The mineral cordierite $(Mg, Fe)_2Al_4Si_5O_{18}$ is used as the carrier material. Because of its system of channels, the carrier has an active surface of 30 000 m^2. The channels of the monolith are covered by a "wash-coat" of γ-Al_2O_3. An alternative wash-coat carrier is a special stainless steel with 5% Al and micro-alloyed with yttrium and cerium. By a carefully controlled heat treatment in an oxidizing environment Al_2O_3 whiskers are formed. On the wash-coat a layer of platinum metals is applied, which is responsible for the catalytic function. Platinum with 20% rhodium dominated earlier but nowadays palladium-rich alloys or pure palladium are mainly used. In 2001, the automobile industry accounted for nearly 72% of the total palladium demand.

The converter function presupposes careful monitoring of the oxygen activity in the exhaust gases. This occurs with a λ-sensor or a λ-probe. The probe electronically orders the engine to keep the λ-value (the air/fuel ratio) at an optimum, often near 1. For description of the λ-probe see section 17.10.2.3 (Yttrium). The placing of the probe in the converter is shown in Figure 32.4.

The legislation in different countries makes use of catalytic converters necessary. The 1990 *Clean Air Act* in the USA took a comprehensive approach to reducing pollution from motor vehicles. The Act provides for cleaning up fuels, cars, trucks, buses and other motor vehicles. Auto inspection provisions are included in the law to

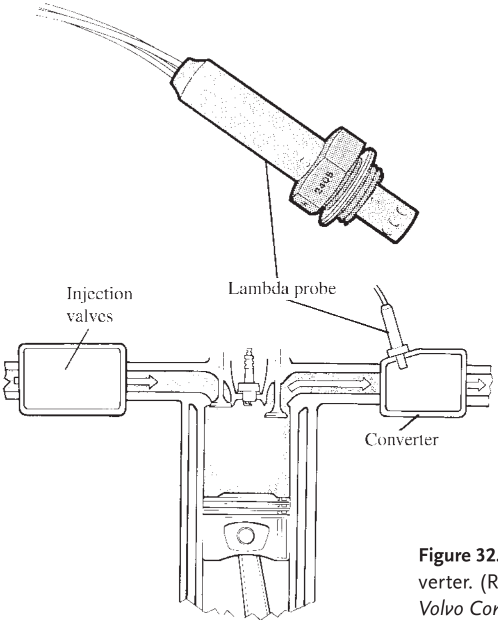

Figure 32.4 The placing of the λ-probe in the converter. (Reprinted from the booklet *Petrol Engine Volvo Components*. With permission.)

make sure cars are well maintained. The 1990 law also includes transport policy changes, which can help to reduce air pollution. According to the *Clean Air Act* 1990 a 40% reduction of the hydrocarbon emissions and a 60% reduction of the emissions of nitrogen oxides should occur during the following 10-year period.

In March 1996, the California Air Resources Board decided that among the cars sold in California in 2003 10% should have zero emissions.

The European Commission proposed new legislation in June 1996, valid until 2010. In step 1, for the year 2000, a 20–40% reduction of auto emissions, compared to 1996 is prescribed. In addition a reduction is demanded in the sulfur content of petrol and diesel oil. From 2010 step 2 starts, which will reduce the emissions to a level of 50–70% of the values in 1996.

32.7.3.2 **Other Applications**

10% of the palladium demand comes from the electronics industry, which uses tiny ceramic capacitors in components for personal computers, telephones, fax machines and other electronically controlled devices. The capacitors consist of many sandwiched layers of palladium and ceramics.

Another 10% end-user of palladium is dentistry. By alloying it with palladium dental gold can be made harder and more wear resistant. The introduction of more gold covering of porcelain crowns has increased this palladium use.

32.7.4
Rhodium

32.7.4.1 Some General Applications

Rhodium is a hard and wear resistant PGM. Advanced optical equipment is plated with thin layers of rhodium in order to get good corrosion and wear protection. Rhodium-alloyed platinum is used in perforated crucibles for making glass fibers. Organic rhodium compounds have been found to be effective catalysts (homogenous) in industrial hydrogenation and in pharmaceutical production of, for instance, the drug L-Dopa for the treatment of Parkinson's disease [32.8].

32.7.4.2 And a Very Special One

Platinum alloys with rhodium are widely used for thermocouples for measuring high temperatures in furnaces and laboratory equipment. A thermocouple, Figure 32.5, consists of two wires of different materials, welded together to form a hot *junction*. This end is placed in the hot furnace and the free ends are connected to a voltmeter, which records the thermal emf (electromotive force) in the circuit. The higher the temperature in the furnace the higher the emf. It is thus possible to graduate the voltmeter in degrees. ANSI (American National Standard Institute), ASTM (American Society for Testing and Materials), and ISA (Instrument Society of America) have standardized five types of base-metal and three types of noble-metal combinations for thermocouples as set out in Table 32.6.

Figure 32.5 A thermocouple for determining temperatures at the level of 1000°C.

The most important combinations for temperatures 700–1200°C are the thermocouple types S and R. Long distances between the hot junction and the voltmeter lead to high costs if noble-metal wires are used the whole way. A large part of the connection may be made of inexpensive "compensation wires", giving no contribution to the emf.

ble 32.6 Standardized noble metal combinations for thermocouples [32.11]

Type of Thermo-couple	Wire 1 (negative)		Wire 2 (positive)		Max. temperature, °C	Thermo-electric output
	Material	Melting point, °C	Material	Melting point, °C		
S	Pure platinum	1769	Pt with 10% Rh	1850	1480	11.5 μV/°C at 1000°C
R	Pure platinum	1769	Pt with 13% Rh	1860	1480	Slightly more than S-type
B	Pt with 6% Rh	1826	Pt with 30% Rh	1927	1700	11.3 μV/°C at 1400°C

32.7.5
Iridium

32.7.5.1 Suitable for Severe Environments

Iridium is the most corrosion-resistant metal known, and was used in making the standard meter bar of Paris, which was a 90% platinum–10% iridium alloy. This is now obsolete as is also the old Pt–Ir kilogram block. Length and mass definitions are now based on fundamental physical constants.

Resistance to high temperatures in severe environments is the background to the use of iridium as the electrode material in spark plugs. In this application it is more resistant than platinum. As a consequence the electrode can be reduced in size, leaving more room for the spark in the chamber.

In modern high-speed plating processes the anodes are insoluble. In the traditional processes with low current densities, anodes of the metal to be plated were used. It is now difficult to find a material that resists the hard attack in the anode process. An anode consisting of a titanium substrate, covered with a mixed oxide IrO_2–Ta_2O_5 has shown a high stability to oxygen attack in an acid medium.

32.7.6
Osmium

32.7.6.1 Mechanical and Medical

Osmium is used as an alloying metal to make soft platinum and palladium hard. The metal is also used to tip gold pen points. It is technically very interesting that a platinum alloy with 25% osmium has very good creep properties at a temperature as high as 1600°C. Because of its high melting temperature Karl Auer used osmium for the first metal-filament lamp.

The oxide OsO_4 improves the effect of contrast in electron microscopy. It is the ease of reduction of oxide to metal that is used. The ability of osmium ions to exchange electrons at high rates is also the base for the medical use of a type of osmium-containing sensors. They are implanted in diabetes patients and check the blood glucose levels continuously.

32.7.7
Ruthenium

32.7.7.1 Old and New Applications

Ruthenium is used as an alloying element for platinum and palladium, making these metals harder by solution hardening. A content of 0.1% Ru in titanium improves the corrosion resistance of this metal. Stable anodes for chlorine production are made of titanium, coated with ruthenium.

A new technique for an improved storage capacity on hard disks uses ruthenium. The product, called AFC media (antiferromagnetically coupled) has a thin layer, three atoms thick, of ruthenium between two magnetic layers on a disk. According to IBM, who have developed this product, it will be possible to store 100 gigabits of data per square inch of this hard disk.

32.8
The Varying Value of Platinum Metals

It is a common apprehension that platinum is much more expensive than gold. The prices of noble metals varies, depending on supply and demand. In the middle of the 1990s, platinum and gold prices were on the same level but the increased industrial use for catalytic purposes has increased the PGM prices considerably. Table 32.7 illustrates this with examples from three occasions.

Table 32.7 Prices in US$ per troy oz on three occasions

	July 1996	July 2000	January 2003
Platinum	397	567	609
Palladium	128	708	243
Rhodium	300	2452	496
Iridium	65	415	124
Gold	383	285	330

1 troy ounce = 31.1 g

32.9
Biological Roles of Metals in the Platinum Group

The concentrations of platinum group elements are extremely low in natural environment. Nor do the elements any role in life. The drug cisplatin is of course, like all potent drugs, very toxic. The oxides RuO_4 and OsO_4 are also toxic.

The mean contents in the earth's crust of all the platinum group elements are as mentioned very low. In the light of this fact it is astonishing that very high concentrations of iridium have been found in sedimentary rocks from the time of transition from the cretaceous to the tertiary geological period. At this time, about 70 million years ago, extinction of many biological species, including the dinosaurs, occurred. The iridium in these rocks is supposed to have arrived with a giant meteorite, the impact of which raised debris in such quantity that solar radiation was absorbed for a long time, changing the earth's climate [32.9].

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33

Zinc

33.1 Zn
Facts about Zinc

33.1.1 Zn
The Element

Symbol:	Zn
Atomic number:	30
Atomic weight:	65.39
Ground state electron configuration:	[Ar]$3d^{10}4s^2$
Crystal structure:	Hexagonal fcc with $a = 2.66$ Å, $c = 4.95$ Å

33.1.2 Zn
Discovery and Occurrence

Discovery: Centuries before zinc was recognized as a distinct element, zinc ores were used for making brass. The metal was known in India before 1000 AD and in China soon after 1000 AD.

Most important mineral: Sphalerite, zinc blende (Zn,Fe)S (figure M47)
Smithsonite $ZnCO_3$
Calamine is a general term often used for the oxidized ores of zinc, silicates and carbonates (non-sulfidic).

Ranking in order of abundance in earth crust:	24
Mean content in earth crust:	70 ppm (g/tonne)
Mean content in oceans:	0.0049 ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	33 ppm
Content in a man's body (weight 70 kg):	2.3 g

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33.1.3 Zn

Chemical Characterization

Zinc is a bluish-white metal, soluble in both acids and alkalis. It is unaffected by dry air but in moist air it is oxidized and becomes coated with a carbonate film that protects it from further corrosion. Zinc is a metal with many industrial applications. Coating with zinc, via hot-dip galvanizing or electroplating, protects iron from corrosion. Pure zinc is the negative electrode in electrical dry cells. Many zinc components are produced by die-casting, a process in which molten zinc is injected to the mold under pressure. Zinc is an ingredient of various alloys, especially brass (copper and zinc). Zinc is essential for life. It is a component in many enzymes, which take an active part in metabolism, and it is of great importance for replication of the genetic codes of DNA and RNA.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Zn^{II} as in ZnO, ZnS and ZnF_2	$Zn(g) \rightarrow Zn(g) + e^-$	906	$Zn(g) + e^- \rightarrow Zn^-(g)$
	$Zn^+(g) \rightarrow Zn^{2+}(g) + e^-$	1733	–
	$Zn^{2+}(g) \rightarrow Zn^{3+}(g) + e^-$	3833	
	$Zn^{3+}(g) \rightarrow Zn^{4+}(g) + e^-$	5731	

Standard reduction potential: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^0 = -0.763$ V

Electronegativity (Pauling): 1.65

Radii of atoms and ions: (WebElements™)		
	Atomic:	135 pm
	Covalent:	131 pm
	Van der Waals	139 pm
	Zn^{2+} (4-coordinate, tetrahedral):	74 pm
	Zn^{2+} (6-coordinate, octahedral):	88 pm
	Zn^{2+} (8-coordinate):	104 pm

33.1.4 Zn
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
7135 kg m^{-3} 7.135 g cm^{-3}	9.16 cm^3	692.7 K 419.5 °C	1180 K 907 °C	388 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
117	117	112	104	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$24.5 \cdot 10^{-6}$	$30.2 \cdot 10^{-6}$	$32.8 \cdot 10^{-6}$	–

Resistivity nΩm

78 K	273 K	373 K	573 K	773 K	1473 K
11	55	78	130	370	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-2.20 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
108 GPa	43 GPa	74 GPa	0.25

33.1.5 Zn
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	7.35 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	115 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	130 $kJmol^{-1}$
Entropy S^0 at 298 K	41.63 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	19.5	25.40	28.8	31.4	31.4	–

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$2Zn + O_2 \rightarrow 2ZnO$	–637	–597	–496	–340	–

33.1.6 Zn
Nuclear Properties and X-ray

Isotope range, natural and artificial	57–81

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half-life**	**Decay mode**	**Decay energy Q**
^{64}Zn	Stable	48.6	0+	–	–	–	–
^{66}Zn	Stable	27.9	0+	–	–	–	–
^{67}Zn	Stable	4.1	5/2-	0.8755	–	–	–
^{68}Zn	Stable	18.8	0+	–	–	–	–
^{70}Zn	Active	0.6	0+	–	5 · 1014 y	–	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{67}Zn
Reference compound	$Zn(NO_3)_2/D_2O$
Frequency MHz (^1H = 100 MHz)	6.257
Receptivity D^P relative to ^1H = 1.00	$1.18 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	0.673
Magnetogyric ratio, $radT^{-1}s^{-1}$	$1.677 \cdot 10^7$
Nuclear quadropole moment, barn	0.150

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
29	Cu	8.028
30	Zn	8.616
31	Ga	9.231

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	58.2
17.37 keV ($MoK\alpha_2$)	54.6

Neutron absorption	**Thermal neutron capture cross section**	1.10 barns

33.2
Zinc in History

33.2.1
A Metal From the Far East

There are two important types of zinc ores, the sulfide type and the oxidized type. The sulfide type embraces pure blende, sphalerite ZnS and complex sulfide mixtures, containing sulfides of zinc, iron and lead. Calamine is a term for the oxidized ores of zinc (including silicates and carbonates), as distinguished from the sulfide ores. Sphalerite, zinc blende, occurs together with other minerals, especially galena, lead glance. Superficially located sphalerite is oxidized and reacts with carbon dioxide to form zinc carbonate, zinc spar or calamine. At the beginning of our chronology, ores containing zinc spar were known as *kadmeia* (in Greece) and *cadmia* or *cadmea* (in Rome). The Latin word *cadmea* later became used for both the zinc ore and the sublimated zinc oxide. The oxide also had the designation *nix alba*, “white snow”. Ever since antiquity, zinc compounds have been known as a medicine for eye inflammations.

The element zinc escaped discovery for a long time because it simply disappeared when sulfidic ores were roasted. Zinc oxide, formed during the roasting, is very volatile and “went up in smoke”. Methods to catch the fleeing zinc oxide were developed in Persia and India before the turn of the millenium 1000. From the 12th century the methods became known in China, and there large-scale zinc manufacture was developed.

When common oxides, such as for instance of lead, are reduced, they form molten metal. Zinc oxide does not exactly follow the other oxides, because zinc has such a high vapor pressure at the temperature needed that it disappears as a vapor, from which the metal has to be condensed. In view of these facts, it is not strange that the pyrometallurgy of zinc was delayed and so also was knowledge about zinc in its metallic form.

In 1745 the ship *Götheborg*, belonging to the Swedish East India Company, was wrecked on its way home from China. The freight had been loaded in Canton and the big sailing-ship had been on the route home for 18 months. The shipwreck occurred just at the entrance of the home harbor and the valuable cargo was lost. It was old Chinese porcelain, tea and silk. However, part of the cargo was zinc metal, a curiosity and a typical metallurgical product from the Far East. Some 100 years later it became possible to rescue parts of the cargo. The zinc metal then was covered by a 1 mm thick layer of zinc hydroxychloride. The metallic core was unaffected and on analysis showed the approximate composition 99.0% Zn, 0.77% Fe, 0.25% Sb. Copper, nickel, silver, lead and arsenic could not be detected [33.1]. The purity of the metal surprised European metallurgists.

From the beginning of the 17th century, China was the main manufacturer of zinc. Europe was left behind in this field. However, if European chemists had read and given Marco Polo credit for his telling of his adventures from the end of the 13th century, they might have been able to start zinc manufacture hundreds of years earlier than when in fact it happened.

33.2.2
Marco Polo in the Pioneering Region of Zinc Manufacture

Marco Polo made extensive journeys in the East during 1271–1295. In Persia he came into contact with zinc and zinc manufacture. He describes it very concretely, as described in ref. [33.2]:

> Kobenan is a large town. The people worship Mahommet. There is much iron and steel .... They also prepare both Tutia (a thing very good for the eyes) and Spodium; And I will tell you the process. They have a vein of a certain earth, which has the required quality, and this they put into a great flaming furnace, whilst over the furnace there is an iron grating. The smoke and moisture, expelled from the earth of which I speak, adhere to the iron grating, and thus form Tutia, whilst the slag that is left after burning is the Spodium.

It is quite clear that the zinc oxide sublimates at the high temperature of the furnace and is deposited on the iron grating above the furnace. *Tutia* is zinc oxide, while *Spodium* is a mixture of other oxides with low sublimation pressures.

33.2.3
Zinc Metal in India and China

Zinc metal seems to have been produced in India in the 7th century AD and in China in the 11th century [33.3]. Indian metallurgists wrote careful recipes, describing how calamine, an impure zinc oxide, should be mixed with organic matter such as sugar solution, mustard seeds and fruits of different sorts. When the mixture was heated in a covered crucible, a metal, similar to tin, was obtained. This small-scale production was mainly for medical use. In China, the manufacturing technique was developed into an important industry. It is described in the book *Tien-kong-kai-ou*, published in the first part of the 17th century and referred to by W. Hommel in ref. [33.1] (see Figure 33.1).

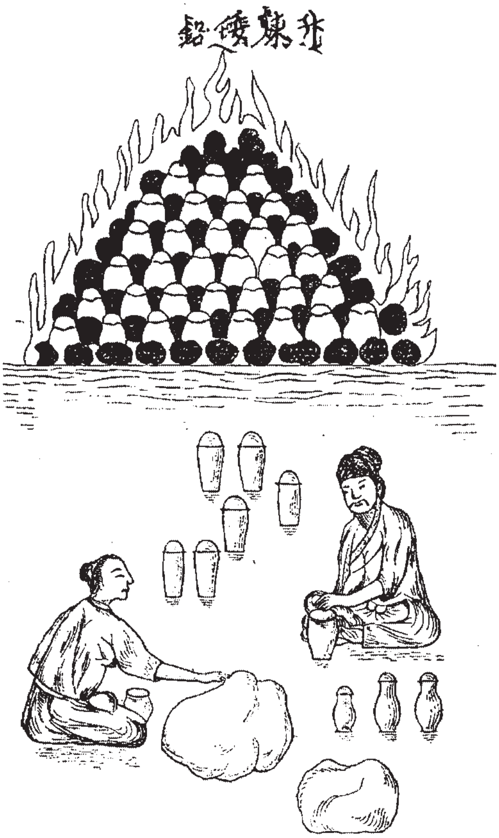

Figure 33.1 Chinese manufacture of zinc metal.

> Zinc ore (calamine) is pressed into clay crucibles, having covers well luted with loam. The crucibles are piled up in a pyramid and heated by burning lumps of coal in-between the crucibles. After heating to redness and cooling a regulus of zinc may be taken out from every crucible.

Hommel states that *Tien-kong-kai-ou* gives no information about reducing agents in the ore when pressed into the crucibles. Perhaps the coal lumps at high temperature formed carbon monoxide, which has passed through pores in the crucible walls and reduced the calamine to zinc. Anyhow new techniques were developed. One method seems to have been a two-step process with the preparation of tutia, zinc oxide, first and then mixing this oxide with carbon powder in the crucible. On heating to a temperature high enough for reduction, very pure metal could be obtained. Perhaps it was such a metal that was delivered to Canton in 1743 and ended up on the bottom of the sea outside Gothenburg in distant Europe.

33.2.4

Zinc Metal in Europe and America

Long before the manufacturing technique was developed in Europe, zinc metal was imported from the Orient by Portuguese merchants. So it was that the metal became known and described. Paracelsus introduced the designation "zinc" for the foreign element. He wrote in 1616 (cited from Mary Weeks):

> There is another metal, zinc, which is in general unknown. It is a distinct metal of a different origin, though adulterated with many other metals. It can be melted, for it consists of three fluid principles, but it is not malleable. In its color it is unlike all others, and does not grow in the same manner; but with its *ultima materia* I am as yet unacquainted, for it is almost as strange in its properties as *argentum vivum* (mercury). It admits no mixture, will not bear the fabrications of other metals, but keeps itself entirely to itself.

The very first zinc metal in Europe might have been manufactured by one *Erasmus Ebener* in Nuremberg as early as 1509 [33.3]. He separated the metal from slag obtained from silver manufacture in Rammelsberg. Brass was made directly from the zinc thus obtained. Around 1620 Agricola observed zinc metal in lead furnaces. The zinc was deposited in wall cracks high up in the furnaces. Discoveries of this type were made by many metallurgists. Gradually a technique for zinc manufacture from lead ores was developed at Goslar in the Harz Mountains in Germany. When the lead ore was reduced in the furnace and lead metal was formed, zinc oxide was simultaneously reduced and its metal vaporized. Caspar Neuman (1683–1737) gives a very detailed description of the Goslar process:

> The greatest quantities of Zinc come from the East Indies, in large oblong pieces; and from Goslar, commonly in round cakes or loaves. Of the origin of the East-India Zinc we have no certain account: The Goslarian is extracted from the Lead- and Silver-ores of Rammelsberg by a particular contrivance in the structure of the furnace. The Zinc, naturally contained in the ore, separates during the fusion from the other metallic matters, being elevated by the heat in form of fume, which passes into a reservoir made for that purpose in the front wall, over the gutter by which the Lead runs off. The reservoir for the Zinc is enclosed, on the inside, by a large flat stone, only some chinks being left for the fumes to enter; and on the outside, by another stone, which is closely luted, and frequently sprinkled during the process with cold water, to cool and condense the fumes. Each smelting lasts twenty hours, beginning at ten in the forenoon and ending at six next morning. When the fusion of the ore is completed, the workman dexterously strikes the outer stone of the reservoir with an Iron rod, so as to loosen some of the luting at the bottom; upon which the Zinc, collected during the process, runs out like Quicksilver. He continues to tap till nothing more will run; then he melts the Zinc again in an iron pot, and casts it into hemispherical masses. I have several times been at this work, and kept at it two days and a night together without leaving the furnace.

In 1746 A. S. Marggraf investigated calamine ores from Bohemia, Poland, Hungary and England, and showed that zinc may be obtained from all of them, if the reduction with carbon occurs in closed crucibles. His conclusion was that Europe has both natural resources and metallurgical knowledge for its own zinc production.

The first European industrial zinc production started in Bristol in the 1740s. *John Champion* developed a technique that became known as the *English method* [33.3]. In this method the reduction was carried out in furnaces for glass manufacture and zinc metal was distilled over to large pots.

In 1800 a Polish pioneer, *John Christian Ruberg*, improved the English technique by evolving horizontal muffles of large capacity. In later years these became the basis for the great Silesian zinc production in Poland.

A man of great importance for the development of large-scale zinc production was an ecclesiastic. Abbé Dony of Liège developed his own pyrometallurgical process for production of zinc and established works in Liège in 1807 with a very modern technique, even for producing brass. The Abbot himself succeeded technically but not financially. He was ruined and died a broken-hearted man. His plant continued, however; a new owner group took over and built up the base for the great company *Société de la Vieille Montagne*, which was founded in 1837. It is an outstanding metallurgical enterprise, which has brought its name from the 19th century into the new millennium.

In the United States, John Hiltz in Washington DC produced the first zinc in the 1850s. Fifty years later the annual US production was 130–230 thousand tonnes, corresponding to 25–30% of world production.

Early zinc manufacture was based on pyrometallurgical processes. In 1881 *M. Letrange* in France presented an electrolytic process. He leached a roasted zinc blende ore with dilute sulfuric acid and electrolyzed the solution. Zinc was precipitated at the cathode. The cell acid thus obtained was used for leaching a new quantity of roasted ore. Several obstacles delayed the utilization of this method for large-scale production. The ore dressing technique for preparing high-grade mineral concentrates was not yet fully developed. In addition, reliable methods for purification of solutions and for slime separation were not available; and finally the cost of electric power was very high. However, at the end of the 1910s commercial production of electrolytic zinc started in different parts of the world.

33.3
Mining of Zinc

33.3.1
Minerals and Zinc Ores

Sphalerite or *zinc blende* (Figure M47) is a yellow, brown, or black mineral (Zn,Fe)S. It often contains manganese, arsenic, cadmium and other elements. It is a widely distributed ore of zinc, commonly associated with galena PbS in veins and other deposits. Sphalerite is the principal ore mineral for zinc in the world.

Calamine is a name often used for the oxidized ores of zinc, silicates and carbonates. In Great Britain the term is used for smithsonite.

Smithsonite $ZnCO_3$ is an ore of zinc, associated with sphalerite. As a mineral it is white to yellow, gray, brown, or greenish.

Zincite is a red to yellow mineral: (Zn,Mn)O.

Willemite Zn_2SiO_4 varies in color from white to brown and it exhibits a bright-yellow fluorescence in ultraviolet light. It is a minor ore of zinc.

Zinc ores occur as a rule together with ores of other metals, mainly lead, copper, silver and other noble metals. In addition, cadmium is found in all zinc ores with an average content of about 0.3% Cd (counted with reference to zinc). This leads to the production of 3 kg of cadmium for every tonne of zinc produced [33.4].

The world total ore reserves are estimated at 190 million tonnes (zinc content) while the reserve base is 440 million tonnes.

33.3.2

Mine Production of Zinc

Zinc mining is very important. In world trade, counted as tonnage, zinc is number 4 among the metals. It comes after iron, aluminum and copper. More than 90% of the zinc comes from zinc blende ores. A typical zinc ore may contain 10% zinc, 4% lead and 80 g of silver per tonne.

Ore dressing separates the different minerals present and produces concentrates for metal production. China and Australia are the greatest producers of zinc concentrates in the world. Other large producers are Canada, Peru and the United States. In the USA the leading zinc mining state is Alaska. The Red-Dog Mine there was opened in 1989; and since then mine production in the United States has exceeded the smelter capacity for zinc in that country.

In Table 33.1 the mine production by country in the year 2000 is shown [33.4].

Table 33.1 Mine production by country in 2000

Country	Zinc production 1000 tonne	Percentage of total production	Country	Zinc production 1000 tonne	Percentage of total production
China	1780	20.27	Bolivia	149	1.70
Australia	1420	16.17	India	144	1.64
Canada	936	10.66	Russia	136	1.55
Peru	910	10.36	Morocco	105	1.20
United States	852	9.70	Brazil	100	1.14
Mexico	393	4.48	Iran	85	0.97
Kazakhstan	325	3.70	Japan	64	0.73
Ireland	263	3.00	South Africa	63	0.72
Spain	201	2.29	Tunisia	41	0.47
Korea North	190	2.16	Namibia	40	0.46
Sweden	176	2.00	Other countries	252	2.87
Poland	155	1.77			
			Total	8780	100

33.4
Modern Zinc Manufacture

More than 90% of the zinc production occurs from sulfide ores. Zinc metal is produced from ore concentrate by pyrometallurgical or electrolytic techniques. Nowadays the latter are dominant. Both methods, utilizing ore as raw material, constitute the *primary* processes, while methods working up zinc scrap are *secondary*.

33.4.1
Primary Production of Zinc From Sulfide Ore

33.4.1.1 Roasting

The concentrate of zinc ore is roasted at 900–1000°C, according to the reaction

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

Sulfuric acid is manufactured from the sulfur dioxide.

The roasting is often carried out in so-called fluidized beds, giving a very intimate contact between solid particles and gas, which reduces the amount of air for the roasting to a minimum. The gas will be rich in SO_2 and suitable for recovery. Sulfides normally contain small amounts of mercury, arsenic, selenium and tellurium. To remove these toxic impurities, sophisticated methods have been developed. This has been necessary because of the risk that they would otherwise enter the food chain.

33.4.1.2 Electrolytic Zinc Manufacture

About 80% of the world's production of zinc is based on electrolytic methods. The roasted concentrate is dissolved in sulfuric acid. Impurities such as Cu, Co and Cd are removed from the solution by adding zinc dust. The precipitation reactions are exemplified by

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu}$$

The purified solution is electrolyzed with lead anodes and aluminum cathodes. To use aluminum as cathode material is artful. As a result of the passive layer on the aluminum surface, the precipitated zinc has low adherence to the cathode and can be shaved off as sheets after the electrolysis.

In fact, zinc precipitation in sulfuric acid electrolyte should not function. As hydrogen is nobler than zinc, the cathodic reaction ought to evolve hydrogen gas instead of precipitating zinc metal:

$$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2$$

In spite of this, zinc precipitation occurs due to the great overvoltage of hydrogen on zinc.

The zinc sheets from the electrolysis are melted in induction furnaces, cast and delivered as billets.

33.4.1.3 Primary Production With Pyrometallurgical Technique

One of the pyrometallurgical methods used is the Imperial Smelting Technique. A roasted zinc concentrate is charged together with coke into a blast furnace. At 1000°C zinc is reduced and its vapor passes from the top of the furnace into a condenser. Here the zinc vapor is cooled by molten lead and the two metals form a molten alloy, which is allowed to cool to 440°C. At this temperature the metal system has separated into a lead phase and a zinc phase. The lead is circulated for continued cooling purposes. Crude zinc produced by this process contains about 2% Pb, 0.3% Cd and 0.05% Fe. It is refined by distillation in two columns [33.5]. In the first one, zinc is purified from lead and iron. The separation is based on the fact that the boiling point of zinc is 907°C, while lead boils at 1749°C and iron at 2861°C. In the second column, zinc is separated from cadmium (boiling point 767°C). Zinc metal with 99.9% purity is obtained.

33.4.1.4 Secondary Production

Zinc-containing scrap is utilized to an increased extent, especially in the highly industrialized countries. This is exemplified in Table 33.2.

Table 33.2 Zinc metal production, total and secondary – four examples

Country	Zinc metal production. 1000 tonne		Percentage secondary of total
	Total	Secondary	
Brazil	199	7	3.5
India	201	25	12.4
Japan	700.5	159	22.7
USA	371	143	38.5

33.4.2
Production Volumes

World total production of zinc, both primary and secondary, by country in 2000 is shown in Table 33.3 [33.4].

Table 33.3 World total production of zinc by country in 2000

Country	Zinc production 1000 tonne[a)]	Percentage of total production	Country	Zinc production 1000 tonne[a)]	Percentage of total production
China	1960	21.5	Netherlands	217	2.4
Canada	787.5	8.6	India	201	2.2
Japan	700.5	7.7	Korea North	200	2.2
Australia	500	5.5	Peru	200	2.2
Korea Republic	474	5.2	Brazil	199	2.2
Spain	386	4.2	Poland	175	1.9
USA	371	4.1	Italy	170	1.9
Germany	356	3.9	Norway	126	1.4
France	350	3.8	South Africa	103	1.1
Kazakhstan	262	2.9	UK	100	1.1
Belgium	252	2.7	Bulgaria	85	0.9
Mexico	235	2.6	Thailand	77.5	0.8
Russia	230	2.5	Other countries	200	2.18
Finland	223	2.4			
			Total	9140	100

a) Primary plus secondary production.

33.5
Uses

There are many applications for zinc. About *three-quarters* of the zinc is used as metal:

- in galvanized steel, which is coated with zinc for corrosion protection;
- in rust-inhibiting paints, containing zinc metal powder;
- as pure zinc metal in batteries (the first, and still the most common, dry battery, the Leclanché cell, utilizes zinc as anode and carbon as cathode);
- in zinc sheets for roofing, utilized from the 1860s when the modern city of Paris was built;
- in anodes of pure zinc in electrolytic processes;
- in zinc-based casting alloys;
- in the copper–zinc alloy brass (treated in Chapter 7 Copper).
  (of all zinc metal produced more than 50% are used for corrosion protection, while about 15% each are used for brass and zinc-base alloy production).

The remaining *one-quarter* is used as zinc compounds for paint and agricultural purposes. Zinc is also an essential element for the growth of humans, animals and plants.

33.5.1
Zinc Alloys – Not Only Brass

A zinc alloy with 4% Al is by tonnage almost as important as brass but not so well known. It has very good casting properties and is primarily intended for pressure die casting. In spite of strong competition from plastics materials, components utilizing pressure die cast zinc alloys have retained a considerable market share for special types of equipment. Complicated and thin-walled parts can be manufactured with narrow tolerances. As the alloy is easily polished, it is used when decorative surfaces are required. This is utilized in, for instance, the automotive and computer industries.

33.5.2
Corrosion Protection

Steel is coated with different metals in order to improve its corrosion resistance. In some cases, such as nickel and copper, the coating metal is nobler than iron. The coating can also be less noble than the substrate material (iron), e.g. zinc and aluminum. The coating on the steel surface may be damaged so that a corroding solution, e.g. salt water, comes into contact with both the coating and the substrate material. Figures 33.2 and 33.3 show that if nickel is to maintain a corrosion protection of steel, the coating must be covering and without defects. Zinc on the contrary protects even if the coating has some small defects.

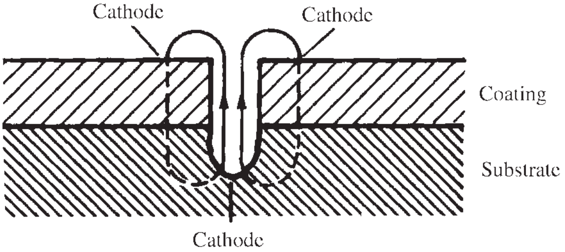

Figure 33.2 A steel surface coated with nickel. At a defect in the surface layer, a galvanic cell is created in which the less noble metal (iron) is attacked. Pitting in the base material (iron) is formed. An example is the rust spots on nickel-coated handlebars. (Reprinted with permission of the Swedish Corrosion Institute.)

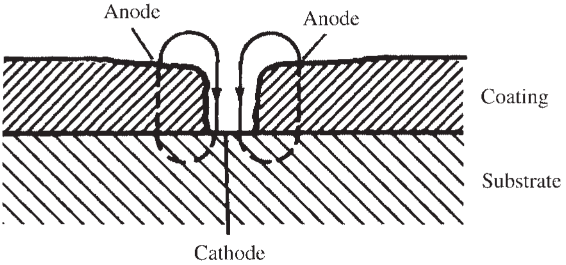

Figure 33.3 A steel surface coated with zinc. At a defect in the surface layer, a galvanic cell is created in which the less noble metal (zinc) is attacked. The iron substrate is protected although its surface is bare. This is galvanic protection. (Reprinted with permission of the Swedish Corrosion Institute.)

This shows that zinc gives an effective corrosion protection, and substantial quantities of zinc are utilized for this purpose. The coating can be applied using a hot-dip process, galvanizing. The hot dipping is made in molten zinc at a temperature of 460°C. Electroplating may be utilized as an alternative. Hot-dip galvanizing involves the following techniques:

- Large components, such as lamp posts, are dipped one by one directly into molten zinc.
- Small components, such as fasteners, are placed in a perforated drum for dipping. After lifting the drum out of the molten zinc, it is centrifuged to throw out any excess zinc.
- A wire or a strip is drawn continuously through molten zinc.

In hot-dip galvanizing the layer is composed of an inner coating of zinc–iron and an outer layer of pure zinc. The entire layer thickness may be about 25 µm. In zinc plating the layer thickness (pure zinc in this case) is less and is adjusted by the plating time. A coating thickness of 5–20 µm is usual.

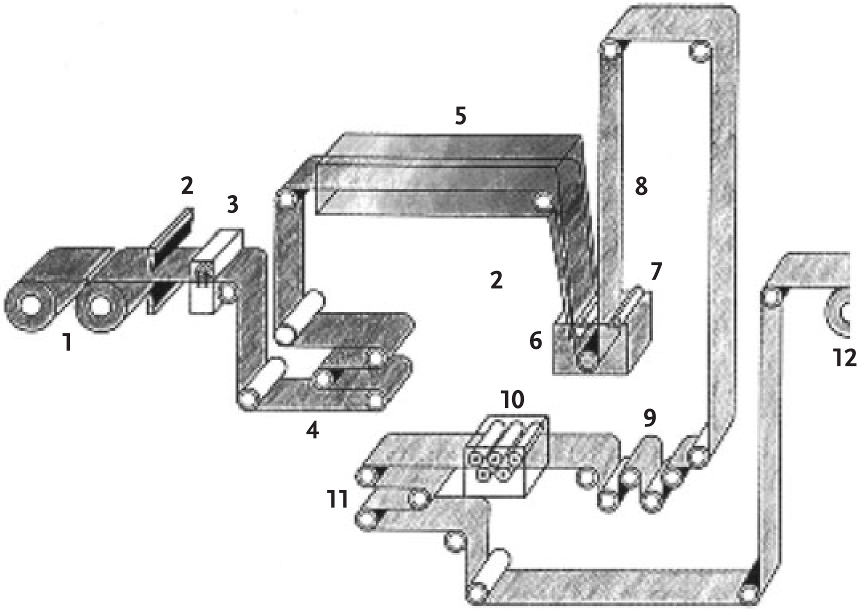

Figure 33.4 Continuous galvanizing of steel strips. The pot with molten zinc is situated at point 6. At point 7, jet-knives wipe off the excess zinc. (Reprinted with permission of Swedish Steel AB (SSAB).)

Steel strips are galvanized in continuous processes as shown in Figure 33.4. A zinc-coating alternative for strips is continuous electroplating. Both techniques are very much utilized for modern automobile body sheets.

Zinc powder is used as a pigment in rust-inhibiting paints. If the zinc content in the paint is high enough for a complete filling, the zinc grains, in contact with each other, give a cathodic protection to the substrate material. Such paints are mainly used for so-called heavy anti-corrosive painting of, for example, bridges.

33.5.3
Chemicals

Zinc chemicals are utilized diversely. Rubber contains about 2% Zn, mainly as oxide ZnO. It works as an activator in the sulfur vulcanization process. Zinc compounds also make components of plastic and rubber more stable against UV radiation. Zinc chemicals are used in pigments and paints (zinc white), as impregnating agents for lumber and textiles, and in lubricants and lubricant carriers (zinc phosphate). They are also used as activators in various batteries and as catalysts. Zinc oxide has a protective effect for running wounds, and zinc ointment contains 10% ZnO.

33.6
Zinc in Life

Zinc is essential for life. It is a component in many enzymes, which take an active part in metabolism, and it is of great importance for replication of the genetic codes of DNA and RNA [33.6]. Lead and cadmium are toxic partly because they take over the position of zinc in important enzyme molecules, which are thus made inactive. In the pancreas, zinc contributes to the preparation of insulin. Zinc deficiency leads to impaired wound healing and loss of hair. In addition, for children, a zinc deficiency may cause delayed mental development, retarded growth and postponed puberty.

An adequate dietary supply of zinc is essential for normal growth. The role of zinc in the synthesis of proteins makes the need for the metal especially pronounced for fetuses and newborn infants. For an adult, a daily intake of 11 mg zinc is recommended, corresponding to 0.15 mg per kilogram body weight. The recommendation for newborns is 6 mg per day, i.e. 1.5 mg zinc per kg body weight. In relation to body weight, the recommended zinc intake is thus 10 times greater for infants than for adults.

In a conference regarding zinc and health [33.7] in was recently concluded that pregnancy and lactation are clearly influenced by maternal zinc depletion. The first six months of life are a period of rapid growth; however, the relatively high zinc requirements during this period can be met satisfactorily from breast milk alone.

Important zinc sources in the diet are fish, meat, offal and whole-wheat bread. Fruit has in general low zinc contents, 0.15 mg per 100 g, while beef and wheat have 4 mg per 100 g. Some vegetable foodstuffs may be zinc-rich but the gut often has difficulties assimilating their zinc content. For vegetarians, sunflower seeds, maple syrup and bran are good foodstuffs, from the zinc point of view.

Zinc is essential for life but it is not without risks. Breathing of molten zinc leads to “fume fever”, which can be serious if the exposure is heavy. Because of that, very good ventilation is necessary in connection with welding of zinc-coated steel.

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34
Cadmium

34.1 Cd
Facts about Cadmium

34.1.1 Cd
The Element

Symbol:	Cd
Atomic number:	48
Atomic weight:	112.41
Ground state electron configuration:	$[Kr]4d^{10}5s^2$
Crystal structure:	Hexagonal with $a = 2.98$ Å, $c = 5.62$ Å

34.1.2 Cd
Discovery and Occurrence

Discovery: Cadmium was discovered by Friedrich Stromeyer in Göttingen, Germany. He found the new element in 1817 when he examined an impure zinc carbonate, $ZnCO_3$.

Most important mineral: Greenockite CdS is the only cadmium mineral of any importance. It occurs as an earthy incrustation on sphalerite. Cadmium is mainly obtained as a by-product when sphalerite is worked for zinc.

Ranking in order of abundance in earth crust:	66
Mean content in earth crust:	0.15 ppm (g/tonne)
Mean content in oceans:	$1.1 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	$50 \cdot 10^3$ years
Mean content in an adult human body:	0.7 ppm
Content in a man's body (weight 70 kg):	49 mg

Encyclopedia of the Elements. Per Enghag

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34.1.3 Cd
Chemical Characterization

Because of its beautiful yellow color, cadmium sulfide was a highly appreciated pigment, *cadmium yellow*. It has been used by painters and in ceramics glazing. Also red pigments, cadmium sulfide/selenide, were used and appreciated. Non-toxic alternatives have to be found. The toxicity of cadmium is due to the fact that the metal replaces zinc in important enzyme molecules, making them inactive. After great intakes, cadmium also destroys the functions of the lungs and kidneys and softens the bones, leading to intense pain. The famous Itai-Itai disease in Japan was a result of such great intakes of rice polluted by zinc refineries. The polluted rice had ten times more cadmium than found in ordinary rice.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
Cd^{II} as in CdO, CdS and $CdBr_2$	$Cd(g) \rightarrow Cd(g) + e^-$	868	$Cd(g) + e^- \rightarrow Cd^-(g)$
	$Cd^+(g) \rightarrow Cd^{2+}(g) + e^-$	1631	–
	$Cd^{2+}(g) \rightarrow Cd^{3+}(g) + e^-$	3616	

Standard reduction potential: $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \quad E^0 = -0.403$ V

Electronegativity (Pauling): 1.69

Radii of atoms and ions: (WebElements™)		
	Atomic:	155 pm
	Covalent:	148 pm
	Van der Waals	158 pm
	Cd^{2+} (4-coordinate, tetrahedral):	92 pm
	Cd^{2+} (6-coordinate, octahedral):	109 pm
	Cd^{2+} (8-coordinate):	124 pm

34.1.4 Cd
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
8650 kg m^{-3} 8.65 g cm^{-3}	13.00 cm^3	594.3 K 321.1 °C	1040 K 767°C	231 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
100	97	95	89	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$26.9 \cdot 10^{-6}$	$30.8 \cdot 10^{-6}$	$36 \cdot 10^{-6}$	–

Resistivity nΩm

78 K	273 K	373 K	873 K	973 K	1473 K
16	68	98	363	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-2.21 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
50 GPa	19 GPa	45 GPa	0.32

34.1.5 Cd
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	6.10 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	100 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	112 $kJmol^{-1}$
Entropy S^0 at 298 K	51.75 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	25.1	25.98	29.0	29.0	20.8	20.8

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Cd + O_2 \rightarrow 2CdO$	−457	−418	–	–	–

34.1.6
Nuclear Properties and X-ray

Isotope range, natural and artificial	97–130

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{106}Cd	Stable	1.25	0+	–	–	–	–
^{108}Cd	Stable	0.89	0+	–	–	–	–
^{110}Cd	Stable	12.49	0+	–	–	–	–
^{111}Cd	Stable	12.80	1/2+	−0.5943	–	–	–
^{112}Cd	Stable	24.13	0+	–	–	–	–
^{114}Cd	Stable	28.73	0+	–	–	–	–
^{116}Cd	Stable	7.49	0+	–	–	–	–
^{113}Cd	Active	12.22	1/2+	−0.6217	$7.7 \cdot 10^{15}$ y	β^-	0.316 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{111}Cd	^{113}Cd
Reference compound	$Cd(CH_3)_2$	
Frequency MHz (^1H = 100 MHz)	21.215	22.193
Receptivity D^P relative to ^1H = 1.00	$1.24 \cdot 10^{-3}$	$1.35 \cdot 10^{-3}$
Receptivity D^C relative to ^{13}C = 1.00	7.07	7.72
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-5.698 \cdot 10^7$	$-5.961 \cdot 10^7$
Nuclear quadropole moment, barn	–	–

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
47	Ag	21.991
48	Cd	22.985
49	In	24.002

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	223
17.37 keV ($MoK\alpha_2$)	28.1

Neutron absorption	**Thermal neutron capture cross section**	2450 barns

34.2
Discovery

34.2.1
A Broad Field of Activities

Friedrich Stromeyer (1776–1835) grew up in Göttingen in Germany. The town is a typical center of learning, and its famous university was opened in 1737. Friedrich studied chemistry and pharmaceutics at the university, and continued with scientific studies and work for N. L. Vauquelin in Paris. There his interest in analytical chemistry was strengthened and he developed into a very clever mineral analyzer. It remained a great interest to him, although he came to devote much of his time to organic chemistry and medicine. He was in fact one of the last in the history of chemistry who, like the 30 years older Klaproth, had an almost complete mastery of the two great fields, mineral analysis and pharmaceutics. In 1802, at the age of 26, he was engaged with the faculty of medicine at the university of his hometown; and in 1810 he was appointed professor at the University of Göttingen. He built up a well-equipped laboratory, which he managed very well too. N. G. Nordenskiöld from Stockholm visited him in 1821 and wrote to Berzelius: “Stromeyer has the finest and neatest laboratory I have yet seen in Germany.”

Germany at that time consisted of a number of independent states. Göttingen was situated in Hannover. The authorities of the state considered it important to inspect the pharmacies, and Friedrich Stromeyer was in 1816 designated to supervisor. The duty was combined with the professorship at the university.

34.2.2
White Zinc Oxide – Yellow!

The superintendence of the pharmacies led to Stromeyer’s discovery of the element cadmium. He himself described the discovery in a letter, dated 1817, to his colleague, Dr J. S. C. Schweigger[1] (cited from Mary Weeks):

---

[1] Schweiggers Journal 21 (1818) 297.

> As I was last harvest inspecting the apothecaries' shops in the principality of Hildesheim, in consequence with the general inspection of the apothecaries of the kingdom having been entrusted to me by our most gracious Regency, I observed in several of them, instead of the proper oxide of zinc, carbonate of zinc, which had almost entirely been procured from the chemical manufactory at Saltzgitter. This carbonate of zinc had a dazzling white color, inclining to orange, though no sensible portion of iron or lead could be detected in it.
>
> When I afterwards visited Salzgitter, during the course of this journey, and went to the chemical manufactory from which the carbonate of zinc had been procured; and when I expressed my surprise that carbonate of zinc should be sold instead of oxide of zinc, Mr. Jost, who has the charge of the pharmaceutical department of the manufactory, informed me that the reason was, that their carbonate of zinc, when exposed to a red heat, always assumed a yellow color, and was on that account supposed to contain iron, though the greatest care had been taken beforehand to free the zinc from iron, and though it was impossible to detect any iron in the oxide of zinc itself.
>
> This information induced me to examine the oxide of zinc more carefully, and I found to my great surprise, that the color ... was owing to the presence of a peculiar metallic oxide, the existence of which had not hitherto been suspected. I succeeded by a peculiar process in freeing it from oxide of zinc and in reducing it to the metallic state ...

The unknown element was isolated in the following way. The impure zinc oxide was dissolved in a quantity of sulfuric acid, so small that the acidity of the solution was restricted. He passed hydrogen sulfide gas in and obtained a yellow precipitate. After filtering and washing, the precipitate was dissolved in concentrated hydrochloric acid and the solution evaporated to dryness. The residue was treated with ammonium carbonate, which dissolved zinc and copper that might have been co-precipitated as sulfides. The new element was not dissolved in ammonium carbonate. The insoluble substance was filtered, washed and ignited to oxide. The brown oxide was mixed with lampblack and heated to moderate redness. A bluish-gray metal with a bright luster was obtained. This happened in 1817.

34.2.3
Accused for Mixing Arsenic Into Medicine – Exculpated by Stromeyer

When the discovery became known, a factory owner, K. S. L. Hermann in Schönebeck, and a Medicinal Counsellor, Dr J. C. H. Roloff in Magdeburg, contacted Professor Stromeyer. Dr Roloff had made a pharmacy inspection some years earlier and confiscated zinc oxide, as it seemed to contain arsenic. From an acid solution of the oxide, hydrogen sulfide in fact precipitated a yellow sulfide, identified as arsenic sulfide. The zinc oxide had been manufactured at Hermann's factory from a Silesian calamine ore. The two gentlemen now sent to Professor Stromeyer both zinc oxide, prepared from the ore from Silesia, and the yellow sulfide with supposed content of arsenic. Stromeyer could rapidly state that the yellow substance was not the sulfide of arsenic but a sulfide of the metal he himself had discovered.

He also made the same investigation of the zinc oxide from Schönebeck as he had originally made with the carbonate from Salzgitter, and got the same result. Hermann was very satisfied. His tarnished reputation as a supplier of medical zinc oxide containing arsenic could be restored. Also Professor Stromeyer was satisfied. Through the contact with Hermann and his ore supplier, he got a large supply of material for further investigation of the new metal and its properties.

34.2.4
A Place in the Discovery Story of the Elements

It was time to give the new element a name. As it followed zinc in calamine ore, Stromeyer found it logical to call upon the old Roman name *cadmia* for zinc spar ores. The new element got the name *cadmium*.

Professor Stromeyer had worked carefully as a supervisor for the pharmacies and he had made Göttingen known due to the great discovery of a new element. This was grounds for the authorities to appoint him to be *Hofrath* or *Court Counsellor*. Certainly this honorary title was a satisfaction to him. The genuine chemist Stromeyer perhaps felt still more satisfaction at having gained a place in the discovery story of the elements. From the mineralogical world he was also honored with the mineral name *stromeyerite* for silver–copper glance CuAgS, a dark steel-gray orthorhombic mineral with a blue tarnish.

> At about the same time as the work was going on in Göttingen, two other German chemists also discovered Stromeyer's element in products emanating from Silesian calamine. Karl Meissner from Halle and Carl Karsten from Berlin announced their discovery the year after Stromeyer. Thus they were passed on the finishing line and are forgotten in all tables of element discoverers. They deserve a mention here.

34.3
Occurrence and Manufacture

The only common cadmium mineral, *greenockite* CdS, is almost always associated with the zinc ore mineral sphalerite. The average ratio between zinc and cadmium in these types of ores is 400:1, which means that the cadmium content is 0.25% with reference to zinc. Of the total output of cadmium in the world, about 80% comes as by-product from primary zinc production and a small amount comes from lead production. The remaining part, about 20%, is obtained from cadmium scrap and other secondary sources, such as for instance dust generated by recycling of iron and steel scrap.

In the selective flotation of zinc–lead sulfide ores, cadmium is distributed between ZnS and PbS concentrates. When heated to high enough temperature (1100°C), as is the case during roasting of lead concentrates, CdS volatilizes without decomposition and is found in the dust collected in bag filters or in electrostatic precipitators. During the roasting of zinc concentrates (950°C), cadmium is mainly found as CdS and CdO in the calcined product.

In connection with pyrometallurgical zinc metal manufacture, cadmium oxide and sulfide are also reduced. In the subsequent zinc refining by distillation, cadmium is effectively separated from zinc, as the two metals condense at different temperatures.

In hydrometallurgical zinc production, with electrolysis, the roasted ZnO concentrate is leached with sulfuric acid. Zinc dust is added to the impure leach solution, which precipitates cadmium and other metals nobler than zinc, in metallic form. From this metal mixture, pure cadmium is prepared by different chemical and physical methods.

To recycle the cadmium from small NiCd batteries, the plastic casings are removed, while the cadmium anode plates are taken out from big industrial batteries. A furnace is charged with this cadmium scrap together with carbon. When heated, cadmium will distill off and is collected in water. The product is reused in new NiCd batteries. Cadmium is also manufactured by recovery from cadmium–tin alloys and cadmium-containing paints.

As a result of great environmental problems with cadmium, both production and consumption declined from 2000 to 2001. In the United States the production of metal declined by 64%, while production of cadmium sulfide and other compounds declined by more than 93%. Such large reduction in production was not registered worldwide, but the decrease in cadmium production is evident. This is expressed in Table 34.1.

Table 34.1 World refinery production of cadmium in the years 2000 and 2001

Country	**Production tonne**		**Change**	**Country**	**Production tonne**		**Change**
	In 2000	**In 2001**	**2000–2001 %**		**In 2000**	**In 2001**	**2000–2001 %**
Japan	2472	2486	+ 0.6	Germany	1130	1100	– 2.7
China	2370	2400	+ 1.3	Russia	925	950	+ 2.7
Canada	2024	1429	– 29.4	Finland	680	700	+ 2.9
Korea Rep.	1911	2000	+ 4.7	Netherlands	628	455	– 27.5
United States	1890	680	– 64.0	Australia	525	378	– 28.0
Mexico	1268	1050	– 6.9	UK	503	485	– 3.6
Belgium	1148	1236	+ 7.7	Other countries	2654	2860	+ 7.8
				Total	20 100	18 200	– 9.5

Source: ref. [34.1].

34.4
Uses

34.4.1
An Outline

Cadmium is a soft, ductile, bluish white metal. It may be alloyed with lead, tin and bismuth in the manufacture of fusible metals for automatic sprinkler systems, fire alarms and electrical fuses. Cadmium has been used as a control or shielding material in atomic energy plants because of its high absorption of low-energy neutrons. Nickel–cadmium batteries are in common use for specialized purposes, but intensive research is going on in order to develop a more ecofriendly anode material as an alternative to cadmium.

Cadmium consumption in 2001 was about 16 000 tonne (according to the World Bureau of Metal Statistics), 17% less than the previous year. Japan used the metal mainly for NiCd batteries and was the largest consumer country. Belgium and the United States followed next.

The International Cadmium Association (ICdA) in Brussels, Belgium, made an estimate of cadmium consumption for different end uses in 2001. Batteries account for 75%, pigments 12%, coatings and plating 8%, and stabilizers for plastics and similar purposes 4%. The remaining small amount of cadmium, 1%, is used in some very special applications such as nonferrous alloys and as cadmium telluride (CdTe) for electronic compounds.

34.4.2
Corrosion Protection and Friction Reduction

The automotive and aircraft industries have been large users of cadmium for surface coating. A cadmium layer plated on steel gives corrosion protection in the same way as has been described for zinc. For cadmium plating the risk of hydrogen uptake and hydrogen embrittlement is considerably less than for treatment with zinc. For this reason critical components in the aircraft industry, e.g. landing gear, have been protected with cadmium even though use of the metal has been banned for environmental reasons. The development of new zinc plating baths, however, has eliminated the use of cadmium for corrosion protection.

The soft and ductile cadmium metal has low friction. Threaded components, such as screws, were cadmium-plated in order to avoid locking. For this use zinc is not suitable, but tin has proved to be a good alternative.

34.4.3
NiCd Batteries

The use of rechargeable batteries has changed dramatically in recent years. Power is required for a lot of portable products, such as telephones, computers and household appliances, as well as for stationary reserve power stations. The answer has been

NiCd batteries. In our modern society this battery type still provides a large fraction of the actual power, in spite of environmental problems with cadmium. However, for small portable appliances, but not for the big reserve power stations, alternatives have been found. In fact the annual cadmium use is increasing for these applications.

The small NiCd batteries are being replaced by nickel metal–hydride, NiMH, batteries (see section 17.10.3.2 on lanthanum). The reason is not only environmental. Prices have been lowered to a level comparable to NiCd batteries and they are better, regarding the so-called *memory effect*. (This expression means that the more times a battery is charged the shorter becomes the lifespan to the next charging.)

In all handling of NiCd batteries the collection of spent batteries is very important. Large industrial batteries are easy to handle and they are recycled to more than 80%. For the small consumer batteries, the difficulties are great. Different, ambitious collection programs have however been developed and tested.

34.4.4
Cadmium Pigments and Cadmium Stabilizers Need Substitutes

Because of its beautiful yellow color, cadmium sulfide was a highly appreciated pigment, *cadmium yellow*. It has been used by painters and in ceramics glazing. Also red pigments, cadmium sulfide/selenide, have been used and appreciated.

In ABS plastics for consumer products such as radios, televisions, telephones, computers and so on, pigments containing cadmium are used. Cadmium-containing stabilizers for improving light and temperature resistance are used in PVC products. An environmental problem arises when all these products are scrapped and enter the combustible fraction of municipal solid waste (MSW).

Cadmium-free alternatives are needed for pigments and stabilizers. It is proving difficult to find them and it will take time.

34.4.5
Cadmium in “Guinness World Records”™

Cadmium in nature consists of 12% of the isotope ^{113}Cd. It absorbs low-energy neutrons very well and is used as a control or shielding material in atomic energy reactors. The isotope is designated stable. Trueb [34.2] states as a curiosity that the isotope in fact is slightly radioactive. It emits β-radiation with an extremely long half-life, $9 \cdot 10^{15}$ years, thus almost 10 million billion years. It was for a while the longest half-life known and gave the isotope a place in several editions of *Guinness World Records*™. The leading position was, from 1998, taken over by ^{128}Te, which has a half-life of $2.2 \cdot 10^{24}$ years.

34.4.6
What to Do With Cadmium?

Many activities are going on in order to find substitutes for cadmium. When this endeavor has been completely successful and there is no need for cadmium, still 15 000–20 000 tonnes will be produced annually in connection with zinc manufacturing. Will this quantity be cast into concrete for terminal storage like burnt-out nuclear fuel? Or will the large difference in toxicity between soluble cadmium compounds and cadmium materials with low solubility, and because of that less toxicity, justify a certain cadmium utilization even in the future?

34.5
Cadmium in the Environment

34.5.1
Cadmium Uptake From Food and Air

Cadmium is not – unlike zinc – an essential element for life. Instead, dissolved cadmium is a poison, which enters the food chain in different ways. Plants absorb cadmium ions from water in the ground. The cadmium ions may have reached surface water through a generally increased leaching in an acid environment. On arable land, the presence of cadmium may also be a result of leaching of phosphate fertilizers and digested sludge. Cadmium absorbed in crops, e.g. rice and wheat, reaches people and animals. In coastal regions the content of cadmium in sea water is low compared to that in the depths of the sea. In the deep Atlantic the cadmium content is about 50 times higher than at the surface. Coastal vegetable matter works as scavengers and absorbs great quantities of cadmium. This is a big advantage for fish and other marine organisms that live in shallow waters.

Food is the most important path for uptake of cadmium in people and animals. Some examples of cadmium contents in foodstuffs are given in Table 34.2. It is recommended that giving up the consumption of kidneys from wild animals should reduce the intake of cadmium.

Table 34.2 Cadmium contents in some foodstuffs

Foodstuff	µg Cd per kg wet weight
Mushrooms, marine mussels, cocoa powder	> 200
Kidney, liver (from pig, cattle, sheep)	≤ 200
Wheat, wheatflour, white bread, potatoes, shrimps	≤ 40
Rye flour, rye bread, tomatoes, eggs, fish	≤ 20
Meat (from chicken, pig, cattle, sheep), fillet of sea fish	≤ 5
Drinking-water, milk, milk products	≤ 1

Source: ref. [34.3].

Cadmium may also be taken up in the body through the lungs. The smaller the cadmium-carrying particles are, the deeper into the lungs the penetration occurs. In cigarette smoke, cadmium is present as very fine particles, and the metal is deposited deep in the lungs. Smoking 20 cigarettes a day leads to a greater cadmium uptake in the body than the daily absorption from food.

34.5.2
Why Is Cadmium Toxic?

The toxicity of cadmium is due to the fact that the metal replaces zinc in important enzyme molecules, making them inactive. After great intakes, cadmium also destroys the functions of the lungs and kidneys and softens the bones, leading to intense pain. The famous Itai-Itai disease in Japan was a result of such great intakes of rice polluted by zinc refineries. The rice had ten times more cadmium than ordinary unpolluted rice.

34.5.3
The Route of Cadmium in the Body

Cadmium is absorbed in the gut and the lungs, and the blood transports it to the liver. There a remarkable reaction with a special enzyme, *metallothionein*, occurs. This enzyme seems to have the task of removing and protecting against the injurious cadmium. Due to this enzyme the body can in fact endure cadmium to a certain extent. When the cadmium intake has been too large for this scavenging protein, the metal is transported further and binds to other proteins. The protecting effect of metallothionein is a result of the fact that it contains cysteine, which binds Cd^{2+} to a complex, containing up to seven metal atoms per molecule. The enzyme, saturated with cadmium, is transported further to the kidneys, which thus concentrate a considerable part of the body content of cadmium.

34.5.4
Successful Environmental Work Regarding Cadmium

When plastics and other products containing cadmium reach municipal waste, they constitute a great source for supplying cadmium to the ground. A big part of the cadmium that enters the waste ends up in the sludge. This may be spread over fields as a fertlizer. Much attention has been paid to this and the situation has been improved. This is indicated by the development of cadmium content in digested sludge from three sewage treatment works near Stockholm (see Figure 34.1).

Another source of cadmium is fertilizers containing phosphate. Moroccan phosphate rock contains more than 50 g/tonne of cadmium and is no longer used as a fertilizer within the European Union. Industries for the production of zinc are a third source. Even here the situation is improved, as is exemplified by the following figures. In 1970 the total cadmium emissions to the atmosphere in Sweden were estimated to be 25 tonne/year. A large metal producer, Boliden, accounted for half this

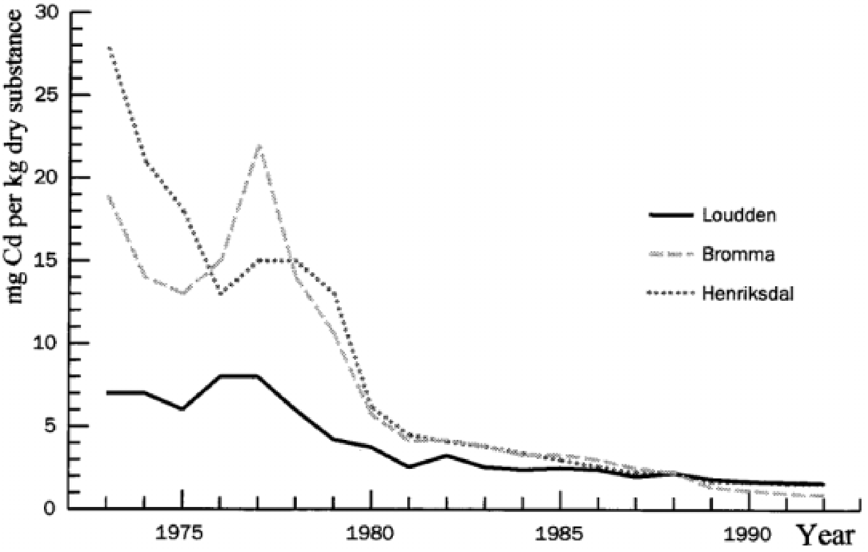

Figure 34.1 Cadmium in sludge from three sewage treatment works in the Stockholm region. At the end of the 1970s, steps were taken to restrict cadmium content in the garbage, which had to be treated [34.3].

quantity. An intensive program of improvement work was started. In 1990 Boliden had decreased its Cd emissions to 0.8 tonne/year and the whole country to 2.5 tonne/year.

34.5.5
Legislation and Government Programs

There is pressure to reduce or even eliminate the use of cadmium. The element is included in a draft list of persistent, bioaccumulative and toxic pollutants prepared by the US Environmental Protection Agency (EPA) in 1999. In many countries the cadmium contents of air, water, food additives, paints and pesticides are regulated.

Spent NiCd batteries are, when incinerated or disposed of in landfills, a source of heavy cadmium emissions. An EU Directive, 2000/60/EC, recommended that the use of 32 chemicals should be phased out within 20 years. According to the recommendation, NiCd batteries should be banned from 2008. The recommendation of 2000 was, however, moderated in 2001. Instead of banning NiCd batteries, new “take-back systems” and deposit schemes should be developed in order to reduce the risk to human health and the environment.

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35
Mercury

35.1 Hg
Facts about Mercury

35.1.1 Hg
The Element

Symbol:	Hg
Atomic number:	80
Atomic weight:	200.59
Ground state electron configuration:	$[Xe]4f^{14}5d^{10}6s^2$
Crystal structure:	Rhombohedral with $a = b = c = 3.005$ Å. $\alpha = 70.52°$

35.1.2 Hg
Discovery and Occurrence

Discovery: Cinnabar, mercury sulfide, was used as a red pigment in ancient civilizations. Elemental mercury was known in antiquity.

Most important mineral: The main source of mercury is the mineral cinnabar HgS (Figure M48). The Almadén mine in Spain has been in continuous operation for cinnabar since 400 BC.

Ranking in order of abundance in earth crust:	67
Mean content in earth crust:	0.085 ppm (g/tonne)
Mean content in oceans:	$3 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	$100 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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35.1.3 Hg

Chemical Characterization

Mercury is the only metal liquid at ordinary temperatures. Its Latin name was *hydrargyrum*, “liquid silver”. The Romans associated the mobile metal with *Mercury*, the messenger of the gods, and this is the reason for the element name *mercury* in English. The designation “quicksilver”, used in many languages, comes from the old German *quecsilabar*, “living silver”. Mercury has been used in thermometers because its coefficient of expansion is nearly constant. In one method of extracting gold and silver from their ores, the metals are combined with mercury into amalgams, from which mercury is removed by distillation. A silver amalgam is used as dental fillings. Organic mercury compounds, especially methylmercury, are dangerous, but the element is also hazardous as a vapor and in the form of its water-soluble salts.

Oxidation states:

Hg^{I} as in Hg_2Cl_2
Hg^{II} as in HgO, HgS, $HgCl_2$ and $Hg(NO_3)_2$
Hg^{III} may exist in complexes but no compounds have been isolated

Ionization energy (kJ mol^{-1}):

$Hg(g) \rightarrow Hg(g) + e^-$	1007
$Hg^+(g) \rightarrow Hg^{2+}(g) + e^-$	1810
$Hg^{2+}(g) \rightarrow Hg^{3+}(g) + e^-$	3300

Electron affinity (kJ mol^{-1}):

$Hg(g) + e^- \rightarrow Hg^-(g)$
–

Standard reduction potential: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(s)$ $E^0 = +0.854$ V

Electronegativity (Pauling): 2.00

Radii of atoms and ions:
(WebElements™)

Atomic:	150 pm
Covalent:	149 pm
Van der Waals	155 pm
Hg^{1+} (6-coordinate, octahedral):	133 pm
Hg^{2+} (4-coordinate, tetrahedral):	110 pm
Hg^{2+} (6-coordinate, octahedral):	116 pm
Hg^{2+} (8-coordinate):	128 pm

35.1.4 Hg
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
13 546 kg m^{-3} 13.55 g cm^{-3} (at 293 K)	14.81 cm^3	234.31 K (triple point) –38.84 °C	629.9 K 356.7 °C	139 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**298 K**	**373 K**	**573 K**	**973 K**
29.5	8.3	–	–	–

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
–	$61 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
58	940	1035	1280	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-2.10 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
–	–	25 GPa	–

35.1.5 Hg
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	2.29 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	59.2 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	64.0 $kJmol^{-1}$
Entropy S^0 at 298 K	76.02 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	24.3	27.98	27.1	20.8	20.8	20.8

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Hg + O_2 \rightarrow 2HgO$	–117	–73	–	–	–

35.1.6 Hg
Nuclear Properties and X-ray

Isotope range, natural and artificial	175–208

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{196}Hg	Stable	0.15	0+	–
^{198}Hg	Stable	9.97	0+	–
^{199}Hg	Stable	16.87	1/2–	0.5059
^{200}Hg	Stable	23.10	0+	–
^{201}Hg	Stable	13.18	3/2–	–0.5602
^{202}Hg	Stable	29.86	0+	–
^{204}Hg	Stable	6.87	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{199}Hg	^{201}Hg
Reference compound	$HgMe_2/C_6D_6$	
Frequency MHz (^1H = 100 MHz)	17.910	6.611
Receptivity D^P relative to ^1H = 1.00	$10 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	5.73	1.13
Magnetogyric ratio, $radT^{-1}s^{-1}$	$4.846 \cdot 10^7$	$-1.789 \cdot 10^7$
Nuclear quadropole moment, barn	–	0.386

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
79	Au	66.990
80	Hg	68.894
81	Tl	70.832

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	212
17.37 keV ($MoK\alpha_2$)	116

Neutron absorption	Thermal neutron capture cross section	375 barns

35.2
Mercury in History

35.2.1
Known in Old Egypt and in China

Heinrich Schliemann is well known for his discovery of the city of ancient Troy, and the excavation work he carried out. Less well known is his finding of a small quantity of mercury in a little coconut-shaped amulet in the great temple at Kurna, Egypt, which was built in 1400 BC. It is probably the most ancient sample of mercury and could be dated to the 15th or 16th century BC.

In China and India findings of mercury from ancient times have also been made. But obviously it took a long time before a common knowledge about the "liquid silver" was established. The Chinese alchemist *Ko Hung* (AD 281–361) wrote:

> Many do not even know that mercury comes out from cinnabar (*tan sha*). When told they still refuse to believe it, saying that cinnabar is red, and how can it produce a white substance? They also say that cinnabar is a stone, which when heated turn to ashes: and how then can anything else be expected of *tan sha*?

35.2.2
Minium and Cinnabar for Decoration

The mineral cinnabar was also known as *minium* in ancient Greece and Rome. The beautiful red powder was mixed with wax and used for decorative purposes. The pigment was often applied to interior walls. Pliny makes some notes about the utilization of minium for adornment in his *Natural History*, XXXIII, Chapters 36 and 40:

> It is in silver mines that minium is found, a pigment held at the present day in very high estimation; and by the Romans in former times – used for sacred purposes as well … for my own part I am quite at a loss to account for the origin of this usage; but it is a well-known fact, that at the present day even, minium is held at great esteem with the nations of Ethiopia, their nobles being in the habit of staining their bodies all over with it … According to

> Juba, minium is a production of Carmania, and Timagenes says that it is found in Ethiopia. But from neither of these regions it is imported to Rome, nor indeed, from hardly any other quarter but Spain; that of most note coming from Sisapo.

Sisapo is identical with the present district of Almadén, the chief source even nowadays for the mineral cinnabar. Thus minium was cinnabar [35.1].

Pliny also was aware of the toxicity of mercury. He looked upon all recipes, recommending its use for medicinal purposes, as highly dangerous. He had also observed that people employed in the factories for preparing minium protected their faces with masks or loose bladder skin in order to avoid inhaling the dust, which is highly pernicious. This outfit obviously was a forerunner of modern dust and gas masks.

35.2.3
"Living Silver" – A Messenger From the Gods

When mercury, the liquid metal, had been prepared, it was looked upon as a sort of silver, and this is the background to the Greek element name *hydrargyrum*, "water silver", and also to the symbol Hg. The designation "quicksilver", used in many languages, comes from the old German *quecsilabar*, "living silver". The Romans associated the mobile metal with the gods' messenger *Mercury*, and this is the reason for the element name *mercury* in the English language.

The appearance and special properties of the metal very much influenced the chemical thinking from its very beginning. The element fascinated people of antiquity and played a big role in the development of alchemy. Yet, the earliest descriptions of mercury are older than alchemy. Even *Aristotle* (384–322 BC) wrote about the liquid silver. *Theophrastos* (ca. 370–285 BC), Aristotle's successor, who published works within zoology and mineralogy, wrote that mercury, which has certain use, is obtained from cinnabar when it is rubbed with vinegar in mortars of brass.

Dioscorides, a Greek army surgeon in the Roman army at the beginning of our era, had the opportunity to see many countries. In his book *Materia Medica* he describes a simple distillation in connection with mercury:

> Quicksilver is made from ammion, which is called cinnabar. An iron bowl containing cinnabar is put in an earthen vessel and covered with a cup-shaped lid smeared with clay. Then it is set on fire of coals and the soot which sticks to the cover, when wiped off and cooled, is mercury.[1]

Thus it is a description of distillation and condensation. The development of chemistry had begun.

Vitruvius, living in the decades BC, gave important information about preparing mercury in ancient Rome. In his book *De Architectura*, VII, 8, he writes:

> Minium is an ore. During the digging it sheds tears of quicksilver which the miners collect and save. The masses of ore as they are taken from the mines are so full of moisture that they are thrown into a furnace or oven in the work-

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[1] cited from ref. [35.1]

> shop to dry, and the fumes that are driven off from them by the heat of the fire, settle down on the floor of the oven and are found to be quicksilver. When the lumps of ore are taken out, the drops, which remain, are so small that they cannot be gathered up, but they are swept into a vessel of water, and there they run together and combine into one.[2]

The great density of the metal he demonstrated by placing a stone in the mercury. It floats! But gold sinks.

Vitruvius also describes amalgamating:

> Quicksilver is used for many purposes; without it neither silver nor brass can be properly gilt. When gold is embroidered on a garment which is worn out and no longer fit for use, the cloth is burnt over a fire in earthen pots; the ashes are thrown into water and quicksilver added to them; this collects all the particles of gold and unites with them. The water is then poured off and the residuum placed in a cloth, which, when squeezed with the hand, suffers the liquid quicksilver to pass through the pores of the cloth, but retains the gold in a mass within it.[2]

This description is from the 1st century BC, and is the earliest known report of the amalgamation with gold. Apparently the main use of mercury in Greek and Roman times was for gilding. The golden horses in the four-in-hand on Piazza del Marco in Venice are made of bronze, which has been rubbed with gold amalgam. On heating, the mercury vaporized and a gold coating with good adherence was left. Many recipes of the *Leyden Papyrus* X [35.2] utilize mercury for amalgamation and for other purposes.

35.2.4
A Major Element for Alchemy and for Experimental Physics

Mercury manufacturing from cinnabar was well established in Europe in the 16th century, with methods like that exemplified in Figure 35.1.

For alchemists, mercury was important as substance and as principle. The purport of the *metallic principle* was just mercury and its mobility made it especially suitable for transformations. The experiments made in order to transform mercury and sulfur to gold are innumerable. Much attention was given to the mineral cinnabar, consisting of mercury and sulfur.

Gradually, and especially after the era of the alchemists, environmental problems were observed. In *Memoires 1719*, edited by the French Academy of Sciences, *Antoine Jussieu* gives a report from a visit to the mines and smelting plants in Almadén in Spain. He was surprised to find that the mercury fumes had not injured the inhabitants. Crops and trees looked fresh and springs near the mine gave good water. But slaves, working and eating in the mine, suffered severely from mercury poisoning.

The first documented use of mercury in physical science was in 1644 when the Italian physicist *Evangelista Torricelli* (1608–1647) filled a glass tube, closed at one end, with mercury. He turned the tube up and down in a container filled with mercury. In

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[2] cited from ref. [35.1]

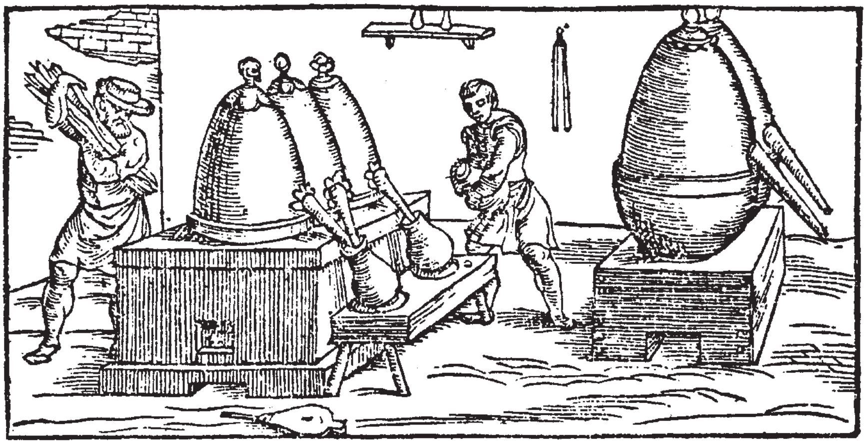

Figure 35.1 Mercury distillation in 1540.
(Reprinted from ref. [35.3].)

this way he was able, for the first time, to measure atmospheric pressure. To honor his achievement, the pressure unit 1 mmHg was called 1 Torr. The unit, however, has been superseded in the SI system. The new unit for pressure is the pascal, Pa, named after *Blaise Pascal* (1623–1662), a French mathematician and religious philosopher. 1 Torr = 1 mmHg = 133.3 Pa.

35.2.5
The Gold and Silver Countries in South America Needed Mercury

The Spaniards discovered mercury mines in Huancavelica in 1566. Probably Inca Indians, who for a long time had been acquainted with mines in which they could find cinnabar, had guided them. This mineral was used for warpaints. Alexander von Humboldt described this discovery in 1836 in his essay *Ensayo politico sobre Nueva Espana* [A political essay about New Spain]. The mine is situated in *Monte Santa Bárbara*, south of the town of Huancavelica. The mining started in 1570, when the Mexican amalgamation technique was introduced to Peru. The method became very important for the silver and gold production of the continent. The technical success, however, had a high price. Many Indians who had been enlisted compulsorily to the dangerous work died of mercury poisoning.

35.3
Occurrence and Manufacture in Our Time

Cinnabar HgS is the dominant mineral (Figure M48). The pure mineral contains 86.2% mercury. It occurs in brilliant red acicular crystals or in red, brownish, or gray masses in veins and alluvial deposits. The main deposit is at Almadén in Spain, but large quantities of the mineral are also found in Kyrgyzstan, Algeria and China. The native metallic element is found as droplets in cinnabar or deposited in hot springs, especially near volcanoes.

Almadén, some 225 km southwest of Madrid, is the richest mercury mine in the world. The mineralization originally occurred in connection with volcanic activity. Both Romans and Moors mined cinnabar there and distilled mercury. In the ore the mercury content is typically 1% but special meter-thick sections may be found with as much as 80% Hg.

Ore from Almadén and other mercury mines is crushed and heated in the presence of oxygen:

$$2HgS + O_2 \rightarrow 2HgO + 2SO_2$$

Mercury oxide is formed, which is spontaneously decomposed to mercury metal at the reaction temperature:

$$2HgO \rightarrow 2Hg + O_2$$

In this treatment sulfur is oxidized to sulfur dioxide and mercury is vaporized. For direct heating a multiple-hearth furnace may be used or alternatively a rotary kiln. These latter furnaces are operated at about 350°C at the charging head and 750°C at the discharge end. In the indirect heating system, two concentric tubes are utilized. The ore passes continuously through the inner tube while the outer tube is heated. When the mercury vapor has been condensed, air is forced through the hot metal melt. Contamination of iron, copper, zinc and lead will be oxidized and form a slag on the surface. For special purposes the mercury is purified by a further distillation.

The world production was annually about 7000 tonne during the 1980s, but during the past ten years the annual world production has averaged about 2000 tonne. Environmental legislation has compelled this reduction, which has been possible partly because mercury is substituted by other materials, and partly because new industrial processes have been developed to utilize recovered mercury. In 2000 the mine production was as low as 1320 tonne, of which Spain accounted for 500 tonne (38%), Kyrgyzstan 257 tonne (19%), Algeria 216 tonne (16%) and China 200 tonne (15%).

35.4
The Toxicity of Mercury

35.4.1
Mercury and Mercury Compounds

There are differences in toxicity between different forms of the element (liquid mercury metal and mercury vapor), inorganic mercury salts and organometallic mercury compounds.

A single oral intake of liquid metal poses a negligible risk for severe poisoning, as the intestinal absorption is low.

However, liquid mercury metal has a tendency to vaporize, expressed by its vapor pressure. At room temperature it has the value 0.002 mmHg (0.27 Pa). This approximately doubles for every 10°C temperature increase. Inhaled mercury vapor accumulates especially in the central nervous system, which is the site of major toxic effects of mercury [35.4]. Injury of the nerve system by mercury vapor gradually affects the facial muscles and eyelids. As time goes on the limbs are also influenced.

The toxicity of inorganic mercury salts increases with their water solubility. Of the chlorides, the divalent $HgCl_2$ has a high solubility, and monovalent Hg_2Cl_2 a low solubility. The latter, called calomel, has been used as a medicine against syphilis, but is toxic enough to cause mercury poisoning in the long run. The patient might have been cured of syphilis but died of mercury poisoning! The protein metallothionein (treated in Chapter 34 Cadmium) to some degree prevents damage by low intakes of mercury.

Organic mercury compounds are dangerous. They are very lipid-soluble and the body absorbs 90–100% of an oral dose. Synthetic methylmercury has been used as an effective treatment of seeds to prevent fungal attack. However, the seeds were consumed by small birds and they were poisoned. In turn, birds of prey, catching the small birds, were also poisoned, and some species were threatened with total extinction. In many counties this type of anti-fungal treatment was forbidden in the 1960s. But in certain parts of the world the treatment was continued and led to mass poisoning. The largest occurred in Iran in 1971, resulting in 459 deaths. This mercury use contributed to making people aware of the injurious effects of mercury.

35.4.2
Minamata Disease

Minamata was originally a fishing and farming village, located on the western coast of Kyushu, Japan's southernmost island. In the 1930s an industry began to manufacture acetaldehyde, used to produce plastics. Mercury was used as a catalyst and began to spill into the bay. The metal accumulated as methylmercury in fish. More than 800 people were poisoned in the middle of the 1950s. Minamata City established contact with Kumamoto University, and in November 1956, the university reported that the disease was a certain type of heavy-metal poisoning, transmitted via fish and shellfish. Gradually the connection between mercury spillage and disease was clarified.

Because of the occurrence of Minamata disease, the importance of pollution problems came to be widely recognized in Japan, and in the whole world, and measures for pollution control were taken. New techniques for trace analysis were energetically developed.

35.5
The Sources of Mercury Emissions

Mercury is present in the atmosphere mainly due to volcanic emissions but also as a result of industrial pollution. The total amount of global emissions of mercury to the atmosphere are not accurately known at present, although there is evidence that the atmospheric concentration of mercury has increased by about 1% per year for the last 25 years. The volcanic emissions are very big, between 25 000 and 100 000 tonne/year. They are responsible for a base level of mercury concentration in the ground and water. Mercury from the atmosphere is enriched in the surface layers of the ground, where it forms complexes with humus. Rain water dissolves and transports humus to streams and lakes. Mercury is enriched in the top layers of the bottom sediments.

In the Amazonian gold rush from about 1975 (see Chapter 5 Gold), the emission of 130 tonnes of mercury per year to the local environment was estimated. It was of course very dangerous for the workers who burned the gold amalgam and for the populations living in the gold-mining areas. The problem was not just connected with these local effects. Mercury contamination in the Amazon Basin is far more complex. Studies carried out hundreds of kilometers downstream from the gold-mining activities indicate that the soil is loaded with natural mercury. *Slash and burn of forest* (from 1960), coupled with important precipitation, lead to leaching of soil into the river and is believed to contribute to the mercury poisoning in this region. Investigation [35.5] shows a considerable increase of mercury uptake among the fish-eating population. Mercury in hair was selected as a bioindicator since it is highly specific for methylmercury.

35.6
The Technical Use of Mercury

As the toxicity of mercury went unrecognized for a long time, the special properties of the element became the basis for a versatile utilization and this remained partly the case up to very recently. As is clear from the following description, mercury may be used in a lot of applications. For all these, the intention is to find substitutes, which both function well without mercury and are acceptable from the environmental point of view.

35.6.1
Metal and Chemicals in Science and Technology

Mercury has been used as a metal in thermometers because its coefficient of expansion is nearly constant, which means that the changes in volume for each degree rise or fall in temperature is the same. It has also had widespread use in many types of scientific apparatus, such as vacuum pumps, barometers, electrical rectifiers, relays and switches.

In the chemical industry, mercury is used as a catalyst for the manufacture from acetylene of acetaldehyde, vinyl chloride and vinyl acetate. Mercury acetate has been used in paints. The intention has been to protect boats against attack of mold fungus. Mercury fulminate $Hg(ONC)_2$ was earlier used in detonators, but is nowadays replaced by lead azide.

35.6.2
Mercury in Lighting

If an electric current is passed through gases, as in the mercury-vapor arc lamp, an intense blue-green light is obtained, which is used for photographic and roadway illumination. For general-purpose illumination the *fluorescent lamp* utilizes an electric discharge in a low-pressure mercury-vapor lamp contained in a glass tube, which is coated on the inside with a fluorescent material known as *phosphor* (which has nothing to do with the element phosphorous). Due to the radiation in the arc, the phosphor fluoresces. Much of the radiation from the arc is invisible ultraviolet light, but this radiation is changed to visible light by the phosphor. By choosing a suitable phosphor, the light from such lamps can be made to approximate the quality of daylight. In addition, the efficiency of the fluorescent lamp is high. A 40 W fluorescent tube produces as much light as a 150 W incandescent bulb. Because of that, fluorescent lamps produce less heat than incandescent bulbs for comparable light production. A modern fluorescent tube contains only 0.01 g mercury, compared to more than 0.035 g in earlier mercury lamp versions.

35.6.3
Mercury in Batteries

The mercuric oxide–zinc cell is a primary battery (not rechargeable). It is made in the shape of a small flat disk and used in this form in hearing aids, photoelectric cells, mini-calculators and so on. The negative electrode consists of an outer zinc casing, filled with a paste of mercuric oxide and zinc hydroxide, in contact with a small steel cathode. The mercury battery voltage is about 1.34 V, stable for a very long time. Mercury contributes to a stable voltage and great capacity. The mercury content in these batteries was originally 0.3%. In modern zinc–air batteries, the mercury content is reduced to an accepted trace level but not quite eliminated.

35.6.4
Amalgamation in Large-Scale Industry

Liquid mercury was once used in the extraction of gold and silver. Added to the crushed ore, it formed liquid amalgams with the noble metals. After the amalgams were squeezed out of the ore, the mercury was removed by distillation, leaving metallic gold or silver.

In the *chlor–alkali process* for chlorine production, a sodium chloride solution is electrolyzed with mercury as the cathode material. Na^+ ions are discharged and sodium metal formed spontaneously is alloyed with mercury as a sodium amalgam:

$$2Na^+ + 2Cl^- \rightarrow 2Na(\text{in Hg}) + Cl_2$$

When Na amalgam is removed from the cell and treated with water, sodium hydroxide and hydrogen gas are formed:

$$2Na(\text{in Hg}) + 2H_2O \rightarrow 2NaOH + H_2 + Hg$$

The liquid mercury is recycled back to the electrolytic cell.

A serious drawback with the process described above is mercury loss to the environment. A modern, alternative process without mercury, the membrane cell technique, is described in Chapter 50 Halogens.

35.6.5
Amalgam in Dental Fillings

The tendency of mercury to form amalgams has been utilized in dentistry. An amalgam for dental fillings may be composed of 52% mercury, 35% silver and 13% tin. It is prepared by stirring a silver–tin alloy into mercury. The mixture is vibrated to a plastic mass, which is placed in the bored tooth and compressed.

The health problems caused by dental amalgam have been very much discussed. The average adult has at least 5 g of mercury in fillings. Mercury in solid form vaporizes at a slow rate, but this is increased with temperature, such as with the intake of hot drinks and food. Already in 1987 the Federal Department of Health in Germany issued an advisory warning against the use of dental amalgam in pregnant women. Many countries have similar or more extensive bans or health warnings regarding the use of amalgam. The US EPA decreed that removed amalgam fillings are hazardous and must be sealed airtight and disposed of as hazardous waste. Most European countries require controls on dental waste amalgam emissions to sewers or air, also from crematoria.

The health problems with dental amalgam fillings are treated in many publications. Washington Department of Health (DOH) has reviewed amalgam fillings as a health risk [35.6].

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36
Boron

36.1 B
Facts about Boron

36.1.1 B
The Element

Symbol:	B
Atomic number:	5
Atomic weight:	10.81
Ground state electron configuration:	[He]$2s^2 2p^1$
Crystal structure:	Rhombohedral with $a = b = c = 5.06$ Å. $\alpha = 58.06°$. A deformed cubic close packing

36.1.2 B
Discovery and Occurrence

Discovery: Boron compounds have been known for thousands of years, but the element was not isolated until 1808 by Joseph-Louis Gay-Lussac and Louis Jaques Thénard in Paris and by Humphry Davy in London.

Most important mineral:	Borax, tincal $Na_2B_4O_7 \cdot 10H_2O$ Colemanite $Ca_2B_6O_{11} \cdot 5H_2O$ Kernite $Na_2B_4O_7 \cdot 4H_2O$ Sassolite, boric acid $B(OH)_3$ or H_3BO_3 Ulexite $NaCaB_5O_9 \cdot 8H_2O$. Hydroboracite $CaMgB_6O_{11} \cdot 6H_2O$

Ranking in order of abundance in earth crust:	37
Mean content in earth crust:	10 ppm (g/tonne)
Mean content in oceans:	4.44 ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^6$ years
Mean content in an adult human body:	0.7 ppm
Content in a man’s body (weight 70 kg):	49 mg

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36.1.3
Chemical Characterization

Boron is hard, brittle element on the borderline between metals and non-metals. Although it belongs to group 13 (3A), which would indicate a close relationship to aluminum, it is chemically much more like carbon and silicon. This anomalous similarity is especially evident in the boranes, compounds of boron with hydrogen. Crystalline boron is resistant to attack by boiling HF or HCl. With metals and with carbon, boron forms borides, some of them very hard. Boron carbide is used as an abrasive. Boron has several important applications in the field of atomic energy. In biology, it is a trace element needed for plant growth, but toxic in excess. Boron halides and boron hydrides (boranes) are highly toxic.

Oxidation states:

B^{III} as in B_2O_3, $B(OH)_3$, and $Na_2B_4O_7 \cdot 10H_2O$
B^{-III} (formal) as in B_2H_6
Borides as FeB, ZrB_2, and B_4C do not conform to usual valence concepts

Ionization energy (kJ mol^{-1}):

$B(g) \rightarrow B^+(g) + e^-$	801
$B^+(g) \rightarrow B^{2+}(g) + e^-$	2427
$B^{2+}(g) \rightarrow B^{3+}(g) + e^-$	3660
$B^{3+}(g) \rightarrow B^{4+}(g) + e^-$	25 026

Electron affinity (kJ mol^{-1}):

$B(g) + e^- \rightarrow B^-(g)$
–26.7

Standard reduction potential: $B(OH)_3(aq) + 3H^+(aq) + 3e^- \rightarrow B(s) + 3H_2O(l)$ [acid solution]
$E^0 = -0.890$ V
$B(OH_4)^-(aq) + 3e^- \rightarrow B(s) + 4OH^-(aq)$ [alkaline solution]
$E^0 = -1.811$ V

Electronegativity (Pauling): 2.04

Radii of atoms and ions:
(WebElements™)

Atomic:	85 pm
Covalent:	82 pm
B^{3+} (4-coordinate, tetrahedral):	25 pm
B^{3+} (6-coordinate, octahedral):	41 pm

36.1.4 B
Physical Properties

Density	**Molar volume**	**Melting point**[a)]	**Boiling point**[a)]	**Specific heat c_p at 298 K**
2340 kg m^{-3} 2.34 g cm^{-3}	4.62 cm^3	(2348) K (2075) °C	(4273) K (4000) °C	1027 J K^{-1} kg^{-1}

a) Melting and boiling points in paranthesis due to their uncertainty.

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
72	32	19	11	10

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
–	$4.7 \cdot 10^{-6}$	$5.4 \cdot 10^{-6}$	$6.2 \cdot 10^{-6}$

Resistivity nΩm

78 K	**298 K**	**373 K**	**573 K**	**973 K**	**1473 K**
–	$18 \cdot 10^{12}$	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-7.8 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
–	–	320 GPa	–

36.1.5 B
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	22.5 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	508 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	563 kJmol^{-1}
Entropy S^0 at 298 K	5.86 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	1.07	11.09	20.5	24.9	29.5	31.4

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3B + O_2 \rightarrow 2/3B_2O_3$	–796	–765	–674	–593	–512

36.1.6 B
Nuclear Properties and X-ray

Isotope range, natural and artificial	7–17

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{10}B	Stable	19.9	3+	1.801
^{11}B	Stable	80.1	3/2–	2.689

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{10}B	^{11}B
Reference compound	$BF_3 \cdot OEt_2/CDCl_3$	
Frequency MHz (^1H = 100 MHz)	10.744	32.084
Receptivity D^P relative to ^1H = 1.00	$3.95 \cdot 10^{-3}$	0.132
Receptivity D^C relative to ^{13}C = 1.00	22.6	756
Magnetogyric ratio, radT^{-1}s^{-1}	$2.875 \cdot 10^7$	$8.585 \cdot 10^7$
Nuclear quadropole moment, barn	0.0846	0.0406

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
4	Be	0.109
5	B	0.183
6	C	0.277

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	2.32
17.37 keV ($MoK\alpha_2$)	0.371

Neutron absorption	Thermal neutron capture cross section	761 barns

36.2
Boron in History

36.2.1
Preludes

The Arabs and Persians knew of borax very early, and it was mentioned as *tincal* or *tincar* in manuscripts two thousand years old. Boron oxide has been detected in Chinese enamels from the 4th century BC. Marco Polo told about borax from Mongolia in the 13th century AD. Borax reached Europe from Central Asia and India via Constantinople and Venice, and for a time the Venetians had a monopoly on the importing of borax from Asia into Europe. This changed in the 1770s when great deposits of boric acid were discovered in Tuscany in Italy. Borax and boric acid were used in the manufacture of glass and also the soldering of gold pieces.

Not until the beginning of the 18th century did something become known about the chemistry of borax and boric acid. *Willem Homberg* (1652–1715) found in 1702 that heating borax in an iron sulfate solution gave a sublimate, which he called *sel volatil narcotique du vitriol*. It was known for a long time as *sedative salt* and was used as a pain-relieving medicine. In 1785 Torbern Bergman in Uppsala showed that the substance was not a salt at all but an acid. Homberg had, without knowing it, prepared the acid of borax. With his experiment Homberg had started the long era of the preparation of medicines from borax products. In fact, boron compounds, found in nature, were used in ancient times in skin ointments.

> Willem Homberg was born on the island of Java, where his father worked for the Dutch East India Company. Back in Amsterdam, Willem had the possibility of studying in different European seats of learning. In Würtenberg he became a doctor of medicine. He worked with Robert Boyle in England, and went to see mines in Germany and Sweden. At the end of his life, he lived in Paris and died there in 1715.

P. J. Macquer (see Chapter 11 Sodium and Potassium) asserted in the middle of the 18th century that borax contains an alkali of the same type that is found in sea water (cited from Mary Weeks):

> Though borax is of great use in many chymical operations, especially in the fusion of metals, yet the late years Chemists were quite ignorant of its nature, as they still are of its origin; concerning which we know nothing with certainty, but that it comes rough from the East Indies and is purified by the Dutch.

In the 1770s the merchant *Johan Abraham Grill* described borax from Tibet, called *poun-xa*. He had got it from the *supercargeur Petter Johan Bladh* at the Swedish East India Company. A native Catholic missionary, Vitalis Kuo had delivered it. J. A. Grill and Gustav von Engeström at Laboratorium Chymicum wrote about *Poun-xa or Native Borax* in the Transactions of the Swedish Academy of Sciences, 1772, 321–322. They informed that Padre Kuo had told the following about the winning of *Poun-xa* in the Kingdom of Tibet:

> Poun-xa is won by digging in the ground to a deep of two ells [one ell is an obsolete unit of length, equal to 45 inches, approximately 1.14 m]. From the taste of the earth it is possible to conclude whether the substance is present or not. Different types of it may be present; 1:o Houi Poun is of the size of semolina; 2:o My-Poun is similar to small white beans; 3:o Pin-Poun or crystallized Poun-xa consists of semi-transparent Crystals of the size of walnuts. Poun-xa is present finished in nature and can not be prepared by boiling of the earth. For refining of Poun-xa the method is the following: Water is boiled in an iron pot; Poun-xa is thrown into the boiling water, which is now stirred with a piece of wood until all Poun-xa is well dissolved; after cooling in another vessel the clear water is poured off as is done with the Saltpeter.

36.2.2
The Discovery of Boron

The element boron was discovered in 1808. A gray powder of boron was formed in the reaction between potassium metal and boric acid. This discovery was made by J.-L. Gay-Lussac and L. J. Thénard in Paris and almost simultaneously by Sir Humphry Davy in London. That the name for the new element should contain the syllable *bor* was natural due to its origin in borax. Davy saw similarities between the new element and carbon, and found it logical to use the name *boron*. It also became the name of the element in the English language.

The Frenchman Henry Moissan manufactured boron industrially in 1895 by reduction of boron trioxide B_2O_3 with magnesium.

36.3
Boron Occurrence in Our Time

36.3.1
An Unexpected Find at the Building of a Sanitarium

In 1913, some 150 km northeast of Los Angeles, in a region with fresh air and unspoiled countryside, a sanitarium was built for people suffering from lung disease. Water was needed and a deep drilling was carried out, during which a find of the mineral colemanite, a calcium borate, was made. It was of geological interest but did not stop the building of the hospital and the arrangements for its water supply. The observation was not forgotten, however, and in 1925 an extensive geological prospecting of the whole region was undertaken. This revealed very large deposits of boron minerals, mainly borax and kernite, two sodium borates with different contents of water of crystallization. The place where the drilling revealed the secret of the ground nowadays bears the name *Boron*.

36.3.2
Borate Deposits in the World

Boron in California is one big sedimentary deposit, but not the only one. Another great one was found at Kirka in Turkey. These two deposits supply more than 80% of the world's demand for borates. Similar deposits, although on a smaller scale, occur in Argentina and Chile. Borosilicate minerals are found in Russia, and magnesium borate minerals in Russia and China. Table 36.1 shows mineral types and locations for different boron minerals [36.1–2].

The production of boron products in the year 2000 counted as content of boron trioxide B_2O_3 is shown in Table 36.2.

Table 36.1 Boron mineral deposits and their locations

Country/location	Mineral types[a]
The Boron mine, California, USA	Borax Kernite Ulexite
Kirka, Western Turkey	Borax Ulexite Colemanite
Argentina	Borax Ulexite Colemanite Hydroboracite
Chile	Ulexite
Provinces of Liaoning and Jilin, China	Szaibelyite[b] Hydroboracite Borax Ulexite
Vladivostok region in far east of Russia	Szaibelyite[b] Datolite and danburite[c]

a) Formulas given in "Facts About Boron" at the beginning of the chapter.

b) Szaibelyite $MgBO_2(OH)$ is the principal Russian source of boron compounds.

c) Datolite $CaBSiO_4(OH)$and danburite $CaB_2(SiO_4)_2$ are found in skarn-type, metamorphic rock complexes.

Table 36.2 World production of boron minerals in 2000

Country	Mineral production	
	B_2O_3 ktonne	Percentage of world production
Turkey	1450	31.1
United States	1070	23.0
Russia	1000	21.5
Argentina	580	12.4
Chile	338	7.25
China	145	3.1
Other countries	77	1.65
Total	4660	100

Source: ref. [36.2].

36.4
Common Boron Products and Their Uses

Boron is mainly used for glass and ceramic products (55% of world boron consumption), soaps and detergents (15%), agriculture (6%) and fire retardants (4% and increasing). In addition boron is used in many very special applications, such as in strong ferromagnetic materials, as an alloying element in steel and as boron carbide and boron nitride for tools. Boron has important applications in the field of atomic energy, and boric acid is used medically. Boron is also used in pyrotechnic flares, utilizing its distinctive green color, and as an igniter in rockets.

Boron has an increasing use in high technology in connection with the introduction of the iron–boron–neodymium magnet. This has been treated in the neodymium section in Chapter 17 Rare Earth Metals.

36.4.1
Borax and Boric Acid

Borax $Na_2B_4O_7 \cdot 10H_2O$ is prepared by water leaching of the mineral tincal and crystallization. By heating of borax in sulfuric acid, boric acid $B(OH)_3$ is obtained. This acid is very weak and is used for its astringent and antiseptic properties. Boric oxide B_2O_3, prepared by heating boric acid, is an important raw material for manufacturing of other boron products.

Borax is used as a so-called lubricant carrier in metal-working processes, such as for instance wire drawing. It forms a lubrication system together with lubricants such as sodium or calcium stearate. At the high pressure in the drawing die, the stearate melts and fulfills the lubrication needs. Borax is not fused but will be dispersed as small solid particles in the stearate. It makes the liquid soap more viscous and it is not so easily squeezed off from the deformation zone. The lubricating effect is improved.

36.4.2
Borax Glass Products

The common soda-lime glass cannot withstand a thermal shock, as its coefficient of thermal expansion is very high. Its dimensions change considerably with temperature. This was a great problem for the lanterns in early days. In rain, the hot glass fractured. Adding B_2O_3 to the glass melt solved the problem. The *borosilicate glass* obtained has a low coefficient of thermal expansion and thus a good thermal shock resistance. It is widely used in chemical laboratories and in modern kitchens. Trade names for the glass are Pyrex and Duran, to name just two. Calcium aluminoborosilicate glass contains 6–12% boron oxide. Comparison between thermal expansion of different glass types is found in chapter 43, Lead, table 43.5.

Glass filaments with the size of 20 μm are made from borosilicate glass by drawing through platinum bushings. Very thin fibers are spun from molten glass and used for thermal isolation.

The US Department of Energy (DOE) plans to store spent nuclear fuel enclosed in stainless-steel containers lined with borosilicate glass.

36.4.3

Boron in Laundry Products

Sodium perborate has the correct full formula $Na_2[B_2(O_2)_2(OH)_4] \cdot 6H_2O$. It is obtained by treating sodium borate with hydrogen peroxide H_2O_2. The peroxide group, built into the molecule, makes the compound a color-safe bleaching alternative in laundry. The formula commonly used, $NaBO_3 \cdot 4H_2O$, is misleadingly simple. Sodium perborate has been an important ingredient of washing and dishwashing powders and tablets. It is also used as a monohydrate, which is said to be more effective at low temperatures compared to the tetrahydrate.

36.4.4

Boron in Agricultural Products

Boron is a nutrient that is essential to all plants, and lack of the element may stunt growth. Trees need more boron than other plants, but crops like sugar beet, celery and cauliflower are sometimes affected of boron deficiency. The olive groves in Greece and Spain have suffered from lack of boron and gave poor yields, but boron additives improved the situation. The real function of the boron atom in the plant is not known, but large quantities of fertilizers containing borax or kernite are used throughout the world. They are applied by spraying or incorporating into other fertilizers, herbicides, or irrigation water.

36.4.5

Flame Retardants

Fire safety requirements imply the use of flame retardants. They constitute a large and heterogenous group of substances, among which are polybrominated diphenyl ethers (PBDE) and polybrominated biphenyls (PBB). As these compounds are questionable from an environmental point of view, there is a desire to replace them with less hazardous substances.

In special cases, for the protection of lumber, wooden products, fiberboard, textiles and paper, borax and boric acid are important alternatives. They function not only as flame retardants but also as protection against mould fungus.

Fire in cotton mattresses and bedding causes a great many deaths. The Consumer Product Safety Commission (CPSC) in the United States has introduced rules to improve fire safety by utilizing absorbed boric acid as a fire retardant for cotton mattresses.

36.5
Special Boron Products and Applications

36.5.1
Elemental Boron

In the periodic table, many elements show more similarity with the neighbors obliquely down to the right than with their successors in the same group. This is the case also for boron, which is a stranger in its group 13. In its properties it is very unlike its successor, aluminum, but has similarities with silicon in group 14 (see Table 36.3). Its electrical conductivity varies markedly with temperature, which is characteristic for semiconductors.

Table 36.3 The element boron and its neighbors in the periodic table

	Group 13		**Group 14**		**Group 15**	
Period 2	5	B	6	C	7	N
Period 3	13	Al	14	Si	15	P
Period 4	21	Ga	22	Ge	23	As

The oxide B_2O_3 may be reduced by magnesium at high temperature to a product with a boron content of 86–88%. It is often called "amorphous boron". Industrially, boron with high purity is manufactured by reduction of boron trichloride with hydrogen. The annual production of boron, amorphous and elementary together, in the world is about 50 tonnes.

Burning boron, forming boric oxide, develops 50% more energy per unit weight than burning carbon to carbon dioxide. For this reason, so-called amorphous boron has been used as a fuel in rockets. Boron is also used in pyrotechnic flares, in which the distinctive green color it gives to stars and Catherine wheels is utilized. Mixtures of boron and potassium nitrate are also used as an igniter for ammunition, mines and fireworks.

Although very toxic, sodium azide (NaN_3) is used in some airbags in automobiles. As an igniter, 0.1–0.3 g boron mixed with potassium nitrate or another oxidizing agent is used. On collision, the system is activated within a few milliseconds, the azide is decomposed and nitrogen gas produced blows up the airbag.

36.5.2
The Special Boron Isotope ^{10}B

Boron consists of two isotopes, ^{10}B and ^{11}B. The former, which accounts for 20% of natural boron, is a very strong neutron absorber and for that reason is used for the control rods in nuclear reactors and as a shield for nuclear radiation. A 1 cm thick layer of boron enriched in the isotope ^{10}B gives the same shielding action against neutrons as 20 cm of lead or 5 m of concrete (an alternative to boron is gadolinium). The pure boron isotope is however very expensive. In many applications natural boron is utilized instead. The emergency cooling systems in nuclear reactors and in nuclear-powered submarines utilize boric acid or borax with natural isotopic composition. The situation is the same for plastics surrounding sensitive instruments and the rubber clothes for personnel.

36.5.3
Boron Carbide

Boron carbide B_4C is very hard, 9.6 on the Mohs scale[1]. There are only two substances that are harder, namely cubic boron nitride (9.8) and diamond (10). Boron carbide is manufactured through the reaction between boron trioxide and carbon at 2000°C in an electric arc furnace.

Boron carbide is used as an abrasive material for grinding, lapping and polishing. It is also used to some extent as an industrial ceramic in nozzles for sand-blasters, turbines for turbojet engines and mortars.

36.5.4
Boron Nitride – Soft as Graphite and Hard as Diamond

Boron has a distinct relation to nitrogen, two steps to the right in the periodic table (see Table 36.3). The boron atom has *one* 2p electron, whereas the nitrogen atom has *three*. Thus for boron nitride, a "mean" atom B/N can be looked upon as one atom with *two* 2p electrons. This is however just what the carbon atom has.

So it is not by chance that boron and nitrogen form boron nitride, one modification of which is similar to graphite regarding structure and properties. Due to its color, it is called *white graphite*. Like common black graphite, it can be transformed to a cubic modification at high temperature and pressure. Cubic boron nitride is the second hardest substance known, after diamond.

Boron nitride BN is formed in the reaction between boron and nitrogen at 1100°C. In its α-modification, white graphite, it is soft and has good lubricant properties. It is especially used for lubrication at high temperatures. A very special application of white graphite is for cosmetics, lipsticks and skin creams. The finely ground nitride has neither color nor scent, but it is said to lend to the beauty preparation a discreet luster and a pleasurable sensation of velvet. The leap from this to tools suitable for machining in hardened steel is great, but boron nitride takes it.

White graphite is transformed to the cubic β-modification of boron nitride at a pressure of 70 000 atm (ca. 7000 MPa) and a temperature of 1600°C. The cubic boron nitride (CBN) can be used as a tool for the machining, turning, milling and drilling of hard alloys, including steels. Diamond, which is harder still, cannot be used for steel machining, as the locally very high temperature destroys the tool due to graphite formation.

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[1] Mohs scale is a standard with ten minerals by which the hardness of a mineral may be rated. The standard minerals are (hardness in parentheses): talc (1), gypsum (2), calcite (3), fluorite (4), apatite (5), orthoclase (6), quartz (7) topaz (8), corundum (9) and diamond (10).

36.5.5
Boron in Batteries and Fuel Cells

Millennium Cell [36.3] has patented boron-based batteries. The anode reaction is

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-$$

and the cathode reaction is

$$8e^- + 4H_2O + 2O_2 \rightarrow 8OH^-$$

The total reaction will thus be

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O$$

or

$$NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O$$

The total reaction is very energetic. Another advantage is that the components are very light in weight. In comparison with zinc batteries, boron-based batteries are said to be several times better. A borohydride fuel cell for generation of electricity has also been patented.

36.5.6
Boron in Steel

Boron is used as an alloying element for steel. For that reason, the alloy ferroboron, with 20% boron, is manufactured in electrometallurgical processes and used as a raw material. Low boron contents, as low as 0.003% B, have a marked effect on the hardenability of steels with medium high carbon contents. It leads to hardening through the component section without alloying the steel with expensive elements such as chromium and nickel. Boron steels of this type have been very much utilized for agricultural machinery.

The ability of steel to withstand moderate stress without plastic deformation and fracture at high temperature is its *high-temperature strength*. In steam turbines, hardened chromium steels with 9–12% Cr are used. If they are alloyed with some tenths of a percent of boron, small boride precipitations are formed in the iron matrix. These act as obstacles to dislocation movements (slips in the crystal grains) and by that means improve the high-temperature strength.

36.6
Boron in the Life of Animals and Humans

Despite the importance of boron in plants, it has been stated that boron has no essential role for animals and human beings. New investigations, however, have shown that a relationship exists between the amount of boron in soil and drinking water and the incidence of arthritis in a population. In the most arid areas of the world, the incidence of arthritis tends to be dramatically lower than in the humid areas. Arid areas also have the highest concentrations of boron in the drinking water and soil. This is natural, as boron is leached out of the soil in wet climates. Thus farmers ought to check the level of boron in their soil. If boron concentrations are low, they may give their crops or livestock supplemental feed containing this important trace element.

Boron halides and boron hydrides (boranes) are highly toxic.

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37
Aluminum

37.1 Al
Facts about Aluminum

37.1.1 Al
The Element

Symbol:	Al
Atomic number:	13
Atomic weight:	26.98
Ground state electron configuration:	[Ne]$3s^23p^1$
Crystal structure:	Cubic fcc with $a = 4.05$ Å

37.1.2 Al
Discovery and Occurrence

Discovery: In 1825 H. C. Oersted in Copenhagen prepared the element aluminum for the first time. Between 1827 and 1845, Friedrich Wöhler improved Oersted's process. In 1886 Charles M. Hall and Paul Héroult independently developed the method for aluminum manufacture by electrolysis of fused salts, a technique now known as the Hall–Héroult process. The element's name has its own history. In 1761 de Morveau proposed the name *alumine* for the base in alum. The name *aluminium* was adopted by IUPAC to conform to the „ium" ending of most elements. Aluminum is the IUPAC spelling, and therefore the international standard. In 1925 the American Chemical Society decided to change the name to *aluminum*, still used in American literature and technical descriptions.

Most important mineral: Aluminum oxide, corundum Al_2O_3 (Figure M49) is used as an abrasive.
Bauxite, named after Les Baux de Provence, near Arles in southern France, is the most important ore.
Minerals in bauxite: diaspore or boehmite AlO(OH)
gibbsite or hydrargillite $Al(OH)_3$

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Ranking in order of abundance in earth crust:	3
Mean content in earth crust:	$8.23 \cdot 10^4$ ppm (g/tonne) (8.23 %)
Mean content in oceans:	0.002 ppm (g/tonne)
Residence time in oceans:	100 years
Mean content in an adult human body:	0.9 ppm
Content in a man's body (weight 70 kg):	63 mg

37.1.3 Al

Chemical Characterization

Aluminum is the most abundant metallic element in the earth's crust. It is a silvery white metal with many desirable properties. In contact with air, aluminum rapidly becomes covered with a thin layer of aluminum oxide that reduces further corrosive attack. Architecturally the metal is very important and widely utilized. Aluminum foil, 0.2 mm, thick protects food and other perishables. The metal is also widely used for containers, bottles and cans. The recycling of such containers is increasingly important from an energy-saving point of view. Aluminum is characterized of a low weight-to-strength ratio, which makes the metal and its alloys useful in the construction of aircraft, railroad cars and automobiles. The metal is also appreciated for other applications, in which low weight is particularly important. One such example is conductors for long-distance, high-voltage power transmission.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Al^{III} as in Al_2O_3, $AlCl_3$, and AlN	$Al(g) \rightarrow Al^+(g) + e^-$	578	$Al(g) + e^- \rightarrow Al^-(g)$ −42.5
	$Al^+(g) \rightarrow Al^{2+}(g) + e^-$	1817	
	$Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$	2745	
	$Al^{3+}(g) \rightarrow Al^{4+}(g) + e^-$	11 577	

Standard reduction potential: $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E^0 = -1.676$ V

Electronegativity (Pauling): 1.61

Radii of atoms and ions: (WebElements™)		
	Atomic:	125 pm
	Covalent:	118 pm
	Al^{3+} (4-coordinate, tetrahedral):	53 pm
	Al^{3+} (6-coordinate, octahedral):	67.5 pm

37.1.4 Al

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
2699 kg m^{-3} 2.70 g cm^{-3}	10.00 cm^3	933.5 K 660.3 °C	2792 K 2519 °C	902 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
241	236	240	233	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$12.2 \cdot 10^{-6}$	$23.1 \cdot 10^{-6}$	$26.4 \cdot 10^{-6}$	$34 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
2.1	25	35.5	59	247	321

Mass magnetic susceptibility χ_{mass} at 293 K	$+7.7 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
70 GPa	26 GPa	76 GPa	0.35

37.1.5 Al
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	10.7 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	292 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	325 kJmol^{-1}
Entropy S^0 at 298 K	28.32 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	13.0	24.35	28.0	31.75	31.75	31.75

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3Al+O_2 \rightarrow 2/3Al_2O_3$	–1055	–1013	–907	–798	–690

37.1.6 Al
Nuclear Properties and X-ray

Isotope range, natural and artificial	22–35

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{27}Al	Stable	100	5/2+	3.642

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{27}Al
Reference compound	$Al(NO_3)_3/D_2O$
Frequency MHz (^1H = 100 MHz)	26.057
Receptivity D^P relative to ^1H = 1.00	0.207
Receptivity D^C relative to ^{13}C = 1.00	1180
Magnetogyric ratio, radT^{-1}s^{-1}	$6.976 \cdot 10^7$
Nuclear quadropole moment, barn	0.140

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
12	Mg	1.253
13	Al	1.486
14	Si	1.739

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	49.8
17.37 keV (MoKα_2)	5.18

Neutron absorption	**Thermal neutron capture cross section**	0.23 barns

37.2
Aluminum in History

37.2.1
The Early History of Aluminum is Alum's History

Aluminum is the most common metal in the earth's crust but the element itself was late to be discovered. It is bound so tightly in its oxide that there is no possibility of setting the metal free by the usual means of reduction with carbon. However, even in antiquity, long before people on the whole were aware of the existence of metallic aluminum, interest in alum was great. It was the salt that nowadays has the formula $KAl(SO_4)_2 \cdot 12H_2O$. Thus it is potassium aluminum sulfate, a colorless substance with an astringent taste. It obtained its Latin name from an Indo-European word stem *alu*, meaning bitter. We know that alum stanches bleeding and that it improves the dyeing of textiles. This was already known in antiquity, and started the search for deposits of alum and methods for preparing the valuable substance.

In some volcanic regions the conditions were favorable for the formation of alum during reactions between aluminum and potassium in the ground and sulfur from the volcano. The Eolic Islands to the north of Sicily are volcanic. Stromboli is one of them; Lipari is the largest. A black or dark-colored volcanic glass, called obsidian, may be found there. The term goes back as far as Pliny, who described this mineral from Ethiopia. Obsidian has been used for making arrowheads, other sharp implements, jewelry and art objects. Obsidian from Lipari became an important export product, long before Christ. In this milieu, with great mineralogical activity, alum was discovered. It is mentioned in writings from the 1st century BC that the Romans exported alum from works on Lipari to dye Phoenician textiles.

The alum deposits on the island of Ischia outside Napoli were worked in the 12th century AD, but new applications for alum, such as for instance in the tanning of leather, increased demand so much that alum had to be imported from the Middle East. Roman alum workers were active in Syria, and Roman merchants took care of the deliveries to their home provinces. However, everything was changed by Turkish expansion in the 15th century. The Romans had to return home not only to unemployment but also to the task of finding new domestic deposits of alum. In a barren mountain district at Tolfa near Rome they found the same type of vegetation that they remembered from the alum region in Syria. This work took place with the merchant Giovanni de Castro as leader. They found white alum stones in a quantity large enough for production. It was a great event and was observed by Pope Pius II. Giovanni de Castro was granted an annual endowment and a statue of him was erected in his honor.

The invention of the art of printing increased the demand for alum from the beginning of the New Era in the 16th century. The method with alum impregnation of paper had been introduced, which created a need for the substance in the growing publishing of books and magazines. Alum was eagerly sought all over Europe and deposits were found in Italy, Germany, England and Scandinavia.

In the first place, the search was for actual alum deposits. However, it was discovered that alum also was hidden in some rocks, originally containing iron sulfide, and pyrite. When decomposed, the pyrite FeS_2 formed sulfuric acid, which had reacted with the aluminum and potassium materials of the rock and formed alum. Roasting of this alum shale or alum schist and leaching with water gave a solution containing potassium, aluminum and sulfate ions. After filtering and evaporating of the water, colorless alum crystals were formed.

Large heaps of burned alum remained as red residues after the alum leaching, and are still there today. The uranium content of the alum shale is left in the residues and makes this material unsuitable for house foundations, as such houses will be affected by radon radiation.

Attempts to prepare synthetic alum from raw materials rich in aluminum hydroxide and sulfate were also made.

In the middle of the 18th century alum found many uses in substantial quantities. But what was alum in reality? Several experienced chemists put that question to themselves. Andreas Sigismund Marggraf (Chapter 11 Sodium and potassium), who had shown that aluminum oxide, calcium oxide and magnesium oxide are different “earths”, set about working with the alum problem. He added alkali to an alum solution. The precipitate he obtained after filtering and drying was aluminum hydroxide. He tried to form alum again by dissolving this hydroxide in sulfuric acid but no alum could be crystallized. However, when he added potassium hydroxide to the sulfuric acid solution of the aluminum hydroxide he got, after evaporation, beautiful alum crystals. He had the answer! Alum is composed of the earth aluminum oxide, potassium and sulfuric acid. It was time to pose the next question. Does alum contain an element with metallic “temperament”?

37.2.2
The Discovery of Aluminum

Berzelius and Davy tried to isolate metallic aluminum by fused salt electrolysis with the voltaic pile. They failed! It was instead in Denmark that the metal became visible for the first time. The year was 1825.

Hans Christian Oersted (1777–1851) was born on the Danish island of Langeland. He studied, mainly all by himself, to such an extent that he became qualified for studies at the University of Copenhagen. At the age of 17 he began to study science, philosophy and medicine. At 22 he became a Doctor of Medicine, but after Volta's discovery his main interests were physics and electricity. In 1806 he was appointed to professor of physics at the university and started a research program, that was to last several years, on the relations between electricity and magnetism. In 1820 he made a discovery of great significance. He found that a magnetic needle is influenced by an electric current and takes a direction perpendicular to the current. This discovery of the magnetic effects of an electric current was a result that constituted the basis for electromagnetism, which later was developed by Ampère, Faraday and Maxwell [37.1]. Oersted had become a recognized scientist, yet in a domain other than chemistry.

When he set to work in 1825 with the aluminum problem, he was in fact preparing experiments with the voltaic pile. He was looking for a metallic element in alumina. He carefully mixed charcoal and aluminum oxide and warmed them to red heat in a tube furnace. At the inlet of chlorine gas, aluminum chloride was formed and vaporized. Outside the furnace it was condensed in potassium amalgam, and aluminum amalgam was formed. When the mercury was distilled off, in the absence of air, a metal, similar to tin, remained. The metal, aluminum, was discovered.

Friedrich Wöhler made critical comments on Oersted's investigation and questioned whether he really had obtained aluminum after the mercury distillation. Careful examinations of Oersted's notes and recapitulations of the original experiments confirmed that Oersted had succeeded in isolating aluminum. In all international tables of element discoverers its is Hans Christian Oersted alone who is attached to the discovery of aluminum.

Wöhler continued the aluminum work and produced water-free aluminum chloride with Oersted's method. He reduced the chloride with potassium metal without mixing in mercury. He got aluminum in his crucible, but always as a gray powder. After a very energetic and exhaustive investigation, typical of Wöhler, in 1845 he succeeded in getting metal of such purity that he could melt the powder to a regulus of aluminum.

37.2.3

Aluminum – More Elegant Than Gold in the Imperial Service

Henri Sainte-Claire Deville (1818–1881) introduced the first industrial aluminum production. He improved Wöhler's method and reduced its costs by utilizing aluminum oxide from bauxite and replacing potassium by sodium metal for the reduction. When he found it possible to produce shining spheres of aluminum, he decided to make the process commercial. But how? Henri was a teacher and his experiments had been done in the chemical laboratory at École Normale Supérieure. He had no means for building a factory. Support came from a totally unexpected source. The emperor, Napoleon III, placed means at his disposal, which made it possible for him to continue his experiments on a larger scale. In 1854 he was prepared to produce aluminum in a quantity of one or two tonnes per year. It was a breakthrough but still the metal was exclusive and expensive. The emperor's personal commitment to the process maybe makes the rumor plausible that he served his most eminent guests on plates of aluminum while guests of the rank below had to content themselves with gold service!

37.2.4
Electrolysis in Molten Cryolite – Basis for Modern Aluminum Production

37.2.4.1 Time for Change

During the last two decades of the 19th century, people in Europe and America entertained a great interest in technology and science. The metal aluminum fascinated – the silvery appearance, the low weight and the good corrosion resistance. But it was a semi-precious metal and very costly, used mostly for jewelry and artwork. A demonstration of that was a cap of aluminum placed on the top of the Washington monument in 1884.

The time was ready for a new development. The aluminum pioneers had passed away, Oersted in 1851, Sainte-Claire Deville in 1881 and Wöhler in 1882. An electrolytic process utilizing fused salt baths became more and more practical at the end of the 19th century. Siemens' development of the electrical generator had created the requirement for a sufficient supply of electric energy. Tentative efforts had been made with melts. Deville had electrolyzed fused cryolite Na_3AlF_6 but the results were unsatisfactory. The Russian chemist A. Tuyrin also proposed an electrolyte of fused cryolite and sodium chloride in 1883. Two young men, Charles M. Hall in the USA and Paul Héroult in France, in 1886 took the decisive steps in the development of the new aluminum technique. The two show an almost improbable simultaneity in the story of inventions, although they were born and lived in quite different parts of the world. Their year of birth was the same, 1863, and both of them died in the same year, 1914. At the age of 23 they both, and independently, invented the electrolytic process for aluminum manufacturing, which still dominates today. The method is also called the *Hall–Héroult process*.

37.2.4.2 Charles M. Hall

Charles M. Hall grew up in Ohio, USA, and went to college in Oberlin. In 1880 he got Professor Frank Fanning Jewett as his teacher in chemistry. This man had just returned from four years' teaching at the Imperial University of Japan. In earlier years he had studied in Göttingen, Germany, and was able to tell his pupils about the complex of aluminum problems in Europe. Hall became very interested and inspired, and decided to devote himself to the chemistry of aluminum [37.2]. He had been aware that every clay bank could be looked upon as an aluminum mine. Professor Jewett continued to have contact with and to support Hall, and helped him to arrange a small laboratory in a shed at his own home. There he started many simple experiments, in order to isolate aluminum metal. He failed when he tried to reduce clay with carbon and when he electrolyzed acidic aqueous aluminum solutions. Why shouldn't aluminum precipitate on the cathode as copper does? He got hydrogen gas instead of aluminum metal.

When Hall continued his studies in physical chemistry and thermochemistry, he got the idea that he should find a substance, other than water, that could dissolve aluminum oxide and make it possible to isolate the metal by electrolysis of a fused salt. In February 1886 he began to work along these lines. He tried to dissolve alumina in fluorspar and in magnesium fluoride. However, both compounds had too high melting points. Then he melted cryolite in a carbon crucible and dissolved alumina in it. After passing a current through the melt for about two hours he found a number of small globules of aluminum. He had discovered the process he was searching for! As always with a new technique, many practical problems came up – about anode material among others. Other complications also arose. In a legal dispute about whether the young Mr Hall really had made the invention himself, Professor Jewett again supported his former student. He told the court that he clearly remembered that, one day in 1886, he was working in his private laboratory. That day the young discoverer rushed in with a few shining buttons in his hand and excitedly shouted, "I have got it! I have got it!"

Judge Taft, later President Taft, decided in favor of Hall, saying that "Hall's process is a new discovery and a step forward in the art of making aluminum. ... Hall was a pioneer, and is entitled to the advantages which that fact gives him in the patent law."

These first globules are carefully preserved as the "Crown Jewels" of the Aluminum Company of America (Alcoa), in Pittsburgh. Alcoa, founded on Hall's invention, is today a company with more than 50 000 employees.

In 1888 the first aluminum companies were founded in the USA, France and Switzerland.

37.2.4.3 **Paul Héroult**

Paul Héroult was born in 1863 in the north of France and was seven years of age at the outbreak of the Franco-German war in 1870. He was then sent to his grandfather in London. Staying there for three years, he acquired a good knowledge of the English language. He returned to France and to his studies there. He learned chemistry and became very interested in Henri Sainte-Claire Deville and his research on aluminum. At this time aluminum was as expensive as silver. It was used mostly for luxury items and jewelry. Héroult wanted to make it cheaper.

At the age of about 22 he inherited a small tannery and, with it, a steam engine and a dynamo. At 23 he experimented with the electrolyses of cryolite and of mixtures of cryolite and sodium aluminum chloride, containing small amounts of aluminum hydroxide. He got molten aluminum at the iron cathode, yet very much mixed up with iron, and he observed that the carbon anode was attacked. He concluded that he had a process in his hand that was capable of producing aluminum from aluminum oxide. Metal was formed on the cathode and oxygen developed on the anode, reacting with the carbon to carbon monoxide and carbon dioxide. However, he got the same type of electrode problems as Hall had reported from his very first experiments. Héroult's process was patented.

37.2.4.4 **Different in the End**

After the aluminum process invention, Charles M. Hall became a famous industrialist. He was the owner of one-quarter of the stocks in Alcoa. Before his death in 1914 he bequeathed great means to his old school in Oberlin and to education of young people in the Orient.

Paul Héroult continued as an inventor. He is renowned for the Héroult furnace, which he patented in 1907. It is an electric arc furnace for steel that gradually became the "melting machine" for scrap in the modern steel industry (see section 8.9.3). In 1905, Paul Héroult was invited to the United States as a technical adviser to several companies, and in particular to the United States Steel Corporation.

37.3
The Raw Materials for Aluminum Manufacture

37.3.1
Bauxite

On the weathering of rocks rich in feldspar in a tropical or subtropical climate, bauxite is formed. The minerals in this rock can be described as $AlO_x(OH)_{3-2x}$ where x varies between 0 and 1. Different values of x give different mineral members within the bauxite family, as exemplified in Table 37.1.

Table 37.1 Minerals in the bauxite family

Value of x	Formula	Alternative formula	Mineral name
0	$Al(OH)_3$	$Al_2O_3 \cdot 3H_2O$	Gibbsite or hydrargillite
1	$AlO(OH)$	$Al_2O_3 \cdot H_2O$	Diaspore or boehmite

Bauxite was formerly regarded as an amorphous clay mineral consisting essentially of hydrated alumina, $Al_2O_3 \cdot 2H_2O$. It is a "mean formula" for bauxite, corresponding to x=0.5, thus $AlO_{0.5}(OH)_2$. Bauxite is named after Les Baux de Provence, a locality near Arles in southern France.

Bauxite, the main raw material for aluminum manufacturing, is found in deposits that may be very large. As a rule mining is carried out in open casts from strata typically some 4–6 m thick. The world mine production was 137 million tonnes in 2001. Australia was the largest producer with 54 million tonnes, 40% of the total. Guinea, Brazil and Jamaica produced about 10% each, China and India 6% each, Russia, Suriname[1] and Venezuela 3% each. In Europe, Serbia, Croatia, Slovenia, Hungary and Greece are important producers [37.7].

In the bauxite deposit at Gove in northern Australia, an ore with the composition 50% aluminum oxide, 3% silicic acid, 18% iron oxide, 3% titanium oxide and 25% wa-

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[1] The Republic of Suriname is situated in the north of South America. It borders French Guyana in the east, Brazil in the south, Guyana in the west and the Atlantic Ocean in the north. The larger part of the country consists of uncultivated rainforest. The capital Paramaribo lies about 20 km south of the coast at the West Bank of the Suriname River. It has 150 000 inhabitants.

ter of crystallization is obtained. A diaspore-bearing clay in Missouri, burley clay, has an alumina content averaging 45–65%.

Bauxite is not used as such in aluminum production. First pure aluminum oxide has to be prepared from the ore.

37.3.2
Aluminum Oxide

In nearly all commercial operations, alumina is extracted from bauxite by the *Bayer process*, according to Figure 37.1. The process was developed by *Karl Bayer* in Austria in 1888. The process involves four steps: digestion, clarification, precipitation and calcination.

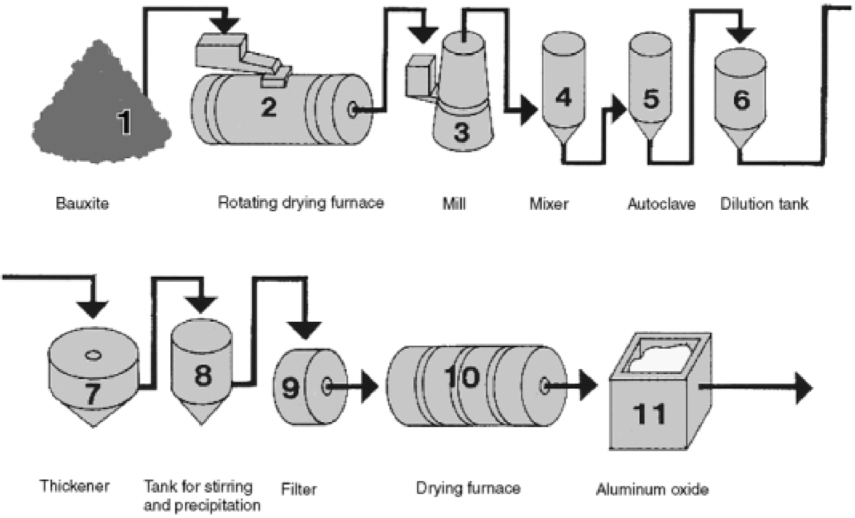

Figure 37.1 The Bayer method for the manufacture of aluminum oxide from bauxite. (Reprinted from the booklet Aluminumlära, SAPA Technology, Finspång, Sweden. With permission. See further ref. [37.3].)

The finely ground bauxite is mixed with water to a slurry that is pumped into a pressure vessel, in which it is digested with a hot sodium hydroxide solution at 200–240°C and a pressure of about 30 atm. The alumina in the bauxite reacts with the caustic soda, forming a saturated solution of sodium aluminate $NaAl(OH)_4$. The insoluble substances, mainly iron hydroxide, are separated from the solution and the red mud residue is thickened in filter presses and washed. The clear solution is passed into large, silo-like precipitators. Seed crystals of $Al_2O_3 \cdot 3H_2O$ are added, which start the precipitation of $Al(OH)_3$ that is filtered off and heated in rotary kilns at about 1100°C. The final product of this process is aluminum oxide Al_2O_3, white and pure.

37.3.3
Cryolite – "Ice Stone"

The mineral cryolite Na_3AlF_6 is rare. It has been found chiefly in a pegmatite at Ivigtut, Greenland, and was called *ice stone*. A melt of this cryolite was used as the electrolyte at the beginning of aluminum manufacturing via the Hall–Héroult process. Nowadays synthetic cryolite is utilized, produced by dissolving aluminum oxide in hydrofluoric acid and addition of sodium carbonate. The cryolite has two properties, which have made it indispensable for the manufacture of aluminum metal: its melting point is low, 1000°C, compared with 2015°C for pure aluminum oxide; and the fused cryolite easily dissolves aluminum oxide. Furthermore the melting point is lowered when Al_2O_3 is added. There is a eutectic (lowest) melting point of 935°C at a composition of 81.5% Na_3AlF_6 and 18.5% Al_2O_3. In practice the melt has a content of 3–8% Al_2O_3 and a working temperature of about 960°C.

37.4
Aluminum Manufacture

37.4.1
Primary Aluminum

Aluminum produced from ore is *primary*, unlike *secondary* that is produced from recycled aluminum.

In the primary production of aluminum, the electrolyte is cryolite, with some excess of aluminum fluoride AlF_3. The electrolyte is melted in steel pots with dimensions up to 10 m length, 4 m width and 1.5 m depth (Figure 37.2). Each pot is lined with carbon, acting as a cathode in the electrolytic cell. Carbon anodes are inserted into the electrolyte from the top. The voltage is 5 V, and the amperage very high – depending on the furnace size, the latter can be between 30 000 and 300 000 A.

Al_2O_3 is added to the melt regularly. The oxide is split into Al^{3+} and O^{2-} ions. Reduced aluminum metal is formed as a melt below the cryolite, while the oxygen ion is oxidized to oxygen at the anode. It attacks the anode, which forms CO and CO_2. Therefore, the carbon anodes are consumed and need to be replaced periodically. The gases formed during the electrolyses contain fluorides (from the melt) and tar residues (from the carbon anodes). They constitute an environmental problem. This is nowadays mastered by careful housing of furnaces and by gas cleaning. In the so-called *dry gas cleaning* the gases pass over a bed of aluminum oxide. The fluorides are bound there as aluminum fluoride. This fluorine-containing aluminum oxide is brought back to the furnaces. Thus both fluorine and aluminum can be utilized in the process.

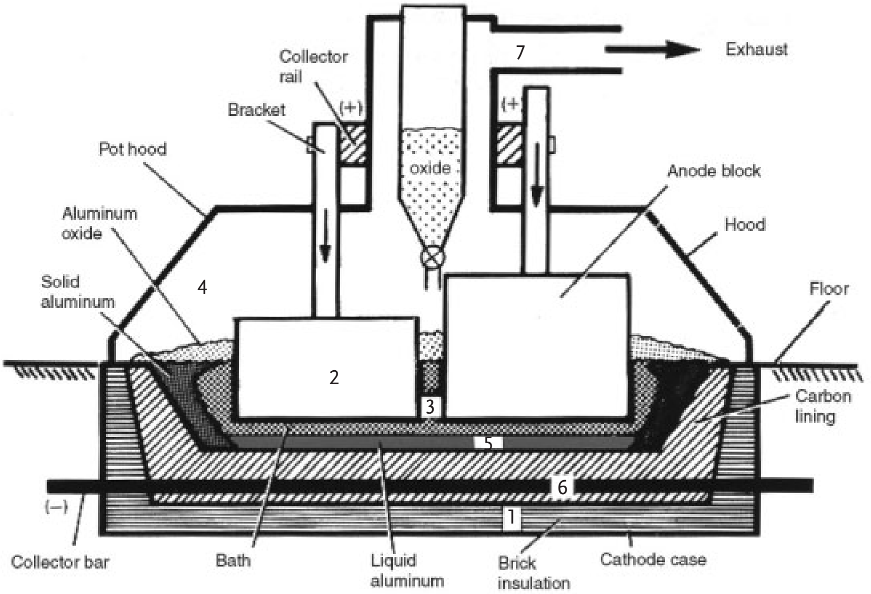

Figure 37.2 Electrolytic cell for the manufacture of aluminum via the Hall–Héroult process. (Reprinted from the booklet Aluminumlära, SAPA Technology, Finspång, Sweden. With permission. See further ref. [37.3].)

For the manufacture of 1 tonne of aluminum, the consumption is as follows:

– aluminum oxide, Al_2O_3	1900 kg
– electrical energy	13 000 kWh[2]
– carbon material for anodes	500 kg
– electrolyte (cryolite and AlF_3)	30 kg

One cell produces more than 1 tonne of molten aluminum in each 24 hours. A modern smelter, with an annual capacity of 200 000 tonnes, needs several hundred pots.

Liquid aluminum is removed from the furnace bottom by vacuum to a ladle, a container for molten metal, in which alloying elements may be added. The alloyed metal is cast into rectangular slabs for rolling or cylindrical billets for extrusion.

37.4.2
Recycled Aluminum (Secondary Aluminum)

Recycling of aluminum saves considerable amounts of energy. As the aluminum is already in the metallic state, all the energy spent in purifying/refining the ore and reducing it to the metal is saved. A great part (more than 25%) of aluminum manufac-

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2) Early Hall–Héroult plants needed 50 000 kWh.

turing is based on recycled metal. For recycling, organizing the collection of spent aluminum products (old scrap, post-consumer scrap) is very important. Aluminum scrap has a high economic value and all aluminum that is collected for recycling is converted into a new generation of aluminum products. Major quantities of old scrap arise from end-of-life cars and from the building sector. Effective collection systems are required for small consumer components, such as beverage cans, food packaging and foil. Such systems, important for both environment and economy, are in fact in function nowadays [37.4].

37.4.3
Manufacture of Rolled Products (Plate, Strip, Sheet, Foil) and Extruded Profiles

Slabs are hot-rolled to plates or coiled to hot-rolled strips for further cold-rolling to strip, sheet and foil. During cold-rolling the strength of the material increases considerably. In order to reach the required thickness of thin products, one or more intermediate annealings may be necessary.

Profiles are manufactured by extrusion, a technique for which aluminum and aluminum alloys are very suitable. A heated billet, a blank, is forced through a tool, a die, prepared to the same cross-section as is required for the profile. The principle is shown in Figure 37.3. Extrusion is the principal method for making structural shapes, tubes and a great number of small and big sections.

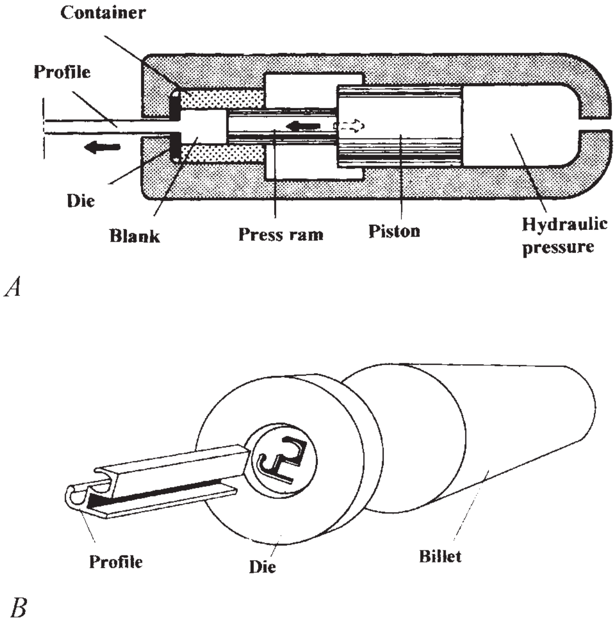

Figure 37.3 Principle of the extrusion of aluminum: A, the extrusion press; B, the die and the profile. (Reprinted from SIS Handbook No. 12, Aluminum. With due permission from Swedish Standards Institute (SIS), Stockholm, Sweden.)

37.4.4
World Production of Aluminum

Aluminum has been produced commercially only for about 150 years and is still a very young metal. At the start of the 20th century, some 8000 tonnes of aluminum was produced annually, whereas 80 years later it was 16 million tonnes, thus 2000 times more. Mankind has been using copper, lead and tin for thousands of years and yet today more aluminum is produced than all other non-ferrous metals together. The total world production of primary aluminum was 24 million tonnes in 2001. In addition, some 7 million tonnes of secondary aluminum were produced.

Primary aluminum is produced in many countries. The biggest producers are Russia, China, the United States and Canada with 11–13% each of total world production. Considerable quantities are also produced in Australia with 7.5% share, and in Brazil and Norway with 4–5% each [37.7].

37.5
An Alloy Family With Possibilities

37.5.1
The Properties of Aluminum

Aluminum has low density and good corrosion properties. The metal's density is 2.7 g/cm^3, compared to 7.9 for iron and 4.5 for titanium. Aluminum is characterized by the spontaneously formed passive layer on its surface. In this respect it has the same behavior as chromium and titanium (for more about "passive layers" see Chapter 24 Chromium). The passive layer is the basis for the good corrosion properties of aluminum. The metal, however, is resistant only within a rather narrow pH range about the neutral point, and is attacked severely by strong alkaline solutions and strong acids. An exception is nitric acid, in which the passive layer is maintained and strengthened. Aluminum has a good resistance against air pollutants and against salt water.

The strength of pure aluminum metal is low. Annealed it has a tensile strength of 75 N/mm^2 (MPa). The strength of aluminum varies according to alloy type and treatment. An alloy with 1.6% Cu, 2.5% Mg and 5.6% Zn in the aged condition (after precipitation hardening) has a tensile strength of 570 N/mm^2. As a comparison it may be mentioned that AISI 1035 steel, with 0.35% C, has a tensile strength of 600 N/mm^2 after hardening and tempering to impart great toughness to the steel. The Young's modulus of elasticity is however considerably lower for aluminum alloys than for steel, 70 000 N/mm^2 and 210 000 N/mm^2 respectively.

37.5.2
Aluminum Alloys

37.5.2.1 Hardenable and Non-Hardenable Alloys – Precipitation Hardening

Aluminum cannot be hardened in the same way as steel by heating and quenching. For aluminum metal and many alloys, the only "hardening" method is cold deformation.

Some aluminum alloys can however be hardened by heat treatment. The process is a *precipitation hardening*, often designated *PH-hardening*. If, for instance, an alloy with 4% Cu is heated up to 550°C, copper will go into solid solution in the aluminum matrix (point 2 in Figure 37.4). On rapid cooling, known as quenching, to point 1, copper remains in solution, although it cannot be dissolved at equilibrium.

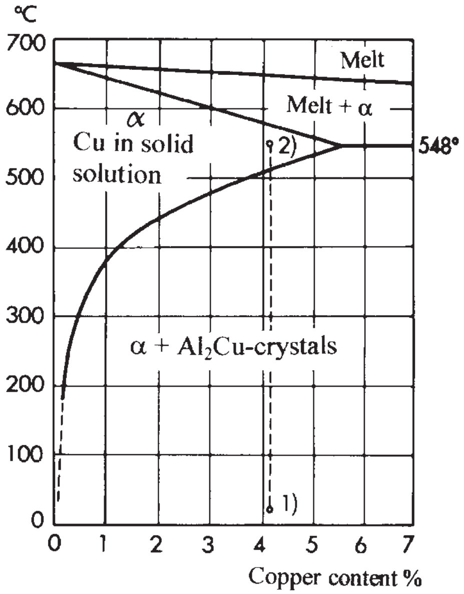

Figure 37.4 Solution treatment and quenching before aging. The first two steps in the precipitation hardening of an aluminum alloy containing 4% Cu, "duralumin". See the text for an explanation of points 1 and 2.

On aging, either natural aging at room temperature or artificial aging at elevated temperature, a great number of small particles Al_2Cu are precipitated. These precipitations will be obstacles for dislocation movements and slip in the crystal planes. These phenomena increase the yield and tensile strength. The alloy has been hardened.

Precipitation hardening has been developed to a modern and very important hardening technique for many alloy types. The method is always constituted by three elements:

- solution heat treatment,
- quenching,
- aging, natural or artificial.

The conditions that must be fulfilled if the precipitation hardening is to function successfully are as follows:

- The alloy must contain elements that dissolve in the base metal matrix at elevated temperature.
- The alloying element remains supersaturated in the solution after quenching.
- On aging, precipitation of many small particles occurs, obstructing the slippage of the crystal planes of the alloy.

Regarding aluminum alloys, there are three types that are PH-hardenable, namely alloys containing

- copper Cu (4%),
- magnesium Mg (0.5–1%) *and* silicon Si (0.5%);
- magnesium Mg (1.2–2.5%) *and* zinc Zn (4.5–5.5%).

37.5.2.2 **Wrought Alloys**

Wrought alloys are ductile and plastically formable, in contrast to cast alloys. A system for classifying wrought aluminum alloy types is given in Table 37.2, showing the different groups within the Aluminum Association system. In Table 37.3 a few examples of specific alloys, their composition and their utilization, mainly within the automotive industry, are given.

Table 37.2 Alloying elements in the seven standard groups according to the Aluminum Association (AA)

Series	Alloy type
1000	Pure aluminum. Al 99% or more
2000	Copper is the principal alloying element in this group. The alloy can be hardened by precipitation hardening
3000	Manganese is the principal alloying element. These alloys have a superior combination of corrosion resistance and formability
4000	Silicon is the major alloying element in this group. See further "cast alloys" (section 37.5.2.3)
5000	Magnesium is the alloying element in this group
6000	Alloys in this group utilize magnesium *and* silicon, which makes them hardenable by precipitation hardening
7000	Zinc is the principal alloying element in this group. In combination with magnesium and in some cases copper, the strength will be very high after precipitation hardening

Table 37.3 Examples of specific wrought alloys, their composition and utilization

Alloy	Compostion %					Application examples
AA	Al	Cu	Mg	Si	Zn	
1200	>99					Metal with high ductility. Suitable for components that will be anodized
5052	(97)		2.5			Suitable when formability requirements are high. Used for truck bumpers and body panels
6063	(99)		0.7	0.4		Moderate strength after extrusion. Used for thick materials, body components and hollow profiles. Precipitation hardenable
7030	(93)	0.3	1.2		5.3	Precipitation hardenable. Alloy of high strength. Used for passenger car bumpers

37.5.2.3 **Cast Alloys**

Casting of aluminum is carried out as *sand casting* in molds of packed sand, as *permanent mold casting* in molds of cast iron or steel, and as *pressure die casting* in automated machines with permanent dies of tool steel. Cast aluminum alloys have a high silicon content, resulting in good castability. An alloy with 10% Si, AA4255, is used for thin-walled pipes and for propellers. Another alloy, also with 10% Si but in addition 0.35% Mg, AA4253, can be precipitation hardened to a higher yield strength. It may be used in marine motor components and for flywheel casings. An alloy intended for pressure die casting has the composition 3% Cu and 10% Si, AA4250. It has a very good machinability and is used for pressure die cast components in engine blocks.

37.6

Surface Treatment of Aluminum and Aluminum Alloys

37.6.1

Surface Treatment of Aluminum – Why?

As a result of its passive surface layer, aluminum alloys have a good corrosion resistance and a rather constant surface appearance. There are however some reasons, exemplified in Table 37.4, for surface treatment of aluminum and its alloys.

Table 37.4 Different reasons for and methods of surface treatment of aluminum

Desirable effect	Method
Improve surface appearance	Anodizing (electrolytic oxidation) Anodizing and coloring Lacquering
Increase surface hardness and wear resistance	Hard anodizing
Improve the adherence of lacquered layers	Chromating
Decrease the electrical transition resistance. Facilitate soldering	Tinning

37.6.2
Anodizing

Anodizing is performed in such a way (Figure 37.5) that the aluminum components are coupled as anodes in an electrolyte, usually dilute sulfuric acid. In the anodic process the component surface is oxidized to a thin film of aluminum oxide, which covers the surface and isolates it electrically. The applied voltage, 20 V, leads to dissolution of the film at certain points which makes it possible for continuous current transport. An anodized layer is built up, the outer regions of which are porous. The layer thickness is 5–25 μm.

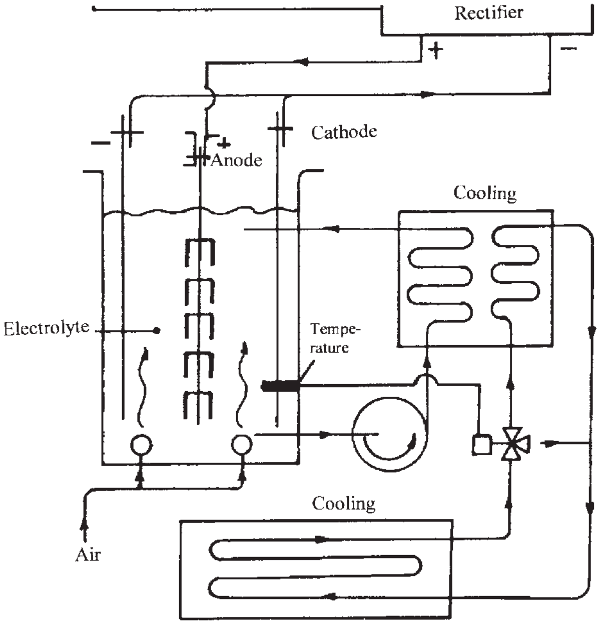

Figure 37.5 Equipment for anodizing. (Reprinted from Anodizing Methods, Svenska Eloxal AB, Tyresö, Sweden. With permission.)

The alloy type influences the result of the anodizing. Pure aluminum (AA group 1000 in Table 37.2) will have a bright and metallic appearance. If very pure (99.9% Al) the sheet will be shiny. Alloys of the type 5000 (AlMg) and 6000 (AlMgSi) take on a silvery appearance, while the result of anodizing alloys with high copper content (4000) is aesthetically less satisfactory. The situation is the same for cast alloys with very high silicon contents.

The pores are important for the coloring of the surface layer according to Figures 37.6 and 37.7. In the *dipping method*, dyes with different colors are absorbed in the pores. In the *electrolytic coloring process*, the anodized component is immersed in a bath containing an inorganic metal salt, of which tin sulfate is dominant. An alternating current is then applied, which deposits colored metal compounds at the bottom of the pores. The colors light to dark brown, black and maroon may be obtained. This technique is the most important for coloring of sheet and profile, and gives, unlike dipping, good color stability and light durability.

The so-called *integral coloring* (Figure 37.8) is a one-step process that produces oxide layer and coloring simultaneously. Bronze and black shades are obtained.

Sealing of the pores is carried out in hot water after anodizing and coloring. In this process aluminum oxide on the inner sides of the pores swells to aluminum hydrox-

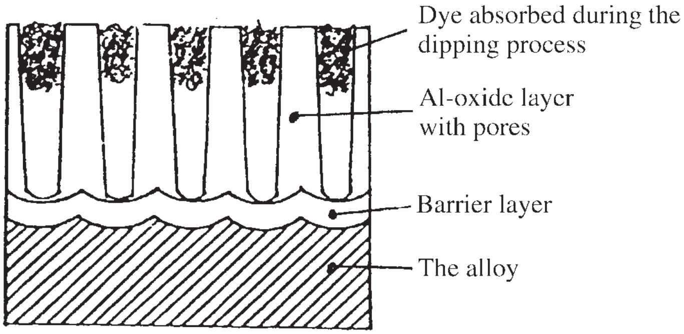

Figure 37.6 Coloring of anodized films with the dipping method.

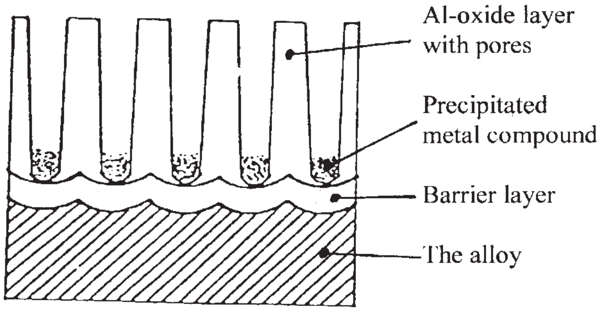

Figure 37.7 Coloring of anodized films with the electrolytic method.

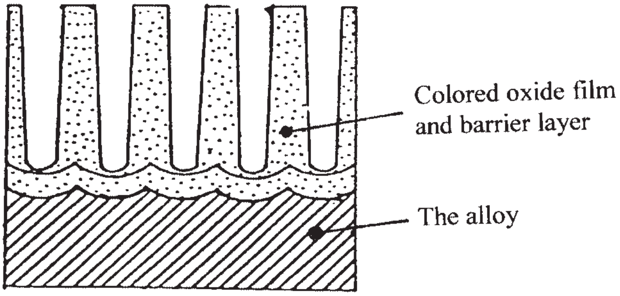

Figure 37.8 Integral coloring of anodized film and barrier layer in a one-step process.

ide. This closes the pores in the anodic film and makes the surface more resistant to staining, abrasion, crazing and color degradation.

Anodizing at very low temperature, almost 0°C, may give layer thicknesses up to 100 μm with low porosity. The method is called *hard anodizing*. The surfaces obtained are in fact not harder than ordinary anodized films, but due to the great layer thickness they are characterized by good wear and corrosion resistance.

A thorough presentation of anodizing for aluminum alloys is given in ref. [37.5].

37.6.3
Chromating

Chromating is a conversion coating process that is used before lacquering and powder coating of aluminum components. The chromate layer improves both the corrosion resistance of the alloy and the adhesion between metal surface and lacquer coating. *Yellow chromate* layers are obtained by dipping in or spraying of a solution containing about 5 g CrO_3 per liter at a temperature of 20–40°C. The pH of the solution is 1.2–1.8. The layer is 0.5–2.0 μm thick. *Green chromating* is also called phosphochromating because phosphoric acid is added to the solution besides chromic acid and hydrofluoric acid. The layer obtained is green because it contains chromium in the trivalent oxidation state.

37.7
Uses of Aluminum and Aluminum Alloys

37.7.1
Exclusive and Ordinary

When aluminum manufacturing was new, at the end of the 19th century, many artists chose the different and unique metal for their works. The well-known Eros statue in Piccadilly Circus, London, was thus made of aluminum in 1893.

Gradually production techniques were developed and the price lowered. Now the utilization has concentrated on applications in which the special technical properties of aluminum are favorable:

- low density,
- good corrosion resistance,
- formability,
- increased strength by alloying and precipitation hardening,
- the possibility of anodizing and coloring.

This has resulted in a very great utilization of aluminum in building and construction, as well as in the packaging, transport, mechanical and electrical sectors.

We meet aluminum use in all types of applications in which the combination of low density, good corrosion resistance and high strength relative to weight is a factor in material selection. In the aircraft industry, aluminum has an especially strong position. Aluminum makes up more than 80% of the weight of a modern passenger airliner.

For automobiles, railroad cars, boats and ships, larger quantities than for aircraft are used. Bodywork may be made entirely of aluminum, and in the automotive industry an important change from cast iron to aluminum in the cylinder blocks of engines has considerably increased the use of cast aluminum alloys (Figure 37.9). This decreases the weight and thus gasoline consumption, which is good for the environment. The increased use of aluminum in hubcaps, bumpers and body components

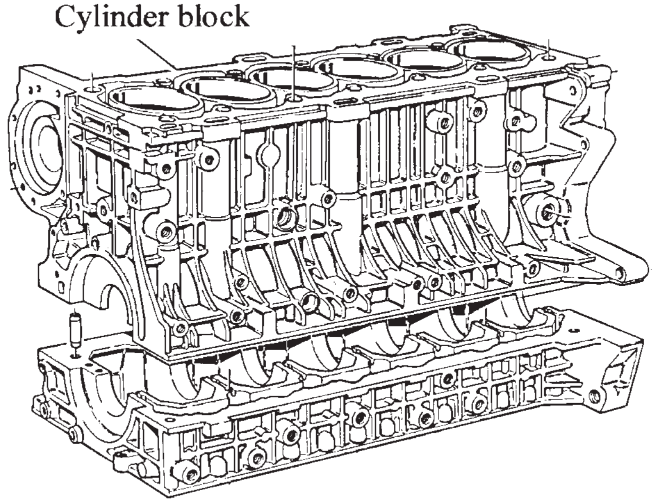

Figure 37.9 A cast aluminum cylinder block. The block has vertical and horizontal strengthening on the outside. This reduces the vibrations in the block and makes the engine run more quietly. (Reprinted with permission from Volvo Information, Petrol engines (Bensinmotorer), 1990.)

also contributes to the weight reduction. For trucks, the light metal is used in loading platforms and tanks.

As is shown in Figure 37.10, the use of aluminum has increased very much in all sectors during the last 50 years. The use is five times higher today than in the 1950s and the growth continues.

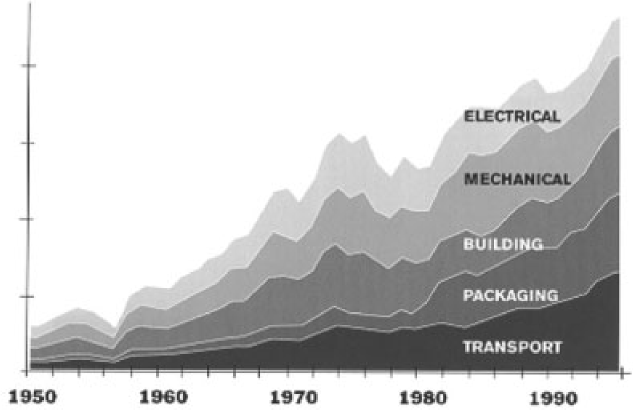

Figure 37.10 The relative use of aluminum in different sectors since 1950 shows a fivefold increase. (Reprinted from SAPA Technology Information Brochure. With permission.)

In modern houses, aluminum has many uses, from anodized facings to interior fittings and window settings. Foils for foodstuffs and cans for drinks are other large applications, as is also household appliances.

In the food and chemical industries, process and storage equipment is largely made of aluminum. Aluminum alloys are also very much utilized in furniture for the home and office, as well as in equipment for sport and recreational activities.

For electrical wire and cables, the combination of conductivity and low weight is very important. In the metallurgical industry, aluminum is used as a deoxidation agent in steel manufacturing (see Chapter 8 Iron) and as an alloying element in magnesium, titanium and copper alloys.

37.7.2
The Right Alloy for Specific Purposes

The utilization of aluminum is very diversified and here only some typical examples can be mentioned (see Table 37.5).

Table 37.5 Aluminum alloys with fields of application

(a) Non-hardenable alloys

Alloy	Field of application
Pure aluminum	Decoration strips. Signs. Foils, thickness 0.007–0.02 mm. Bottle caps, cans, tubes for toothpaste. Lamellae for heat exchangers
Alloy with 1% Mn	Cooking utensils, kitchen equipment. Roofing and facing plates
Alloys with 2.5–4.5% Mg	Boats. Containers for food and chemical products. Corrosion-resistant
Alloy with 1% Mg	Suitable for decorative anodizing
Cast alloy with 10% Si and 2.5% Cu. The Cu content improves the strength but is too low to give hardenability	Cylinder blocks for private cars

(b) Hardenable alloys

Alloy	Field of application
Alloy with 0.5% Mg and 0.4% Si. Hardenable due to presence of Mg and Si	The most usual alloy for extruded profiles
Alloy with 0.7% Mg and 0.4% Si. Hardenable due to presence of Mg and Si	Masts for sailing boats
Alloy with 0.9% Mg, 1.0% Si and 0.7% Mn. Hardenable due to presence of Mg and Si	Structural parts in buses, trucks, trailers, cranes, bridges, ladders, crash barriers
Alloy with 1.2% Mg and 5.5% Zn. Hardenable due to presence of Mg and Zn	Bumpers for cars
Cast alloy with 10% Si and 0.4% Mg. Hardenable due to presence of Mg and Si	Components in marine engines

37.8
Aluminum in Life

Aluminum hydroxide has a very low solubility in neutral water but the solubility increases at both low and high pH values. Acid rain therefore leaches aluminum from minerals in the soil, which increases the aluminum ion concentrations in streams and lakes.

Aluminum is not an essential element for vital functions. For mankind the daily intake with food and drink is restricted to 3–5 mg aluminum. It passes out in the urine and only 10 µg is absorbed [37.6]. In a changed environment with high content of sulfurous oxide in the air, the rain gets more acid. Water in lakes and streams will dissolve more aluminum from the ground, which may lead to ecological damage. A consequence is an increased intake of Al^{3+} in living organisms. An injurious effect of this is that the availability of phosphorus may be limited as it is bound as very insoluble $AlPO_4$. This can restrict the availability in the body of vital phosphorus.

There is another very special consequence of the acidification of the environment, connected with aluminum. If Al^{3+} is dissolved from the soil, due to acid rain, and is transported to a large lake with neutral pH, aluminum hydroxide is precipitated. It may to some extent be deposited on the gills of fish, resulting in trouble with oxygen uptake.

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38
Gallium, Indium and Thallium

38.1 Ga
Facts about Gallium

38.1.1 Ga
The Element

Symbol:	Ga
Atomic number:	31
Atomic weight:	69.72
Ground state electron configuration:	[Ar]$3d^{10}4s^24p^1$
Crystal structure:	Orthorhombic with $a = 4.52$ Å, $b = 7.66$ Å, $c = 4.53$ Å

38.1.2 Ga
Discovery and Occurrence

Discovery: In 1875 Paul-Émile Lecoq de Boisbaudran in Paris found the new element gallium. After the discovery it was shown that gallium is Mendelev's eka-aluminum.

Most important mineral: Gallium follows aluminum and zinc in minerals and is contained in flue dusts from coal burning, which may contain up to 1.5% gallium. The element is obtained as a by-product in the production of aluminum, zinc and copper.

Ranking in order of abundance in earth crust:	34–35
Mean content in earth crust:	19 ppm (g/tonne)
Mean content in oceans:	$3 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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38.1.3 Ga
Chemical Characterization

Gallium is blue-gray as a solid and silvery as a liquid. The metal remains liquid over a wider temperature range than any other element. It melts at 30°C and boils at 2403°C. This makes gallium usable in high-temperature thermometers. Gallium arsenide is capable of converting electricity directly into coherent light, and gallium arsenide is a key component of light-emitting diodes (LEDs).

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ga^{I} as in Ga_2O	$Ga(g) \rightarrow Ga^{+}(g) + e^{-}$	579	$Ga(g) + e^{-} \rightarrow Ga^{-}(g)$
Ga^{II} as in GaO, GaS, and $[Ga_2Cl_6]^{2-}$	$Ga^{+}(g) \rightarrow Ga^{2+}(g) + e^{-}$	1979	–29.1
Ga^{III} as in Ga_2O_3 and Ga_2Cl_6	$Ga^{2+}(g) \rightarrow Ga^{3+}(g) + e^{-}$	2963	
Ga^{III} in the so-called III–V compounds, for instance GaAs	$Ga^{3+}(g) \rightarrow Ga^{4+}(g) + e^{-}$	6180	

Standard reduction potential: $Ga^{3+}(aq) + 3e^{-} \rightarrow Ga(s)$ $E^0 = -0.53$ V

Electronegativity (Pauling): 1.81

Radii of atoms and ions: (WebElements™)		
	Atomic:	130 pm
	Covalent:	126 pm
	Van der Waals:	187 pm
	Ga^{3+} (4-coordinate, tetrahedral):	61 pm
	Ga^{3+} (6-coordinate, octahedral):	76 pm

38.1.4 Ga

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
5905 kg m^{-3} 5.91 g cm^{-3}	11.81 cm^3	302.92 K (triple point) 29.77 °C	2676 K 2403 °C	371 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
43	41	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$18.3 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
27.5	136	272	310	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-3.9 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	–	–

38.1.5 Ga
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	5.59 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	256 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	277 kJmol^{-1}
Entropy S^0 at 298 K	40.88 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	18.5	25.86	27.8	27.8	27.8	27.8

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3Ga+O_2 \rightarrow 2/3Ga_2O_3$	–665	–620	–507	–	–

38.1.6 Ga
Nuclear Properties and X-ray

Isotope range, natural and artificial 61–84

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{69}Ga	Stable	60.11	3/2–	2.017
^{71}Ga	Stable	39.89	3/2–	2.562

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{69}Ga	^{71}Ga
Reference compound	$Ga(NO_3)_3/D_2O$	
Frequency MHz (^{1}H = 100 MHz)	24.001	30.497
Receptivity D^P relative to ^{1}H = 1.00	0.0419	0.0571
Receptivity D^C relative to ^{13}C = 1.00	239	326
Magnetogyric ratio, radT^{-1}s^{-1}	$6.439 \cdot 10^7$	$8.181 \cdot 10^7$
Nuclear quadropole moment, barn	0.17	0.10

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
30	Zn	8.616
31	Ga	9.231
32	Ge	9.856

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	62.4
17.37 keV ($MoK\alpha_2$)	57.7

Neutron absorption	**Thermal neutron capture cross section**	2.9 barns

38.1 In
Facts about Indium

38.1.1 In
The Element

Symbol:	In
Atomic number:	49
Atomic weight:	114.82
Ground state electron configuration:	$[Kr]4d^{10}5s^25p^1$
Crystal structure:	Tetragonal with $a = b = 3.25$ Å, $c = 4.95$ Å

38.1.2 In
Discovery and Occurrence

Discovery: Ferdinand Reich and Hieronymus Richter at the Bergakademie Freiberg in Germany discovered the element in 1863.

Most important mineral: Indium is present in ores of zinc, lead, copper and tin, regularly in very low contents, yet sometimes up to 1%. The element is obtained as a by-product in the working of the ores.

Ranking in order of abundance in earth crust:	64
Mean content in earth crust:	0.25 ppm (g/tonne)
Mean content in oceans:	0.02 ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

38.1.3 In
Chemical Characterization

Indium is a soft malleable, silvery white metal. Due to its low friction properties, it is used in bearing alloys. Certain indium compounds have unique semiconductor properties. Films of ITO, indium–tin oxide (80% In_2O_3), are transparent to visible light but not for infrared light. In addition they have good electrical conductivity. The electrical conductivity of the thin coating is utilized on windshields for railway locomotives and airplanes to make it possible to warm them up with electric current for defogging.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
In^I as in InCl and In_2S	$In(g) \rightarrow In^+(g) + e^-$	558	$In(g) + e^- \rightarrow In^-(g)$
In^{II} as in InO and $InCl_2$	$In^+(g) \rightarrow In^{2+}(g) + e^-$	1821	−31
(perhaps I,III-chloride)	$In^{2+}(g) \rightarrow In^{3+}(g) + e^-$	2704	
In^{III} as in In_2O_3 and InN	$In^{3+}(g) \rightarrow In^{4+}(g) + e^-$	5210	

Standard reduction potential: $In^{3+}(aq) + 3e^- \rightarrow In(s)$ $E^0 = -0.338$ V

Electronegativity (Pauling): 1.78

Radii of atoms and ions:		
(WebElements™)	Atomic:	155 pm
	Covalent:	144 pm
	Van der Waals:	193 pm
	In^{3+} (4-coordinate, tetrahedral):	76 pm
	In^{3+} (6-coordinate, octahedral):	94 pm
	In^{3+} (8-coordinate):	106 pm

38.1.4 In
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
7310 kg m^{-3} 7.31 g cm^{-3}	15.71 cm^3	429.8 K 156.6 °C	2353 K 2080 °C	233 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
92	84	76	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$25.4 \cdot 10^{-6}$	$32.1 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
18	80	121	367	470	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-7.0 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
11 GPa	–	–	–

38.1.5 In

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	3.26 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	230 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	243 kJmol^{-1}
Entropy S^0 at 298 K	57.82 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	23.3	26.74	29.7	29.7	29.7	23.9

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$4/3In+O_2 \rightarrow 2/3In_2O_3$	–554	–512	–403	–297	–

38.1.6 In

Nuclear Properties and X-ray

Isotope range, natural and artificial 100–134

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half-life**	**Decay mode**	**Decay energy Q**
^{113}In	Stable	4.3	9/2+	5.523	–	–	–
^{115}In	Active	95.7	9/2+	5.534	$4.4 \cdot 10^{14}$ y	β^-	0.496 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{113}In	^{115}In
Reference compound	$In(NO_3)3/D_2O/HNO_3$	
Frequency MHz (^1H = 100 MHz)	21.866	21.913
Receptivity D^P relative to ^1H = 1.00	0.0151	0.338
Receptivity D^C relative to ^{13}C = 1.00	86.3	1920
Magnetogyric ratio, radT^{-1}s^{-1}	$5.885 \cdot 10^7$	$5.897 \cdot 10^7$
Nuclear quadropole moment, barn	0.80	0.81

Characteristic X-radiation Z	 Element	 Kα_2 keV
48	Cd	22.985
49	In	24.002
50	Sn	25.044

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	237
17.37 keV (MoKα_2)	29.9

Neutron absorption **Thermal neutron capture cross section** 194 barns

38.1 Tl
Facts about Thallium

38.1.1 Tl
The Element

Symbol:	Tl
Atomic number:	81
Atomic weight:	204.38
Ground state electron configuration:	[Xe]4f^{14}5d^{10}6s^{2}6p^1
Crystal structure:	Hexagonal hcp with $a = 3.46$ Å, $c = 5.52$ Å

38.1.2 Tl
Discovery and Occurrence

Discovery: Thallium was discovered in 1861 by W. Crookes in London and isolated in 1862 by C.-A. Lamy in Paris.

Most important mineral: $(Cu,Tl,Ag)_2Se$ is a rare mineral, named crookesite, after Sir William Crookes. Thallium is however obtained as a by-product of zinc and lead production. The element is finely dispersed in feldspar and pyrite, as well as in zinc and lead ores.

Ranking in order of abundance in earth crust:	60
Mean content in earth crust:	0.85 ppm (g/tonne)
Mean content in oceans:	$1.9 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

38.1.3 Tl

Chemical Characterization

Thallium is a soft, malleable metal that develops a bluish-gray tinge, resembling lead. In the periodic table it is situated low down in the boron group, and does not have the ability of gallium and indium to form valuable phosphides and arsenides. Nevertheless some special applications are known. A mercury–thallium alloy, which forms a eutectic at 8.5% thallium, is reported to freeze at −60°C, about 20 degrees below the freezing point of mercury. This is utilized in low-temperature thermometers, relays and switches. The electrical conductivity of thallium sulfide changes with exposure to infrared light, and this compound is used in photocells. Thallium is dangerous, like mercury and lead, but is much less of an environmental problem as it is, up to now, little used in industry. The monovalent thallium ion has a certain similarity with the potassium ion and disturbs potassium in its transfer of nerve impulses in the body. Thallium is very toxic because of that.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Tl^{I} as in Tl_2O and Tl_2SO_4	$Tl(g) \rightarrow Tl^+(g) + e^-$	589	$Tl(g) + e^- \rightarrow Tl^-(g)$
Tl^{III} as in Tl_2O_3 and $TlCl_3$	$Tl^+(g) \rightarrow Tl^{2+}(g) + e^-$	1971	−21
	$Tl^{2+}(g) \rightarrow Tl^{3+}(g) + e^-$	2878	

Standard reduction potential: $Tl^{3+}(aq) + 3e^- \rightarrow Tl(s)$ $E^0 = +0.72$ V
$Tl^+(aq) + e^- \rightarrow Tl(s)$ $E^0 = -0.336$ V

Electronegativity (Pauling): 1.62 (Tl^+); 2.04 (Tl^{3+})

Radii of atoms and ions: (WebElements™)		
	Atomic:	190 pm
	Covalent:	148 pm
	Van der Waals:	196 pm
	Tl^+ (6-coordinate, octahedral):	164 pm
	Tl^+ (8-coordinate):	173 pm
	Tl^{3+} (4-coordinate, tetrahedral):	89 pm
	Tl^{3+} (6-coordinate, octahedral):	102.5 pm
	Tl^{3+} (8-coordinate):	112 pm

38.1.4 Tl

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
11 850 kg m^{-3} 11.85 g cm^{-3}	17.25 cm^3	577 K 304 °C	1740 K 1467 °C	129 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
51	47	44	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$25.2 \cdot 10^{-6}$	$29.9 \cdot 10^{-6}$	$34.7 \cdot 10^{-6}$	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
37	150	228	380	850	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-3.13 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
8 GPa	2.8 GPa	19 GPa	0.43

38.1.5 Tl
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	4.27 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	165 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	182 $kJmol^{-1}$
Entropy S^0 at 298 K	64.18 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	24.4	26.32	30.5	30.5	22.7	24.4

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4Tl+O_2 \rightarrow 2Tl_2O$	–294	–254	–168	–	–

38.1.6 Tl
Nuclear Properties and X-ray

Isotope range, natural and artificial	179–210

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{203}Tl	Stable	29.52	1/2+	1.622
^{205}Tl	Stable	70.48	1/2+	1.638

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{203}Tl	^{205}Tl
Reference compound	$TlNO_3/D_2O$	
Frequency MHz (^1H = 100 MHz)	57.123	57.634
Receptivity D^P relative to ^1H = 1.00	0.0578	0.142
Receptivity D^C relative to ^{13}C = 1.00	331	813
Magnetogyric ratio, $radT^{-1}s^{-1}$	$15.539 \cdot 10^7$	$15.692 \cdot 10^7$
Nuclear quadropole moment, barn	–	–

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV
80	Hg	68.894
81	Tl	70.832
82	Pb	72.804

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	219
17.37 keV ($MoK\alpha_2$)	119

Neutron absorption	**Thermal neutron capture cross section**	3.4 barns

38.2
The History Behind Their Discoveries

38.2.1
Thallium (1861)

38.2.1.1 **One Element – Two Spectroscopic Discoveries**

At the age of 15, *William Crookes* (1832–1919, knighted in 1897) entered the Royal College of Chemistry in London as an assistant. In 1851, at the age of 19, he published his first paper, based on investigations of selenocyanides. He had prepared these from a lead chamber slime obtained from a factory in Harz, in which sulfuric acid was made by burning pyrite. This slime happened to play an important role in the discovery of the element thallium.

Crookes adopted the method of spectral analysis, introduced by Bunsen and Kirchhoff, with great enthusiasm. When, in 1861, the German scientists published their spectroscopic discovery of rubidium and cesium, Crookes decided to utilize the technique to examine his old selenium residues, lying in darkness in the laboratory store. His intention was to detect tellurium, the constant follower of selenium. He introduced a small amount of a residue sample into a gas flame and observed clearly the lines and bands of selenium in the spectroscope. In the position he expected to find tellurium lines he instead discovered a green line, totally unexpected. He had found a new element! In March 1861 he published the discovery in *Chemical News*, a journal he himself had founded in 1859. Due to the green spectral line with which the new element revealed itself, he gave it the name *thallium* after the Greek word *thallos* for a green shoot or twig.

Claude-Auguste Lamy (1820–1878), an eminent French scientist, also investigated the slime from a lead chamber process and discovered too the characteristic green spectral line. Yet it was not until March 1862, and it seemed clear that Crookes had beaten him to it.

38.2.1.2 **The Right of Priority Disputed**

During the spring of 1862, William Crookes prepared thallium salts and a gray powder, which he asserted to be the element itself. It has however been questioned if this was the metal and not its sulfide. Lamy on his part worked very methodically with the mapping out of thallium's chemistry and preparation of the element itself:

> A sample of the deposit in the first lead chamber is treated with aqua regia until the acid is almost driven off. The mass is dissolved in boiling water. After cooling yellow thallium chloride crystallizes that is purified in several recrystallizations. When this chloride is submitted to the decomposing action of the electric current from four or five Bunsen cells there appears, at the negative pole, pure thallium.

Already by June 1862 he had presented a small ingot (14 g) of thallium metal to the Académie des Sciences and his results were published in *Comptes Rendus* in the same month. Lamy also established that thallium forms monovalent thallous salts and trivalent thallic salts. The ion Tl^{+} has similarities with the rubidium ion, while the ion Tl^{3+} resembles aluminum.

In the light of these facts, who discovered the element thallium?

A committee from the French Academy, including, among others, Henri Sainte-Claire Deville, credited Lamy with the isolation of thallium metal. However, there is no doubt that Crookes made the spectroscopic discovery of thallium first in 1861. In tables of element discoveries, both are usually credited.

William Crookes continued his thallium work, and in 1873 determined the atomic weight of the new element in research that is still a model of analytical precision.

38.2.2
Indium (1863)

38.2.2.1 Bergakademie Freiberg, the Oldest Technical University in the World

Freiberg is a small town in the German federal state of Saxony. It is situated on the northern slope of Erzgebirge. In the surrounding mountains, deposits of gold and silver were discovered as early as the 13th century AD, and later also zinc was found. Thus Freiberg became the greatest town in Saxony in the Middle Ages. The silver mines were running right up to 1913. Georgius Agricola's life-work (see Chapter 2 The knowledge of Matter) was performed in this region, partly in the adjacent town of Chemnitz, and partly in Joachimsthal on the other side of the Bohemian border. Agricola's work prepared for the founding of a mining school in 1765, a school that developed into the famous *Bergakademie Freiberg* (the Freiberg Mining Academy), the oldest technical university in the world (see Figure 38.1). It became an educational and research institution not only for the South German mining districts but also fairly soon for the whole world.

During the 18th and 19th centuries the authorities of various nations sent many young men to Freiberg to study geology, mineralogy, mining and metallurgy. The geologist, Professor *Abraham Gottlob Werner*, active at the Academy in the two last decades of the 18th century, had a great attraction. Andrés Manual Del Rio and Alexander von Humboldt (see Chapter 21 Vanadium) were fellow-students in Freiberg. After finishing their education in Freiberg many of the students continued to Sweden for complementary studies at the University of Uppsala and the Laboratorium

Figure 38.1 The first buildings at Bergakademie Freiberg [38.1].

Chymicum in Stockholm. The two Spanish brothers *Juan José and Fausto d'Elhuyar* (see Chapter 26 Tungsten) were both sent to Freiberg in 1778. Juan José continued in Uppsala in 1782. Later – in the 19th century – Berzelius and his laboratory became the goal for the visits to Sweden.

38.2.2.2 **Reich, Richter and the Element Indium**

Ferdinand Reich (1799–1882) grew up in Bernburg in Saxony and was educated in Leipzig and Freiberg. At 23 he walked to Göttingen in order to complete his education in chemistry for Professor Stromeyer (see Chapter 34 Cadmium). Before starting, he got an assignment from the Bergakademie to procure valuable literature as well as good laboratory equipment for the chemical laboratory of the Academy. This task he obviously performed well, because in the following year he was sent to Paris for a similar assignment. He returned with platinum tools, certified weights, chemical equipment and minerals for both the Bergakademie and Professor Stromeyer. Equally important – not least for his coming activities – was the fact that he became acquainted with some of the leading scientists of this time: J.-L. Gay-Lussac, L. J. Thénard, Justus von Liebig and Alexander von Humboldt. From 1824 up to his retirement, he was employed at the Bergakademie. He was professor of physics but also taught mineralogy and chemistry.

At the age of nearly 65, in the year 1863, he decided to search for the element thallium in the zinc ores of the Freiberg region. Thallium had been discovered in England two years earlier in residues collected in a lead chamber from sulfuric acid manufacture. The sulfur (and thallium) originated from the mineral pyrite. The complex zinc ores in the Himmelfürst mine near Freiberg contained, besides zinc blende (sphalerite), also pyrite, containing arsenic. It was not unlikely that thallium could be found there. Specimens for examination were brought from the mine to the chemical laboratory of the Academy. As an assistant, Professor Reich had a young man, *Hieronymus Theodor Richter* (1824–1898). Thallium had revealed itself clearly through the green line that Sir William Crookes in London had observed in the spectroscope. It was natural for the two Freiberg scientists to look for the same line in the material from the Himmelfürst mine. They placed a small sample in the loop of a platinum wire and heated it up in a Bunsen burner. The radiation was observed in the spectroscope. They were surprised to find a blue line, an indigo blue, which did not coincide at all with some of cesium's blue lines. They realized that they had missed thallium but instead discovered a new element. The year was 1863. Due to the color of the line, they named the element *indium*.

> They also isolated the new metal by simple chemical methods. The zinc blende sample was dissolved in acid and several metals, Pb, Cu, As and Sn, were removed by precipitation with hydrogen sulfide. The filtrate was oxidized and neutralized with ammonia in great excess. Zinc stayed dissolved while a precipitate of iron hydroxide, also containing indium, was obtained. The hydroxide precipitate was dissolved in acid, and iron (and some indium) was precipitated again by careful addition of sodium carbonate. From the filtrate indium hydroxide was precipitated by sodium carbonate in excess. They prepared indium by reduction of the oxide with charcoal in front of the narrow end of a blowpipe. The new metal was, according to the discoverers, "a soft ductile metal, with which one could mark a paper, and it was of lighter color than lead, similar to tin".

For the 1867 World's Fair in Paris, a one pound bar of the metal was prepared and Richter delivered it personally. But he actually exhibited a lead ingot – indium was a world novelty and could be stolen! He showed the genuine indium bar secretly only to scientific colleagues.

The assistant Richter became an authority of blowpipe analysis and continued the work of *Karl Friedrich Plattner* (1800–1858), the "Pope of the blowpipe", at the Freiberg Academy [38.2]. In 1875 he was appointed Director of the Academy.

38.2.3
Gallium (1875)

Paul-Émile Lecoq de Boisbaudran (1838–1912) in Paris was the very first to confirm Mendeleev's system when in 1875 he identified eka-aluminum and named it *gallium*. Lecoq also discovered the rare-earth metals samarium and dysprosium. His background, both genealogical and scientific, is described in Chapter 17 Rare earths.

Lecoq was fervently interested in spectroscopy and its systematics. He had studied spectra for several years and thought that there was a similarity in the arrangement of the spectral lines emitted from elements within a group of related metals. At the beginning of the 1870s he was thinking that there ought to exist, according to Mendeleev, an element between aluminum, discovered in 1825, and indium, discovered in 1863. The spectra for these two elements were known. This should, according to his theory, facilitate the detection of eka-aluminum. But where could this stranger be found?

Lecoq directed his interest and energy towards zinc ores. From the Pierrefitte mine in the Argelès Valley, Hautes Pyrénées, Lecoq obtained 50 kg of zinc blende ore and began the examination in 1874. One year later he had reached his goal. He had dissolved a quantity of ore in acid and supposed that he had the element he searched for in solution. He carried out a very simple precipitation reaction. When he put a strip of zinc into the solution, a deposit was formed on the strip. He dissolved the deposit, concentrated the solution and absorbed it in a carbon electrode. For *Chemical News* he wrote the following description (cited from Mary Weeks):

> Between three and four in the evening of August 27, 1875, I found indications of the probable existence of a new elementary body ... the new substance gave under the action of the electric spark a spectrum composed chiefly of a narrow violet ray, readily visible, and situated at about 417 on the scale of wavelengths. I perceived also a very faint line at 404.

As the line positions fitted into his theoretical pattern, he asserted that the missing element between aluminum and indium was discovered. Lecoq de Boisbaudran named the new element *gallium* after *Gallia*, an old Latin name for France. The mining company *La Vieille Montagne* was interested in further examination of the new element in its zinc ores and placed substantial ore quantities at Lecoq's disposal. The method for gallium manufacturing was modified. The technique utilized in his early experiments, precipitation of gallium on a zinc strip, appeared to be not a galvanic process like precipitating noble copper from a solution on the less noble zinc. Instead, zinc had consumed acid and neutralized the solution until some basic gallium salt or gallium hydroxide had been formed on the strip. The discoverer gave the following description of the method used for the preparation of gallium metal on a larger scale:

> The ore is dissolved in aqua regia, containing excess of hydrochloric acid. An excess of ore is also used so all the nitric acid is consumed. In the acid filtrate sheets of zinc are placed to deposit noble metals like gold, copper, mercury, indium, cadmium, lead and so one. The process is interrupted before all zinc is consumed and the spongy deposit is filtered off. To the filtrate a large excess of zinc is added and the mixture is heated for several hours. That neutralizes the solution, and basic salts of zinc and hydroxides of aluminum, iron, and gallium are precipitated. The hydrochloric acid solution of this precipitate is buffered with acetic acid and ammonium acetate. With hydrogen sulfide zinc is precipitated and gallium co-precipitated. Gallium hydroxide is prepared and dissolved in potassium hydroxide. From this solution gallium metal is prepared electrolytically on a platinum cathode.

With this method and from a sample of several hundred kilograms of zinc blende, Lecoq prepared the first gram of gallium metal in November 1875. In cooperation with Emile-Clément Jungfleisch, professor at the Collège de France, he later treated 4 tonne of zinc blende at the Javel works and got 75 g of gallium.

When the Russian chemist Dmitri Mendeleev was informed about the discovery and the properties of the new element, he became immediately convinced that eka-aluminum had been discovered. The accordance between the new metal's real properties and those predicted by Mendeleev was remarkable.

38.3
Occurrence

The three metals gallium, indium and thallium are finely dispersed in feldspar and pyrite, as well as in zinc and lead ores, and no large separate mineralizations have been found in the earth's crust.

38.3.1
Gallium

Gallium minerals are very rare and have no practical importance. One example is gallite $CuGaS_2$. The element gallium however is not a rare metal, as the somewhat astonishing comparison, in Table 38.1, with the well-known metals silver, tin and lead will show.

Table 38.1 Common and uncommon elements in the earth's crust

Element	Abundance in earth's crust g/tonne
Silver	0.075
Tin	2.3
Lead	14
Gallium	19

As mentioned in Chapter 4 Geochemistry, the Ga^{3+} ion with radius 0.61 Å "hides" easily in a structure in which Al^{3+} ions with radius 0.53 Å dominate. Aluminum minerals may contain up to 100 g/tonne of gallium, and in bauxite the content is about 50 g/tonne. Coal may have a higher Ga content. Gallium follows aluminum in all industrial processes. This explains why gallium is common but experienced as rare. Gallium also follows zinc in sphalerite, zinc blende. The reason is probably that the lattice constants for ZnS and GaAs are almost identical, 5.4 and 5.6 Å, respectively.

38.3.2
Indium

Indium is present in sphalerite and galena (lead glance) regularly in parts-per-million quantities, but actual indium minerals are very rare. Ores with high indium contents (0.1–1%) are found in Bolivia, England (Cornwall) and Canada (Brunswick). The mentioned indium contents are very seldom found however. A sphalerite with 0.05% In is a rich “indium ore”. A specific iron-black mineral, indite $FeIn_2S_4$, is found in Siberia but it is very rare.

38.3.3
Thallium

Thallium minerals are rare too. N. A. E. Nordenskiöld found one in Sweden in 1866. It had the composition $(Cu,Tl,Ag)_2Se$. In order to honor Sir William Crookes, the discoverer of thallium, he named the mineral crookesite. Thallium is recovered from the roasting of pyrite in connection with the production of sulfuric acid and as a by-product of zinc and lead production from sphalerite and galena. Manganese nodules, found on the ocean floor, contain thallium.

38.4
Manufacture of Metals and Compounds

38.4.1
Gallium

Gallium was earlier prepared from the distillation residues of zinc manufacture and from flue dust in coal-fired power stations. Nowadays gallium is produced as a by-product of aluminum manufacture. In the autoclave treatment in the Bayer process, gallium is dissolved together with aluminum. Up to the 1980s gallium was precipitated electrolytically on a mercury cathode. Gallium amalgam was formed, from which gallium was extracted and purified. From the 1990s the process used has been liquid–liquid extraction. Gallium is extracted from the Bayer lye with oxyquinoline, which effectively takes gallium over to an organic phase. From this the element is brought back to a water phase with small volume. The concentrated gallium solution is electrolyzed and the metal obtained may then be purified by zone melting to a purity of 99.999 999% (for more details about zone melting see section 40.4.4). In 2001 the production of refined gallium was about 80 tonnes.

38.4.2
Indium

Indium is mainly won from residues during the metallurgical treatment of indium-rich zinc and lead ores. The residues are dissolved in acid and indium chloride precipitates at the inlet of chlorine gas. The indium chloride is purified from tin, copper and lead using liquid–liquid extraction. A concentrated indium solution is obtained, from which indium is precipitated on zinc sheets. The spongy metal is scraped off, fused and cast into bars. For normal use, purification by electrolysis is satisfactory. For semiconductor purposes, repeated electrolysis and zone melting create an extreme purity. In 2001 the refined indium production was about 300 tonnes.

38.4.3
Thallium

Thallium is prepared from filter dust obtained after roasting of sulfide ores. The dust is dissolved in sulfuric acid. Then thallium co-precipitates with lead sulfate. The lead manufactured by reduction with coke contains thallium metal. Lead is first removed in two electrolytic processes, and in a second step thallium is precipitated on a steel cathode. As an alternative, thallium can be won from a sulfuric acid solution with an ion-exchange technique. The annual production of thallium compounds corresponds to 30 tonnes of thallium, but the production of the metal is not large – in the whole world less than 10 tonnes.

38.5
Properties and Uses

38.5.1
Gallium

Pure gallium has a beautiful, silvery appearance. Like water, the metal expands on solidifying. Therefore, it should not be stored in glass containers, as they may break as the metal solidifies. Mineral acids attack high-purity gallium only slowly.

38.5.1.1 A Metal With Low Melting Temperature

Gallium is the only metal, besides mercury, cesium and rubidium, that can be liquid near room temperatures. The temperature range for the molten phase is very wide, 30 to 2403°C. This makes the metal usable in high-temperature thermometers. Turnable anodes in X-ray tubes may also be mounted in liquid gallium.

38.5.1.2 Gallium in LEDs and High-Speed Transistor Electronics

Gallium compounds such as GaP and GaAs are formed with the elements in group 15 of the periodic table, the phosphorus group. They have semiconducting properties, and especially GaAs has been very much used in optoelectronic devices as light-emitting diodes (LEDs), photodetectors, laser diodes and solar cells. As a semiconductor, GaAs has an advantage over silicon in that it generates less heat, and it is therefore used for high-speed transistor electronics in supercomputers. The compounds are prepared by direct reaction at high temperature between gallium and phosphorus or arsenic, all the reactants being extremely pure. More than 90% of the gallium consumed in industrialized countries is in the form of GaAs.

As gallium arsenide is capable of converting electricity directly into light, it is a key component of LEDs, which may replace miniature incandescent lamps. The compound is electroluminescent and emits light with wavelengths that may be influenced by doping with other elements. LEDs have a wide range of uses as energy-efficient, reliable signal lamps in all types of electronic equipment, TV sets, cameras, bulletin boards at airports and so on.

A new generation of LEDs is based on the nitrides of gallium and indium, GaN or GaInN. These new LEDs are said to last longer and can be modified to give a discrete high brightness in different colors through the spectrum.

Oxides of gallium and the rare-earth metal gadolinium, magnetizable in only one direction, were used as a so-called *bubble memory* in computers. It was once thought that this would become one of the leading memory technologies, but this promise has not been fulfilled.

Special solar cells are made of germanium coated with gallium arsenide.

38.5.1.3 **Gallium as a Neutrino Detector**

A special and scientifically very interesting utilization of gallium is for detecting neutrinos from the sun. In the Gallium Neutrino Observatory at Gran Sasso, east of Rome, the GALLEX project took data continuously between 1991 and 1997. In April 1998 a new project with solar neutrino observations started. Data for the measuring period May 1998 to January 2002 (43 solar runs) have been analyzed. Gallium is used because the gallium isotope ^{71}Ga is converted to ^{71}Ge, which can be detected. The efficiency is extremely low. To make a detectable transformation possible, 83 tonnes of gallium chloride had to be placed in the Gran Sasso tunnel, waiting for successful hits. To prepare this great chloride quantity, 30 tonnes of gallium metal has to be used, thus a great deal of a whole year's world production of the metal.

38.5.2

Indium

Indium is a very soft, silvery white metal with a bright luster. Like tin, it emits a high-pitched "cry" when it is bent.

38.5.2.1 **Indium in Low-Melting Alloys**

An alloy consisting of 24% indium and 76% gallium is liquid at room temperature. Low-melting tin–bismuth alloys contain indium. They are used for safety fuses, in fire-alarm boxes and in sprinkler systems. Also indium alloys are used as solders for printed circuit boards. Indium alloys are easily composed for a specified melting range. Alloys of this type are used to give a signal "clear" for the Christmas ham or turkey to be taken out from the oven.

38.5.2.2 **Coatings for Bearings and Mirrors**

Indium metal has a very low friction coefficient. It was the basis for the first large-scale application for indium, a coating for bearings in high-performance aircraft engines. Bearings that must function lubricant-free, as for instance in Formula 1 type racing cars, are plated with indium.

Mirrors can be made by plating indium on metals or sputtering indium on glass. They reflect as well as silver mirrors but have better corrosion resistance.

38.5.2.3 Indium–Tin Oxide (ITO) and Indium Phosphide (InP)

Films of ITO, *indium–tin oxide* (80% In_2O_3), are transparent to visible light but not to infrared light (IR). In addition they have good electrical conductivity. Vacuum sputter deposition of ITO affords excellent coating uniformity and adhesion. Film thickness should be in the range 1000–2000 Å for high IR reflectivity, but the thickness has little influence on film conductivity.

The electrical conductivity of the thin coating is utilized on windshields for railway engines and airplanes to make it possible to warm them up with electric current for defogging.

As ITO is not transparent to IR radiation, it is used as a heat-reflecting coating in order to make the heating and cooling of buildings more energy-efficient. On goggles for welders, it is also sputtered as an IR-reflecting coating, protecting the eyes against heat radiation.

Interest in ITO increased considerably when indium–tin oxide thin films were introduced for liquid crystal displays (LCD). They are used for watches, television screens and so on.

Indium phosphide (InP) has been introduced as an advanced semiconductor material. A chip based on InP is the fastest frequency synthesizer known, and operates at seven billion cycles per second. This is more than three times faster than other available synthesizers.

38.5.3
Thallium

The metal is soft and malleable, and can be cut with a knife.

38.5.3.1 Thallium, a Forbidden Rodenticide – But Allowed in Detective Stories!

Thallium sulfate is very toxic. It has in fact been used as an alternative to arsenic by assassins. The sulfate is odorless and tasteless, giving no warning of its presence. It is said that this deadly sulfate has also been used by dictatorial regimes to dispose of opponents. The victims seem to have died from natural causes. Thallium sulfate has been widely utilized as a rodenticide and ant killer. In 1987 many people in Guyana were affected by consuming milk from cows that had eaten molasses treated with thallium sulfate (for use against rats). Some 44 persons died.

The use as a household insecticide and rodenticide has been prohibited in the United States since 1975. Thallium sulfate is however allowed and utilized as an effective poison in detective stories!

38.5.3.2 Some Special Applications

The water-soluble compounds of thallium are toxic, as already mentioned. In spite of that – or perhaps because of that – thallium had a great medical use up to the end of World War I, mainly as a medicine against tuberculosis and syphilis. This has now been emphatically banned.

Thallium, low down in the boron group of the periodic table, does not have the ability of gallium and indium to form valuable phosphides and arsenides. Nevertheless some special applications are known. A mercury–thallium alloy, which forms a eutectic at 8.5% thallium, is reported to freeze at −60°C, about 20 degrees below the freezing point of mercury. Lead, alloyed with a high thallium content, 30–50%, is very corrosion-resistant and has been used as the anode material in continuous zinc plating.

Thallium silicate glass has a higher refractive index than lead glass and is transparent to IR radiation. For that reason, this type of glass is used in the optics of copying machines.

The electrical conductivity of thallium sulfide changes with exposure to IR light, and this compound is used in photocells. Research activities are going on to utilize thallium oxide and thallium cuprate for high-temperature superconductors.

38.6
Ecological Effects

Gallium and indium are not essential for life and seem to have no biological roles. Indium is toxic to some small extent, but due to its low abundance its influence on the environment is insignificant.

Thallium is dangerous, like mercury and lead, but it causes far fewer environmental problems as it has, up to now, been so little used in industry. The monovalent thallium ion has a certain similarity with the potassium ion and interferes with the role of potassium in the transfer of nerve impulses in the body. Because of that, thallium is very toxic. In fact an increased potassium intake counteracts to some extent the effect of thallium poisoning. The chalcophilic character of thallium (its tendency to form sulfides) is perhaps also important as it may replace other metals in essential enzymes. An intake of 1 g is lethal, but some milligrams are enough to create psychoses and neurological disturbances. Exposure to soluble thallium compounds should not exceed 0.1 mg/m^3 (8 h time-weighted average in a 40 h working week).

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39
Carbon

39.1 C
Facts about Carbon

39.1.1 C
The Element

Symbol:	C
Atomic number:	6
Atomic weight:	12.01
Ground state electron configuration:	[He]$2s^2 2p^2$
Crystal structure:	*Diamond*: Cubic with *a*=3.57 Å. *Graphite*: Hexagonal with *a* = 2.46 Å, *c* = 6.71 Å. „Amorphous“ carbon, carbon black, soot, charcoal, and so on are all microcrystalline forms of graphite. *Fullerene*: The structure element is a truncated icosahedron with a carbon atom at each of its 60 vertices. Besides this C_{60} fullerene, also C_{70}, C_{74} and C_{82} have been synthesized.

39.1.2 C
Discovery and Occurrence

Discovery: Graphite and diamond were known to ancient civilizations. Carbon as soot and charcoal was used in prehistoric time. The discovery of the fullerenes is new (1985) and led to a Nobel Prize in 1996.

Most important mineral: Calcite $CaCO_3$ and other carbonates.
Diamond and graphite in nature (Figures M50 and M51).
Wood, peat, coal and natural gas.

Ranking in order of abundance in earth crust:	17
Mean content in earth crust:	200 ppm (g/tonne)
Mean content in oceans:	28 ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	$23 \cdot 10^4$ ppm (23 %)
Content in a man’s body (weight 70 kg):	16 kg

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39.1.3 C
Chemical Characterization

Carbon is found free in nature as diamond, graphite and amorphous carbon (microcrystalline graphite). Graphite is one of the softest materials known, while diamond is the hardest. More recently another form of carbon, fullerene, C_{60}, was discovered. Its molecule consists of 60 carbon atoms in a roughly spherical shape, looking like a soccer ball. Carbon has the unique ability to link with other carbon atoms to form complex chains and rings. This property has created the "organic" chemistry with an almost infinite number of carbon compounds. Plants, using photosynthesis, convert carbon dioxide from the atmosphere into organic carbon compounds, which are subsequently consumed by other organisms. Carbon is however also very important in many industrial applications. In 1961 the International Union of Pure and Applied Chemistry (IUPAC) adopted the isotope ^{12}C as the basis for atomic weights. ^{14}C, a radioactive isotope with a half-life of 5730 years, is used to determine the age of materials like wood, archeological specimens, etc.

Oxidation states:
This concept is rarely used for carbon due to its special bonding characterization, even if a formal oxidation state of IV often, but not always, comes out conspicuously.

Simple molecular compounds:	CO_2, CO, CCl_4 and CS_2
Carbides:	CaC_2, B_4C, WC, TiC and $Cr_{23}C_6$

Ionization energy (kJ mol^{-1}):		**Electron affinity (kJ mol^{-1}):**
$C(g) \rightarrow C^+(g) + e^-$	1087	$C(g) + e^- \rightarrow C^-(g)$
$C^+(g) \rightarrow C^{2+}(g) + e^-$	2353	–122
$C^{2+}(g) \rightarrow C^{3+}(g) + e^-$	4620	
$C^{3+}(g) \rightarrow C^{4+}(g) + e^-$	6223	
$C^{4+}(g) \rightarrow C^{5+}(g) + e^-$	37 831	

Standard reduction potential:	$CO_2(g) + 2H^+(aq) + 2e^- \rightarrow CO(g) + H_2O(l)$	$E^0 = -0.106$ V
	$CO(g) + H_2O(l) + 2e^- \rightarrow C(s) + H_2O(l)$	$E^0 = +0.517$ V
Electronegativity (Pauling):	2.55	
Radii of atoms and ions:	Atomic:	70 pm
(WebElements™)	Covalent:	77 pm
	Van der Waals:	170 pm
	C^{4+} (4-coordinate, tetrahedral):	29 pm
	C^{4+} (6-coordinate, octahedral):	30 pm

39.1.4 C
Physical Properties

Density	Molar volume	Melting point
2250 kg m^{-3} (graphite) 2.25 g cm^{-3}	5.34 cm^3 (graphite)	4000 K (graphite, triple point, 10.3 MPa) 3727 °C
3510 kg m^{-3} (diamond) 3.51 g cm^{-3}	3.42 cm^3 (diamond)	4100 K (diamond, triple point, 12.4 GPa) 3827 °C

Boiling point	Specific heat c_p at 298 K
4100 K (graphite, sublimation point) 3827 °C	711 J K^{-1} kg^{-1} (graphite) 510 J K^{-1} kg^{-1} (diamond)

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
70–220 (graphite)	80–230	75–195	50–130	35–70
– (diamond)	1000	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$0.05 \cdot 10^{-6}$ (diamond)	$1 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$	$3.7 \cdot 10^{-6}$

Resistivity nΩm

78 K	293 K	373 K	573 K	973 K	1473 K
–	$1.375 \cdot 10^4$ (graphite) 10^{20} (diamond)	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-6.3 \cdot 10^{-9}$ m^3kg^{-1} (graphite) $-6.2 \cdot 10^{-9}$ m^3kg^{-3} (diamond)
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	33 GPa	–

39.1.5 C
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	–
Enthalpy of vaporization ΔH_{vap} at b.p.	715 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	717 $kJmol^{-1}$
Entropy S^0 at 298 K	5.74 $JK^{-1}mol^{-1}$ (graphite) 2.38 $JK^{-1}mol^{-1}$ (diamond)

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	1.67 (graphite)	8.52 (graphite) 6.11 (diamond)	16.84 (graphite)	21.61 (graphite)	25.09 (graphite)	25.90 (graphite)

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$2C+O_2 \rightarrow 2CO$	–274	–311	–400	–485	–575
$C+O_2 \rightarrow CO_2$	–394	–395	–395	–395	–395

39.1.6 C
Nuclear Properties and X-ray

Isotope range, natural and artificial 8–20

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half-life**	**Decay mode**	**Decay energy Q**
^{12}C	Stable	98.90	0+	–	–	–	–
^{13}C	Stable	1.10	1/2–	0.7024	–	–	–
^{14}C	Active	0.00	0+	–	5730 y	β^-	0.156 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{13}C
Reference compound	$Si(CH_3)_4$
Frequency MHz (^1H = 100 MHz)	25.145
Receptivity D^P relative to ^1H = 1.00	$1.75 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	1.00
Magnetogyric ratio, radT^{-1}s^{-1}	$6.728 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation

Z	**Element**	**Kα_2 keV**
5	B	0.183
6	C	0.277
7	N	0.393

X-ray radiation absorbed by the element

Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	4.53
17.37 keV (MoKα_2)	0.581

Neutron absorption	**Thermal neutron capture cross section**	0.0034 barns

39.2
A Long History

It is probably the case that carbon, in the form of charcoal and soot, was the first element with which mankind came into contact. The forest fires gave charcoal and the coal fire gave soot. In historic times charcoal has been a prerequisite for the development of the metallurgy and manufacture of metals, known since antiquity. The first ink for writing purposes was probably prepared by stirring lampblack into olive oil and adding balsam gum. It gave a very durable writing, proved by old rolls of parchment and by the Dead Sea Scrolls. For writing, a reed pen was utilized. The ink was stored by the writer in an inkhorn.

Knowledge about carbon as a chemical element was developed far later, beginning in the 18th century. In the middle of that century Joseph Black in Scotland showed that when charcoal is burned a gas is formed, the properties of which are different from those of air. This gas, carbon dioxide, was for a long time designated *fixed air*. The difference between graphite and carbon was elucidated only with great difficulty, in connection with the century's important work about iron and steel. This is described in Chapter 8 Iron.

In the same century it was clarified that diamond is a form of carbon. In 1772 Lavoisier and a group round him placed a diamond in a glass case and ignited it with a big burning glass. They collected the gas above mercury, added slaked lime, and got an obvious precipitation of calcium carbonate. The burning glass had heated the air, which had oxidized the diamond carbon to carbon dioxide. At the start of 19th century, Guyton de Morveau fused soft iron in a small crucible and added a diamond with a weight of 1 g (5 carat!). The iron was changed to steel.

Carbon has been of decisive importance for vital processes. Around 25 other elements are also essential, but carbon, with its unique properties, is the central atom of life. At the beginning of the 19th century, the general opinion was that the sole possibility for the formation of an organic compound was the action of a *vital force*. In 1828 Wöhler made his famous synthesis of urea, which constituted some sort of paradigmatic shift. From the middle of the 19th century "organic" chemistry simply became the chemistry of carbon compounds.

39.3
Carbon in Space

Carbon has of course a much longer history than can be traced back to our ancestors' use of charcoal for ore reduction or soot for writing.

A star retains its temperature by the fusion energy set free when four hydrogen nuclei combine to produce one helium nucleus. When the supply of fuel begins to run out in the center of the star, it will be compressed and the temperature increases to still higher values. In our sun, so small that it is, no atoms heavier than helium can be synthesized. In bigger stars three atoms of helium can combine to one carbon atom. The synthesis of elements has started. Carbon forms neon, which forms oxygen, which in its turn forms silicon. When, at the end, silicon starts to synthesize iron, the star is close to catastrophe. A giant star ends its active life in a gigantic supernova explosion, and the elements synthesized are blown out into space. They are partly built into new stars and partly stay in interstellar space. In Table 39.1 the estimated relative number of atoms in our total solar system is compared with the corresponding values for the earth (not the crust but the whole earth).

Table 39.1 The number of atoms (relative to silicon = 1) of the most abundant elements in our solar system and in the whole earth

Element	Abundance, relative to silicon	
	In the solar system	In the whole earth
Hydrogen	27900	0.015
Helium	2720	–
Oxygen	24	3.5
Carbon	10	0.006
Silicon	1	1
Magnesium	1.1	1.1
Aluminum	0.09	0.13
Iron	0.9	1.3

Source: values recalculated from ref. [39.1].

In the solar system, carbon is thus the fourth most abundant element, almost as common as oxygen. There is however a very big difference between the abundance of these elements in the earth, the number of carbon atoms being only about two-thousandths of that of oxygen. When the earth was formed, carbon was present as volatile compounds, CH_4, CO and CO_2. Some of these stayed in the atmosphere, some were trapped in minerals, but to a great extent they escaped from the atmosphere due to the low gravitational force of the small planet earth.

In supernova explosions, various elements are, as already mentioned, thrown out into space. When gases are expanded and cooled, chemical reactions occur and different carbon compounds are formed. Several have been identified in the atmospheres of our neighboring planets, in comets and meteorites and also in interstellar space. Duley and Williams [39.2] have described in detail the carbon compounds present in interstellar space.

The structure and composition of meteorites in general indicate that they have been heated to a very high temperature and thus lost their carbon content. A rare meteorite type is the so-called *carbonaceous chondrite*. It contains carbon as graphite and non-volatile compounds of high molecular weight but also the complex molecules necessary for life, such as amino acids [39.3]. A surprise on examination of Halley's comet in 1986 was the finding that its core contains both solid carbon and carbon-rich compounds of high molecular weight. Knowledge about comets and carbonaceous chondrites is important as it contributes to the elucidation of the material of which our earth was originally formed.

39.4
Back to Carbon on Earth

The most important carbonate minerals are calcite, dolomite and magnesite. They have been treated in connection with the elements calcium and magnesium in Chapter 14. Pure carbon occurs as graphite and diamond. Great quantities of carbon are also present in fossil fuels such as pit coal, brown coal, peat, natural gas and oil deposits, as well as in all living organisms.

Coal is a family of rock-like deposits, which are derivatives of forest-type vegetation, accumulated in fens and compressed a long time ago. They gradually changed to material with increasing carbon content. The organic constituents that comprise the coal mass are designated *macerals*. They are to coal what minerals are to inorganic rock. The coal series begins with peat and ends with graphite (see Table 39.2).

Brown coal was formed less than 100 million years ago in the *Tertiary*, a geological period thought to have covered the time between 65 and 2–3 million years ago. Black coal mainly was formed in the *Carboniferous* period, ranging from about 345 to 280 million years ago.

In the deposits coal is present in beds sandwiched with sand and clay layers.

Table 39.2 Coal types

Type	Description
Peat	A deposit of semi-carbonized plant remains in a water-saturated environment, such as bog or fen, and with a high moisture content. It is an early stage in the development of coal. Carbon content is about 60% and oxygen content 30%
Brown coal, lignite	A brown to brownish black coal. In brown coal the original plant structures may usually be seen
Coal (pit coal) (Figure M50)	A combustible rock containing more than 50% by weight and more than 70% by volume of carbonaceous material. Differences in the kinds of original plant materials, in the degree of metamorphism, and in the range of impurities are characteristic of coal and are used in classification
Anthracite	Coal of the highest rank, in which carbon content is between 92% and 98%. It is hard and black, and has a semi-metallic luster. Anthracite ignites with difficulty and burns with a short blue flame, without smoke
Graphite (Figure M50)	A hexagonal mineral, a naturally occurring crystalline form of carbon

Source: mainly from ref. [39.4].

39.5
Coal for Power Generation and Metallurgical Coke

39.5.1
Different Fields of Application

For coal there are at least three large fields of application:

- generation of electrical energy in power stations;
- production of hot water for distribution in cities;
- raw material for producing metallurgical coke.

Burning coal generates about 40% of the electricity in the world. Coke is produced by pyrolysis of coal – heating in the absence of air. Coke contains 90–95% carbon, the rest being ash. It was once very much used as a fuel for heating houses but has now been replaced by oil, gas and electricity. In the blast furnaces used for the production of raw iron, coke is indispensable. It works both as a means of reduction and as a heat generator. The high content of carbon in the raw iron also comes from the coke.

At one time Germany and England were the most important coal countries in the world. The coal industries in these two countries are nowadays under strong pressure. Government subsidies, which have delayed closing-down, are being prohibited by EU energy policies. The mining of brown coal, mainly in eastern Germany and the

Czech Republic, has been reduced considerably due to environmental problems. China and the USA are now the largest producers in the world, and account for 30% each of the total world production.

39.5.2
Environmental Problems of Burning Coal

Coal contains substances that are set free on burning and can lead to environmental problems. This has made it difficult for coal to compete with other energy generators. The harmful emissions can however be reduced to a considerable extent by different methods. A *scrubber* washes away sulfur dioxide with water and lime. A *precipitator* removes 99% of the ash that follows the flue gases. A special problem is that of the nitrogen oxides formed on burning coal. Their formation increases with increased burning temperature.

The modern burning technique in a *fluidized bed* was developed in order to find a combustion process without the need for external emission controls such as scrubbers. In the fluidized bed solid fuels are suspended on an upward-blowing stream of air. The tumbling action is similar to a bubbling fluid. This results in a turbulent mixing of gas and solids in the combustion process and effective heat transfer. Fuel is burned at temperatures of about 850°C, well below the threshold at which nitrogen oxides form. The flue gases are brought into contact with limestone or dolomite for absorption of sulfur dioxide. More than 95% of the sulfur pollutants in coal can be captured.

39.6
Carbon Black and Active Carbon

Carbon black is a well-defined, industrially produced product and consists of finely dispersed carbon with specified grain size. It should not be confused with *soot*, formed during uncontrolled and incomplete combustion in a Bunsen burner or a candle. Soot may contain additional complex organic molecules, some of which may be carcinogenic.

Carbon black with a grain size below 1 μm is prepared primarily from petroleum-based feedstock. The oil is heated above 1100°C. This process "cracks" the oil to produce carbon black powder. Alternatively, combustion of natural gas or other organic compounds may be utilized. Together the carbon particles form an aggregate with the ability to bind other compounds to their very large specific surface of 50–100 m^2/g. This property is utilized in the various technical applications of carbon black. It is used as a pigment in printing inks and as a transfer material in carbon paper, typewriter ribbons and laser printers, as well as in photocopying machines.

Carbon black is also an essential ingredient in rubber goods and improves their strength and durability. The rubber mixture for the treads of tires may contain, by weight, more than 50 parts carbon black per 100 total. It is also used as an intensively black filler for polymers and lacquers. The carbon mixed in also acts to conduct away static electricity.

A very important and technically advanced use of carbon black is as a raw material for making hard carbides in the manufacture of hard metals. Powders of tungsten or of other carbide-forming metals are weighed together very carefully to stoichiometric mixtures, which are heated to a very high temperature. The intended carbide is formed.

Active carbon has a specific surface of 500–1500 m^2/g. This makes active carbon suitable for adsorption purposes, such as for instance in groundwater purification and the dechlorination of process water, as well as for adsorption of gases and droplets in gas masks. Within medicine it is also used to adsorb poisons in the stomach and intestine.

39.7
Graphite

Graphite exhibits the properties of both a metal and a non-metal. This makes it suitable for many industrial applications. The metallic properties include thermal and electrical conductivity; the non-metallic properties include high thermal resistance and lubricity. Some of the major end uses of graphite are in refractories, high-temperature lubricants, brushes for electrical motors, friction materials, batteries and fuel cells.

Graphite is a modification of carbon. It takes its name from the Greek word *grapho*, to write, which alludes to the utilization of graphite in pencils. Graphite is soft and unctuous. It conducts electricity well and is immune to most acids.

39.7.1
The Atomic Arrangement Determines Its Properties

Graphite has a density of 2.25 g/cm^3 and is built up of layers of carbon atoms arranged in a hexagonal ring system (Figure 39.1). Within a plane the atoms are bound to each other with covalent bonds. Between the planes no covalent bonds exist but weak so-called van der Waals forces. This is the reason why graphite easily colors the paper black when writing with a pencil. It is also possible to “feel” the crystal structure if graphite is rubbed between thumb and forefinger. On a macroscale the slip of the atomic planes against each other appears as lubrication ability. Graphite is also used as a lubricant for some plastic deformation operations, especially when the temperature is so high that conventional lubricants would be destroyed. In the drawing of high-speed steel wire at 300–400°C graphite is used for lubrication within the die.

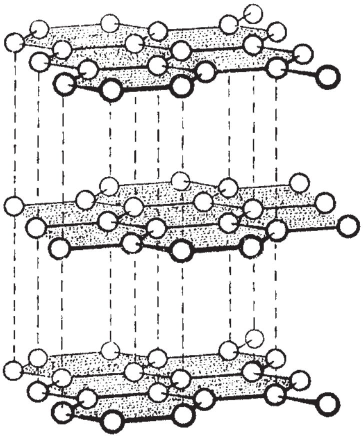

Figure 39.1 The crystal structure of graphite. The separation of the sheets is 3.35 Å. The C–C bond length in the sheets is 1.42 Å.

39.7.2
Natural and Synthetic Graphite

Graphite is a naturally occurring crystalline form of carbon. Graphite in deposits is designated *natural graphite,* while *synthetic graphite* is manufactured. Graphitization of natural graphite has occurred in geological processes through intrusion contact at high temperature between igneous rock and carbonaceous matter. Synthetic graphite is obtained by the treatment of non-graphitic carbon at high temperature. Vapor deposition from hydrocarbons is also a graphitization method.

Fine-grained, generally sooty graphite is called amorphous graphite. The word is not formally correct as all graphite is crystalline, but the designation is frequently used for graphite formed during the thermal transformation (metamorphism) of coal. Graphite that is not amorphous is often referred to as crystalline even if different subgroups exist.

39.7.3
Occurrence and Production

Graphite occurs naturally in metamorphic rocks such as marble, schist and gneiss. It is mined from both open pit and underground mine operations. The ores are crushed, ground and enriched by different flotation processes. World production of natural graphite was about 870 000 tonnes in the year 2001. About half of the total (450 000 tonnes) was produced in China, while India was in second place with 140 000 tonnes. Other large producer countries were Brazil, Madagascar, Mexico, the Czech Republic, North Korea and Canada. The eight mentioned countries accounted for 92% of the world's production.

39.7.4
Applications for Graphite

Graphite is stable over a wide range of temperatures and is a good conductor of heat and electricity. For these reasons it is used in metallurgy as a refractory material for crucibles, ladles and molds for molten metals and as an electrode material in electric arc furnaces. Mixed with alumina or zirconia, graphite is pressed into components for the continuous casting of steel and shielding for pyrometers. Within steel metallurgy, large amounts of graphite are also used as a carbon-raiser additive in steel-making. In chemical technology, graphite is used for the anodes in aqueous electrolytic processes for the production of chlorine and fluorine.

The versatility of graphite is illustrated by the fact that it is used both to increase friction, in the brake linings for automobiles, and to decrease friction, as an additive to lubricants.

Because of its conductivity, graphite is an important material for electrical purposes. Graphite brushes for rotating electric motors transfer electric current effectively while the lubricity of the material keeps the friction wear low. Graphite also plays an important role as cathode material in batteries and fuel cells. This will increase the demand for very pure graphite (synthetic or purified natural) concurrently with the development and increased utilization of hybrid vehicles.

In nuclear technology, graphite is used as a *moderator* to slow down the neutrons released during fission. This is necessary for continuous fission to be maintained. The Chernobyl accident happened with a reactor using graphite as moderator and ordinary water as coolant. This combination caused instability. Better stability is achieved in reactors using a graphite moderator and pressurized CO_2 as the coolant. However, the most common reactor type nowadays uses pressurized water as both moderator and coolant.

When fibers of organic material, such as rayon, are heated to a very high temperature, volatile matter is driven off, giving carbon residues with graphitic structure. They are used in a new graphite application: strong carbon fibers for reinforcing plastics. These composites are used in tennis rackets, golf clubs and lightweight aircraft.

39.8
Diamond

39.8.1
Graphite and Diamond

Graphite is the stable modification of carbon at low pressure and moderate temperature. It can however be transferred to diamond by applying a very high pressure at high temperature according to the phase diagram of carbon, shown in Figure 39.2. When the shock wave technique is utilized graphite is placed in an explosive. At the explosion it will be transferred to diamond grit. It corresponds to the area in the figure at about 1100 kbar and 3000 K.

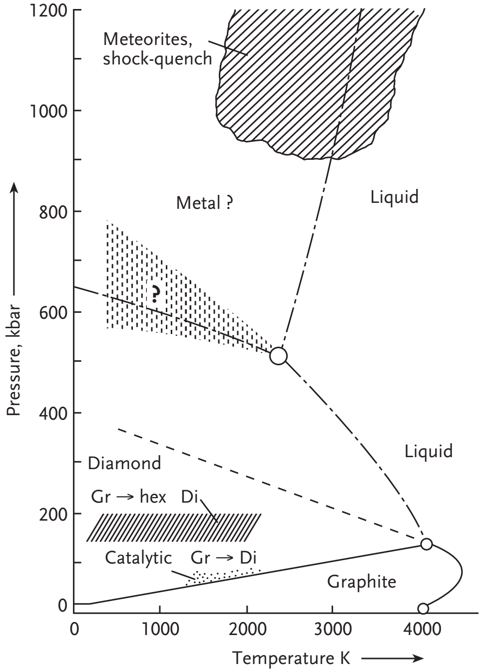

Figure 39.2 The phase diagram of carbon. Reprinted from Ullmann's Encycl. Ind. Chem. 5th ed. 1986. Vol. A5, Carbon, p. 97.

The equilibrium diagram however includes a *liquid-graphite-diamond triple point* near 130 kbar and 4000 K. Along the equilibrium line between graphite and diamond at for instance 1800 K and 70 kbar diamond may also be formed under favorable circumstances. It is utilized at the modern syntheses of diamond, described in section 39.10. Perhaps this was also what happened in nature when the natural diamonds were created in gelogical processes deep in the earth.

Diamonds found in nature in the earth's crust are called *natural diamonds*. Some of them (familiar as the precious stones used for jewelry) reach gem-quality standards for clarity, color and size; others may be used as *industrial diamonds* to make various tools for abrasive machining of hard materials, etc. (Figure M51). The main part of the latter, however, are *synthetic diamonds,* manufactured from graphite, and used for many purposes in industry. Diamond is the hardest material known and has the highest thermal conductivity of all materials at room temperature.

39.8.2
Structure and External Symmetry

Diamond, like graphite, is pure carbon, but with another arrangement of the carbon atoms, another crystal structure. Each atom in diamond is surrounded in space by four neighbors, quite symmetrically, as shown in Figure 39.3. All the atomic sites and all the bonds are completely equivalent. The loose and weak interplanar packing of the atoms in graphite and the very tight and strong packing in diamond explain the differences in physical properties. The density is 2.25 g/cm^3 for graphite and 3.51 g/cm^3 for diamond. Graphite is greasy and flexible and has low hardness. Diamond is the hardest material known, and thus has the highest number, 10, in Mohs' scale. In fact the hardness of diamond gave rise to its name: the Greek word *adamantos* means irrepressible.

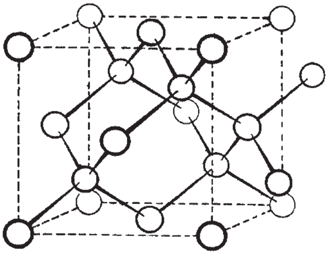

Figure 39.3 The crystal structure of diamond. The C–C distance is 1.54 Å. The edge of the unit cell is 3.57 Å.

Diamond has cubic crystal symmetry. The principal external habits or crystal forms are mostly the *octahedron*, the *cube* and the *dodecahedron*, as shown in Figure 39.4. Slightly rounded faces and slightly curved edges as well as combinations of the forms and twinning are common. The cleavage is perfect along the four octahedral planes and is used to split larger stones. Very high optical refraction together with strong color dispersion gives diamond jewels their highly appreciated charm of "colored fire". The unique combination of the highest thermal conductivity at room temperature of all known materials (four times higher than for copper) and high electrical resistivity makes diamond suitable for some advanced technological purposes.

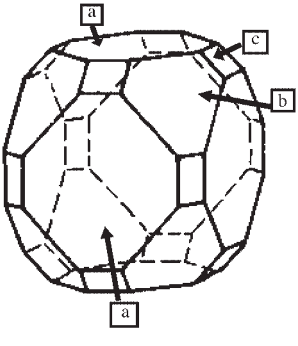

Figure 39.4 A possible shape for a diamond, showing a combination of the following crystal forms, with faces labeled: (a) cubic or hexahedral, (b) octahedral and (c) dodecahedral. The crystal is holohedral, which means that it is a crystal within its system (cubic in this case) showing maximal symmetry. The most usual however is the pure octahedron.

39.8.3
Diamonds in the Ground

Diamonds are formed in magmas 200 km below the surface of the earth, which corresponds to an extremely high pressure. In combination with a high temperature, above 1400°C, this has caused diamond formation from magmas containing carbon. The process has similarities with the modern manufacture of synthetic diamonds. Through gas-rich eruptions, steep narrow throats in the shape of "carrots" (Figure 39.5) were formed and filled with kimberlite, a volcanic breccia[1] and the mother rock of diamond.

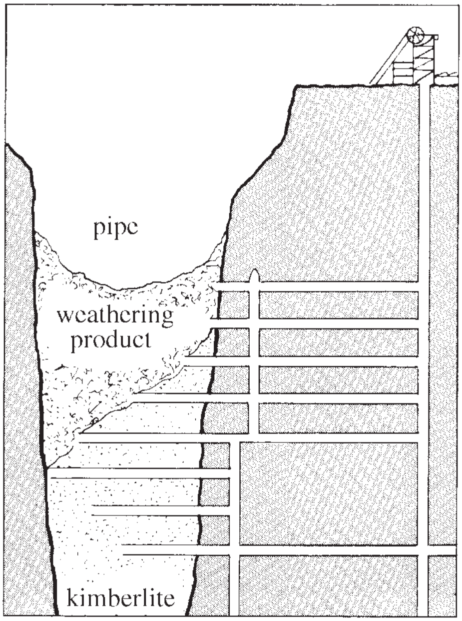

Figure 39.5 Mining of kimberlite [39.5].

Diamonds are also found in *placers*. These so-called secondary deposits are formed when kimberlite weathers to a yellowish soil, which is transported away by water and glaciers. Placers are important sources of natural industrial diamonds.

39.8.4
Winning of Diamond

In older times, up to the beginning of the 18th century, most diamonds came from India. In 1725 the situation changed. Considerable deposits were discovered in Brazil, *Minas Gerais*, where now the town of *Diamantina* is situated. After the Brazilian

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[1] Breccia is a coarse-grained rock composed of angular broken rock fragments held together by a mineral cement.

boom during the 18th and 19th centuries, South Africa took over the role as diamond leader. The town of *Kimberley* in the Cape Province of South Africa was founded in 1871 after sensational finds of diamonds were obtained.

The town was for a long time the world center for the winning of diamonds and trading in the valuable precious stones. On top of the famous mine "Big Hole", a *yellow ground* was found, which was a weathering product of the underlying kimberlite, called the *blue ground*. The mine was worked from 1871 to 1908 with simple methods, but in spite of that a depth of 1070 m was reached. In all 14.5 million carats of diamond (2900 kg) were obtained. For this extraction a rock quantity of about 24 million tonnes of kimberlite had to be broken.

Modern South African diamond winning occurs nowadays as underground mining. The mineralization has a small width but considerable depth. Special machines have to be utilized that are suitable for the special working conditions in very deep mines – some 3300 m depth and a working temperature of +50°C. The *one man–one machine* drilling technique (Figure 39.6) was developed in the 1950s by the Swedish companies Atlas Copco and Sandvik Rock Tools. Today, a selection of standard "slim size" machines is available, allowing mechanized mining in 2 m wide drifts.

Figure 39.6 One man–one machine, a drilling technique in diamond mines. (Reprinted with permission of Atlas Copco Rock Drills AB, Sweden.)

39.8.5
World Supply of Natural Diamonds

Diamond "size" is expressed in carats; 1 carat = 0.2 g. The mines at Kimberley have produced a total of more than 200 million carats since the 1870s. Almost half of South Africa's diamonds are of gem quality. The largest producer of gemstone diamonds in southern Africa – and in the world – however is Botswana. The world production of natural diamond in the year 2001 is shown in Table 39.3 [39.6].

Table 39.3 Production of natural diamond in the year 2001

Country	Gemstone quality thousand carats	Industrial quality thousand carats
Botswana	20 100	5060
Russia	11 600	11 600
Australia	10 700	13 100
Congo (Kinshasa)	9100	9100
Angola	4650	520
South Africa	4 470	6 700
Canada	2600	–
Namibia	1490	–
Brazil	1000	–
Ghana	700	170
Sierra Leone	450	150
C. African Republic	360	120
Tanzania	300	50
Guinea	270	90
China	235	950
Other countries	475	390
Total	68 500	48 000

39.8.6
Use of Natural Diamonds in Industry

Natural diamond is used by industry for many different purposes, such as for instance drill bits, saws, diamond wheels, drawing dies, and as a loose grain abrasive for polishing. However, the role of diamond for industrial applications has to a great extent been taken over by synthetic diamond.

There is a drawback associated with using natural diamond as the tool material for some applications. This may be exemplified by the utilization of diamond in drawing dies for the production of special quality wires made of stainless steel, nickel–chromium resistance alloys, tungsten or molybdenum metals. Due to its special crystal structure, natural diamond has small variations in hardness in different directions. Die wear therefore varies depending upon the direction. A cylindrical hole in a die can change to hexagonal after drawing of a lot of wire. This is demonstrated in Figure 39.7 for the drawing of resistance wire. The picture to the left shows a new natural diamond (ND) die whereas the figure to the right is a used ND die. An exaggerated quantity of wire was drawn just for demonstration purposes (the wire manufactured using this die cannot of course be accepted as a quality product).

There is a second drawback with diamond, natural or synthetic, in some applications. If a tool is used for machining of a steel component by turning, milling or drilling, the temperature at the contact point between tool and steel becomes so high that the diamond is destroyed. It will be transformed to graphite. For steel machining, a tool made of cubic boron nitride (CBN) may be used instead.

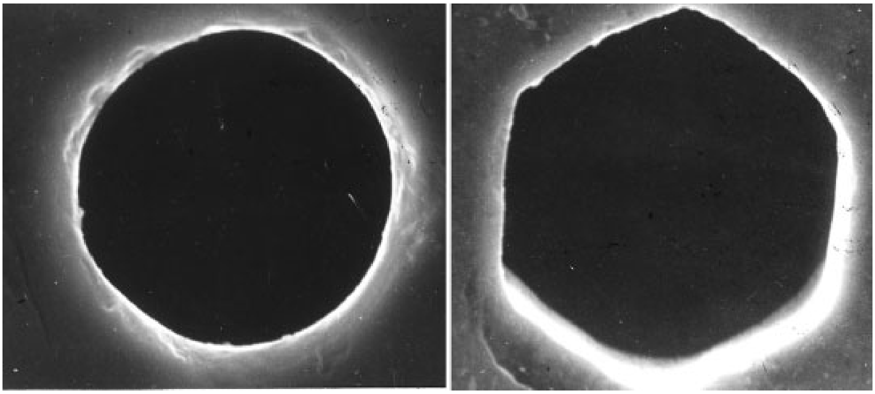

Figure 39.7 A demonstration of the behavior of natural diamond dies. The picture to the left shows a new die (of size 0.02 mm) made out of natural diamond. The picture to the right shows a used die (in this case the size was initially 0.03 mm) after drawing a large quantity of wire. During drawing, wear has preferentially occurred in special crystal directions. The hole, round at the beginning, has been turned into a hexagon. A die of synthetic diamond does not change its cross-sectional shape in this manner.

39.8.7
Gemstone Diamonds

39.8.7.1 Working of Diamonds

Diamonds from a mine are separated into gem-quality, near-gem-quality and industrial-grade diamonds. The diamonds are then grouped into sizes, big (more than 1 carat), small (between 1 and 0.1 carat) and "sand" (less than 0.1 carat). Diamonds larger than 15 carats are handled individually. The ultimate purpose of sorting is to estimate an asking price for the rough diamonds.

A rough diamond is cut into pieces along carefully selected cleavage planes. Although practiced in India in very early times, the art of cleaving was developed very much in Europe by the English chemist William Hyde Wollaston (1766–1828; section 32.4.1). The tool used is a copper or bronze disk coated with diamond grains. Grinding occurs on a rotating horizontal steel disk covered with diamond powder and oil (Figure 39.8).

In the process of grinding, the direction in which the grinding disc moves across the facet that is being worked is not immaterial. Owing to the fact that the hardness of diamond, as well as other precious stones, is different in different directions, the working occurs more easily when the softer parts of the rough diamond come into contact with the hard, cutting directions in the diamond grains on the rotating disk. As a consequence the grinding of diamond facets can be accomplished with comparative ease in some directions, while in others the process is extremely tedious.

When the grinding wheel came into use at the end of the 15th century it was possible to develop the faceting that is so typical of diamond as a gemstone. The cardinal *Jules Mazarin* (1602–1661), a French statesman of Italian descent, came up with the

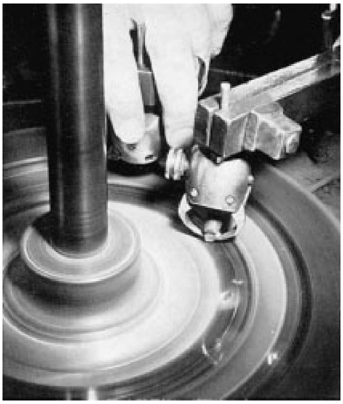

Figure 39.8 Grinding of diamond [39.5].

idea. His name has become attached to the *mazarin stone* that has been made famous in our time in the novel *The Adventure of the Mazarin Stone* by Sir Arthur Conan Doyle.

39.8.7.2 **Brilliant Grinding**

The perfection of diamond as a gemstone is obtained through the modern *brilliant grinding*. This technique gives the stone maximum brilliance. A brilliant ground diamond has the form of an octahedron with two truncated, opposite corners. Stones with the natural shape of an octahedron already have the brilliant form and can at once be faceted by grinding (see Figure 39. 9).

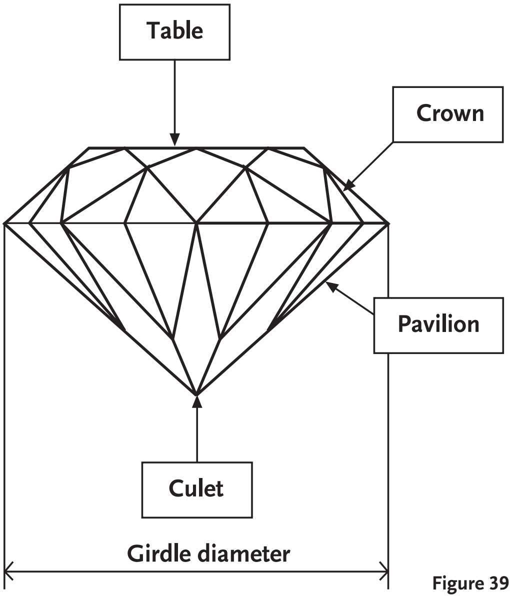

Figure 39.9 A brilliant ground diamond.

As already mentioned, the weight (size) of a diamond is expressed in carats; 1 carat = 0.2 g. The connection between girdle diameter and weight for brilliant ground diamonds is given in Table 39.4 [39.5].

Table 39.4 Girdle diameter and weight for brilliant ground diamonds

Diameter mm	2.2	3.0	4.1	5.2	6.5	7.4	8.2	9.0	9.3	11.0
Weight carat	0.04	0.10	0.25	0.50	1.00	1.50	2.00	2.50	3.00	5.00

As diamonds increase in weight, the price per carat increases because larger diamonds are more rare. A 1 carat diamond costs significantly more than four 0.25 carat diamonds of the same quality. If the price for a diamond with the weight 0.5 carat is $100, the price for a 1 carat diamond would be considerably more than $200, perhaps $400.

39.8.7.3 Two Famous Diamonds – Cullinan and Koh-i-Nor

A handful of diamonds are renowned for their incredible legend and history, magical lore and large size. They have acquired grand names that mark their significance and importance. Behind each of these spectacular diamonds lies a rich, magnificent story of history, discovery and achievement.

The largest diamond ever found was the *Cullinan diamond*. It takes its name from *Thomas Cullinan*, founder of the Premier Diamond Mining Co. in South Africa. There the mine superintendent Frederick Wells discovered the stone in 1905. Cullinan is the largest diamond ever found. Its weight was 3106 carats! Cutting of the huge, rough Cullinan was entrusted to Joseph Asscher, a clever diamond cutter in Amsterdam. Cleaving, sawing and polishing produced nine major stones and 96 smaller ones. The diamond was bought by the Transvaal government and was given to King Edward VII on his 66th birthday. The largest brilliant, named Cullinan I or *The Great Star of Africa*, is the largest existing cut diamond and has a weight of 530 carats. It is a magnificent pear-shaped gem, set in the royal scepter of the British Crown Jewels.

No stone on earth has such a rich and fascinating history as the *Koh-i-Nor diamond*. It is believed that the Rajah of Malwa secretly held it as long ago as 1302. In many wars the diamond was taken as a trophy by conquerors. It was in the Persian Empire that it got the name Koh-i-Nor, meaning “mountain of light”. In the famous Peacock Throne in Teheran it was used as one of the peacock’s eyes. However in 1849, when the British annexed the Punjab, they found the Koh-i-Nor there, took it as a war trophy and presented the diamond to Queen Victoria. The Queen got experts to regrind it from 190 to 109 carats and to repolish the gemstone in order to accentuate its brilliance. Since 1937 the Koh-i-Nor has been the gem in the middle of Queen Elizabeth’s crown. This position – in a royal crown – may be said to be in compliance with the old adage that “he who owns the Koh-i-Nor rules the world”.

39.8.7.4 Diamonds are unstable

According to figure 39.2 diamond is stable only at very high pressure. All the valuable jewelry diamonds, and the industrial diamonds too, should spontaneously form graphite. That diamond really exists at atmospheric pressure and room temperature is of course due to the fact that transformation of diamond to graphite occurs with very low speed at low temperatures.

In an inert atmosphere diamond is rapidly transformed to graphite at 800°C. Because of that diamond tools cannot be used for machining (lathing, drilling) of steel.

39.9
Fullerenes

Diamond is one kind of carbon, graphite is another – yet a third kind is *fullerenes*, discovered in 1985. Harold Kroto (University of Sussex, England) visited Richard Smalley and Robert Curl, Jr at the Rice University in Houston. The scientists intended to simulate carbon nucleation in red giant stars. The method was to direct a pulsed laser towards graphite and examine the species formed in a mass spectrometer. A peak corresponding to a molecular weight of C_{60} was obtained. Later similar molecules, C_{70}, C_{76} and C_{84}, were discovered. The scientists concluded that the C_{60} signal was due to a spherical structure, an icosahedron, similar to the surface panels of a modern soccer ball. The substance was named "fullerene" after *Richard Buckminster Fuller* (1895–1983), the designer of mechanically coupled structures whose geodesic domes also had the appearance of a soccer ball. Some compounds between fullerenes and alkali metals seem to have superconducting properties. Chemically, they are quite stable. Breaking of the fullerene molecule requires temperatures of over 1000°C. The discovery was reported to *Nature* in September and published in November 1985. A new field for chemistry had opened up. Kroto, Smalley and Curl were awarded the Nobel Prize for chemistry in 1996 for their discovery of fullerene.

39.10
Synthetic Diamond

Synthetic diamond accounts for more than 90% of industrial diamonds used in the world. The world production of synthetic diamond was in 2001 about 600 million carats. USA accounted for 50%, Russia for 13%, South Africa and Ireland for 10% each, Japan for 5%, Belarus, Sweden and China for 3–4% each.

39.10.1
Synthesis of Diamond

High pressure and high temperature transforms graphite into diamond. The technical problems were solved in the 1950s as a result of work at ASEA in Sweden, General Electric in the United States and de Beers in Holland. Pioneering work was done

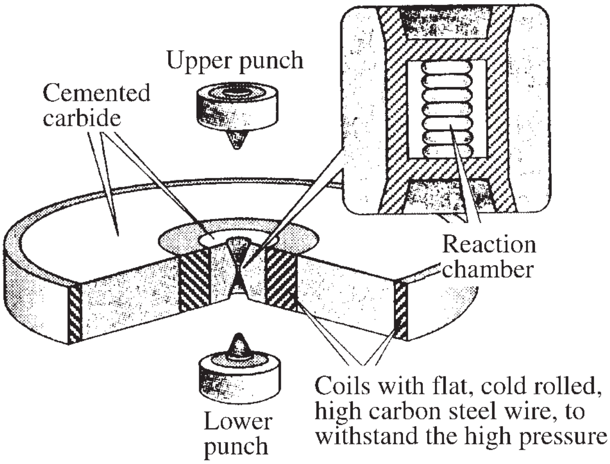

Figure 39.10 Principle of the equipment for diamond synthesis [39.7].

by the Swedish scientist *Baltzar von Platen* (1898–1984), who in this connection developed the hot isostatic high-pressure equipment that later became known as the Quintus Press (section 44.6.1). For the synthesis of diamond, carbon in the form of graphite is mixed with a metal, usually nickel or cobalt. At a temperature of 1600°C the metal melts and dissolves the graphite. When the pressure is increased to 6000 MPa (60 000 atm) the graphite is transformed to diamond (Figure 39.10 – see also Figure 39.2). When the metal is dissolved in acid, the diamond grains are set free.

For the manufacture of diamond tools, diamond powder is sintered in a high-temperature, high-pressure (HTHP) process to form polycrystalline diamond (PCD). As a rule this sintering is performed on a substrate of cemented carbide, which gives a cylindrical core of PCD surrounded by a ring of cemented carbide (Figure 39.11). Every grain of synthetic diamond is a single crystal, like natural diamond. In the whole tool all these crystals are randomly mixed, causing the same properties in all directions. Because of that a tool of synthetic diamond is said to be polycrystalline. In the use of industrial diamonds, the designations ND and SCD stand for natural diamond and single-crystalline diamond, and PCD for polycrystalline synthetic diamond.

As shown in Figure 39.12, diamond is the hardest of all materials, followed by cubic boron nitride (CBN), ceramics and cemented carbides (hard metals). For tools it

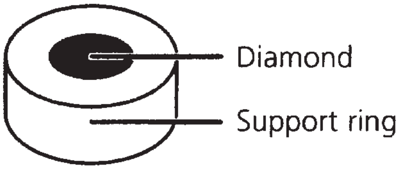

Figure 39.11 A core of synthetic diamond supported by a ring of cemented carbide.

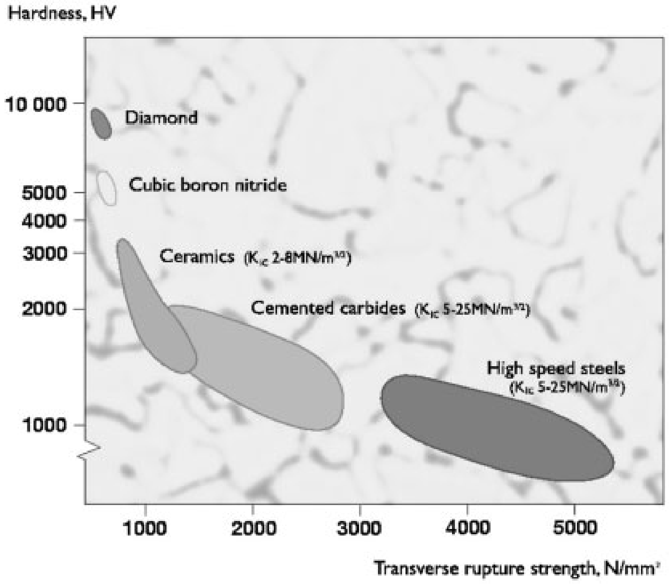

Figure 39.12 Hardness (Vickers hardness HV) of different industrial hard materials. The K_{IC} values express the toughness. High-speed steel (Chapter 26 Tungsten) is the most wear-resistant steel. (Reprinted from *Understanding Cemented Carbide* with permission from Sandvik Hard Materials, Sweden.)

is important not only that diamond is a hard and wear-resistant material but also that it has a high modulus of elasticity and good thermal conductivity. Diamond has the best thermal conductivity of all materials, i.e. much better than copper.

In fact diamond can also be formed at low pressure. With the Chemical Vapor Deposition technique (CVD) diamond can be forced to grow on a substrate surface. As a rule a gas mixture, containing a hydrocarbon and hydrogen, is thermally activated by a combustion flame or plasma technique. Atomic hydrogen and carbon containing radicals are formed, a gas from which diamond starts to grow at a low pressure. In ref. [39.8] a nanocrystalline diamond coating of this type is described. Deposition temperature was 900°C.

39.10.2
Uses of Synthetic Diamond

Synthetic diamond is nowadays very much used in tools for:

– grinding and polishing;
– diamond wheels for cutting purposes;
– plastic deformation processes such as wire drawing;
– machining, such as turning of highly wearing materials like ceramics, graphite, cemented carbide, plastics reinforced with glass fiber, rubber and wood.

Machining of steel with diamond tools must be avoided for the reasons mentioned above.

39.11
The Carbon Cycle

Carbon is a component of all organic substances, plants and animals. Dead sea creatures sink to deeper layers and decompose. Carbonate and hydrogencarbonate (CO_3^{2-} and HCO_3^-) ions are formed and are brought up to the surface by ocean currents. There they react with metal ions and form carbonate sediments. The carbon dioxide in the air compensates for the carbon losses as it is in equilibrium with carbon dioxide dissolved in the seawater and thus with its content of carbonate and hydrogencarbonate ions.

Carbon dioxide in the air is used for photosynthesis by vegetation on land and in surface waters. At the same time oxygen is produced. When terrestrial vegetation dies, a bacterial degradation process occurs. Part of the dead plants is however "saved" as organic humus and this constitutes the carbon reservoir of the earth's crust. During past geological periods the "saved capital" has grown large and constitutes nowadays deposits of peat, coal, oil and natural gas. The greatest part of the carbon dioxide from the degradation process is however brought back to the atmosphere. The situation is the same for large grass and forest fires. As a consequence of these "natural" processes, an equilibrium content of carbon dioxide in the atmosphere is established.

However, the equilibrium has been changed by large-scale burning of fossil fuels in modern society. Power production and automobile exhausts generate huge amounts of carbon dioxide, which are delivered to the atmosphere. A considerable disturbance to the global environment occurs.

39.12
The Greenhouse Effect

39.12.1
General

If the earth reradiated back to the atmosphere just as much energy as it obtained from the sun, its surface temperature would be 255 K (–18°C). This value can be calculated with Planck's radiation law. The fact that the average temperature is not –18°C but perhaps +15°C is due to the *greenhouse effect*. It seems to be a beneficial effect for human beings!

The atmosphere of the earth transmits the sun's radiation, which warms up the earth. The heat radiation, in the infrared, that is reflected by the earth's surface is partly absorbed by the atmosphere. The so-called *greenhouse gases* absorb radiation in the wavelength ranges 5–8 μm (water vapor) and 13–20 μm (carbon dioxide). These normal greenhouse gases have a window of transmittance for heat radiation with a wavelength of about 10 µm. Freons in the atmosphere shut that window. They absorb at 9–10 µm and aggravate the greenhouse effect (in addition to their adverse effect on the ozone layer; see Chapter 47 Oxygen). Aggravate? Is it not a positive benefit that the greenhouse effect changes the earth from a mean temperature of –18°C to a comfortable mean temperature of +15°C?

39.12.2
Let Us Be Speculative ...

The greenhouse effect is obviously demonstrated by our neighboring planets. Venus has an atmosphere of almost pure CO_2. In addition it is covered by white clouds. Its surface temperature is about 430°C. Thus liquid water cannot be present on its surface. If present in earlier periods, also then with high contents of carbon dioxide, the radiation would have increased the surface temperature to levels at which water has vaporized. Water vapor also is an effective greenhouse gas, so the temperature increased by the combined action of water and carbon dioxide. Venus is thus a nightmare scenario of the danger with the greenhouse effect.

The planet Mars has a thin atmosphere, a low greenhouse effect and a low surface temperature, –53°C. In the case of Mars there is almost an equilibrium between radiation in and out.

The earth is different. Since the very first appearance of life, 3–4 billion years ago, the intensity of the sun has increased by about 30%. Why has the surface temperature not increased more than it really has in spite of that? This is thought to be due to the fact that photosynthesis has been developed and lowered the carbon dioxide content of the atmosphere. The influence of the greenhouse effect has decreased and allowed increased radiation out. This has preserved the temperature.

The idea that life itself is capable of adjusting the conditions in favor of its further existence is expressed in the *Gaia hypothesis* [39.9]. Its originator, *James Lovelock*, has also calculated that, without life on earth, the atmosphere would consist of 98% CO_2 and 0% O_2. Our planet would have a surface temperature of 300°C. But then of course there would be no human beings present to talk or write about “our” planet.

39.12.3
... and Realistic

The increased burning of coal and oil in industry and houses, the increased burning of gasoline and diesel oil for automobiles, buses and airplanes, as well as other activities in modern society, have all increased the carbon dioxide content of the atmosphere. An increased temperature also is confirmed. In addition, computer simulations have shown that a doubling of the CO_2 content should result in an increase of the global temperature by 2–4°C.

If the other greenhouse gases are taken into consideration, a considerable effect on the climate could be expected: increased precipitation (rainfall and snow), more hurricanes, as well as increased melting of the polar ice-caps, leading to higher sea levels.

However, it is not unequivocally accepted that the greenhouse gases resulting from human activities are the sole cause of the warming of the earth. Another view has emerged – that the temperature changes are connected with changes in the output of radiation from the sun. These changes could be responsible for a considerable part of the actual warming. This is exemplified by the high solar activity in the 11th and 12th centuries, when the earth was so warm that the Vikings inhabited Greenland. On the other hand, in the late 17th century, solar activity was low and led to the period in history known as the *Little Ice Age*.

D. V. Hoyt and K. H. Schatten have treated the role of the sun in climate change in ref. [39.10].

39.13
Dating With the Carbon-14 Method

The element carbon has four isotopes, according to Table 39.5.

Table 39.5 The isotopes of carbon

Isotope:	^{11}C	^{12}C	^{13}C	^{14}C
Half-life:	20.3 min	Stable	Stable	5730 years

Carbon in the atmosphere consists of 99% carbon-12 (^{12}C) and 1% carbon-13 (^{13}C). In the upper levels of the atmosphere, radioactive carbon-14 (^{14}C) is produced by the influence of cosmic rays on nitrogen. The carbon formed is immediately oxidized to "special" ^{14}C-containing carbon dioxide, $^{14}CO_2$. This will mix with ordinary carbon dioxide in the whole atmosphere. The content of ^{14}C in relation to total carbon is very low, about 10^{-12}. Together with the ordinary molecules, these special carbon dioxide molecules are taken up by green plants in the course of photosynthesis. When the plants generate their carbohydrates via photosynthesis, this ^{14}C is incorporated in the cells. Because ^{14}C is radioactive, it decays (^{14}C is transformed to ^{14}N by β-radiation). But the level of ^{14}C in the tissue of the green plants, or the animals that feed on them, stays constant as long as they are alive, because of compensation by the addition of ^{14}C from the atmosphere. However, when the organism dies, the radioactivity of the ^{14}C decreases due to the radioactive decay at a well-established rate.

Willard Frank Libby (1908–1980) was a professor at the University of California from 1959 and responsible for its Geophysical Institution from 1962 to 1976. He saw the possibility in the ^{14}C decay and developed a workable technique for age determination, a method that has great utility for dating of, above all, archeological finds. For this he got the Nobel Prize for chemistry in 1960.

The method works in the following way. The intensity of the β-radiation from a sample (the total carbon content of which is known) is determined. The sample material may be wood, charcoal, bone, or shell. The content of ^{14}C is calculated from this β-activity, and thus the time that has passed since the death of the plant from which the object was produced may be worked out. As a control, the method has been used – with good results – on specimens up to 5000 years old that could be dated by conventional archeological techniques. The method presupposes that the content of ^{14}C has been constant in the atmosphere. This is not the case – and the fluctuations in the past are not known. Consequently the results obtained have some uncertainty. In specimens older than 70 000 years the content of ^{14}C is so low that the method cannot be used.

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40
Silicon

40.1 Si
Facts about Silicon

40.1.1 Si
The Element

Symbol:	Si
Atomic number:	14
Atomic weight:	28.09
Ground state electron configuration:	$[Ne]3s^2 3p^2$
Crystal structure:	Cubic with $a = 5.43$ Å; diamond structure

40.1.2 Si
Discovery and Occurrence

Discovery: Quartz and silicates are known from time immemorial. J. J. Berzelius discovered the element silicon in 1824. He named the element after the Latin name *silex* for flint stone.

Most important mineral: Quartz, SiO_2 (Figure M52)
Many silicates, which build up the mantle and crust of the earth (Figures M54–M67)

Ranking in order of abundance in earth crust:	2
Mean content in earth crust:	$28.2 \cdot 10^4$ ppm (g/tonne) (= 28.2 %)
Mean content in oceans:	2.2 ppm (g/tonne). (Pacific surface 0.03, at depth 4)
Residence time in oceans:	6300 years
Mean content in an adult human body:	260 ppm
Content in a man's body (weight 70 kg):	18 g

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40.1.3 Si
Chemical Characterization

Silicon is an element with dark gray color with a bluish tinge. It is not attacked by sulfuric, hydrochloric or nitric acids, but it dissolves in hydrofluoric acid, forming the gas, silicon tetrafluoride, SiF_4. It also dissolves in sodium hydroxide, forming sodium silicate and hydrogen gas. The chemistry of silicon is characterized by the fact that it is favorable from an energy point of view for the silicon atom to form single bonds with four oxygen atoms. As each oxygen atom simultaneously must bond to two silicon atoms, the network –O–Si–O–Si– results, as is thoroughly discussed below in the section about silicates. High-purity silicon is required for the manufacture of transistors and other semiconductor devices. Silicon is a major element in modern electronics.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Si^{IV} as in SiO_2, tetrahedron	$Si(g) \rightarrow Si^+(g) + e^-$	787	$Si(g) + e^- \rightarrow Si^-(g)$
$[SiO_4]^{4-}$, Mg_2SiO_4, SiF_4,	$Si^+(g) \rightarrow Si^{2+}(g) + e^-$	1577	–133.6
and SiH_4	$Si^{2+}(g) \rightarrow Si^{3+}(g) + e^-$	3231	
Si^{II} as in SiF_2	$Si^{3+}(g) \rightarrow Si^{4+}(g) + e^-$	4356	

Standard reduction potential: $SiO_2(s) + 4H^+(aq) + 4e^- \rightarrow Si(s) + 2H_2O(l)$ [acid solution]
$E^0 = -0.909$ V
$SiO_3^{2-}(aq) + 3H_2O(l) + 4e^- \rightarrow Si(s) + 6OH^-(aq)$ [alkaline solution]
$E^0 = -1.69$ V

Electronegativity (Pauling): 1.90

Radii of atoms and ions:
(WebElements™)

Atomic:	110 pm
Covalent:	111 pm
Van der Waals:	210 pm
Si^{4+} (4-coordinate, tetrahedral):	40 pm
Si^{4+} (6-coordinate, octahedral):	54 pm

40.1.4 Si

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
2329 kg m^{-3} 2.33 g cm^{-3}	12.06 cm^3	1687 K 1414 °C	(2628 K) (2355 °C)	712 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
330	168	108	65	32

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$-0.4 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	$3.5 \cdot 10^{-6}$	$4.1 \cdot 10^{-6}$

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
–	10^6 10^{12} (if free from impurities)	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-1.8 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
47 GPa	–	100 GPa	–

40.1.5 Si

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	50.2 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	359 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	456 $kJmol^{-1}$
Entropy S^0 at 298 K	18.83 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	7.28	20.00	24.47	26.57	27.20	27.20

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Si + O_2 \rightarrow SiO_2$	−857	−816	−724	−644	−544

40.1.6 Si

Nuclear Properties and X-ray

Isotope range, natural and artificial 22–36

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{28}Si	Stable	92.23	0+	–
^{29}Si	Stable	4.67	1/2+	−0.5553
^{30}Si	Stable	3.10	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{29}Si
Reference compound	$Si(CH_3)_4$
Frequency MHz (^1H = 100 MHz)	19.867
Receptivity D^P relative to ^1H = 1.00	$3.67 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	2.10
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-5.319 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
13	Al	1.486
14	Si	1.739
15	P	2.013

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	64.0
17.37 keV (MoKα_2)	6.73

Neutron absorption	**Thermal neutron capture cross section**	0.167 barns

40.2
A Question From Antiquity Is Answered

Glazed ceramics, dating from about 7000 BC, have been found in archeological excavations in Egypt and Mesopotamia. The technique is thought to have utilized the reaction between sand, lime and alkalis to form a molten glaze to cover the ceramic material. Special glass-making, with no connection to pottery, was developed far later, about 2000 BC. The first craftsmen had certainly posed the question: Which is the *basic element* in glazing, in glass and in quartz? And the alchemists questioned: What is the *principle* of glass?

Rock crystal, pure quartz (Figure M52), was well known to the ancient Egyptians. They manufactured pearls and vases, and could manage, clever craftsmen that they were, to handle the hard and brittle mineral. They even used it for the adornment of palaces and graves as well as for preparing eyes in some statues, to which was attached such great importance in their cult. They learned to make glass by fusing quartz and alkali (soda or potash) together. For this they utilized crucibles of pottery. A very old glass object is kept in the British Museum and has the designation *Tutmosis* (Thotmes III). It has been dated to 1500 BC. The great breakthrough in glass manufacture came about 100 BC, when the blowpipe was introduced. After that, even vessels with thin walls could be made. Plane glass sheets were manufactured by first blowing a cylinder, which was cut up and planed out.

During the centuries of antiquity and the Middle Ages, the technology of glass-making was developed to a high level, regarding both craftsmanship and artistry.

> The question about the central substance in glass and quartz remained unanswered however. And nor did the 18th century, with its great development within chemistry, see the solution of the problem. Torbern Bergman in Uppsala designated quartz as an earth, thus as an oxide, very difficult to reduce. In the early 19th century Humphry Davy attacked the problem. He was convinced that quartz was not an element. Was it instead the oxide of an unknown metal? He utilized powerful methods in order to reveal the content of the white siliceous stone. He dissolved silicic acid in alkali and electrolyzed it with the voltaic pile. He let potassium vapor pass over quartz at high temperature. No substance with metallic *temperament* appeared. J.-L. Guy-Lussac and L. J. Thénard in Paris tried another way. They made silicon tetrafluoride

> SiF_4 by letting gaseous hydrofluoric acid HF pass over quartz. The tetrafluoride formed was allowed to pass over hot potassium metal. In a violent reaction a reddish-brown powder was formed. Perhaps an impure elementary silicon.
>
> J. J. Berzelius began a systematic study in his laboratory in Stockholm. He mixed quartz, iron, carbon and charcoal, and heated the mixture up to a very high temperature. A compound between iron and silicon, an iron silicide, was formed. This he treated with hydrochloric acid and measured the amount of hydrogen evolved. He observed that more gas was formed than what corresponded to the iron content of the sample. The "metal" of the quartz had been present in the beaker!
>
> Berzelius himself told that from this moment it was simple to complete the discovery. He made SiF_4 by reaction between quartz and hydrofluoric gas. When the silicon fluoride reacted with potash, a double fluoride, potassium hexafluorosilicate K_2SiF_6, was formed. In a glass tube he mixed this compound with pieces of potassium metal. On heating, a feeble detonation indicated that the silicon had been reduced and had formed potassium silicide in the test tube. Water attacked potassium but left silicon undissolved. This element was not combustible in oxygen, while chlorine attacked it readily. Berzelius reported that, according to his experiments, silica contains 52% oxygen. (A very good value, as we today know that the oxygen content of SiO_2 is 53%.) This final discovery was made in 1824.
>
> In 1854 *Henri Étienne Sainte-Claire Deville* prepared silicon by electrolysis in connection with his pioneer work with aluminum. He used a fused electrolyte of impure sodium aluminum chloride. The aluminum metal, obtained at the cathode, contained 10% silicon. When dissolved in acid, bright silicon laminae stayed undissolved. It is interesting to note that Deville expressed the opinion that the element silicon is not a real metal.

Today silicon is classified as a nonmetal but sometimes also as a semi-metal because it displays properties similar to those of both metals and nonmetals. Elementary silicon is produced industrially in large-scale by reduction of quartz with coke. The product is commonly and inappropriately called *metallic* silicon (see Figure M53).

40.3
Silicates – The Basic Building Blocks of Rocks[1]

40.3.1
In the Middle of the Periodic Table

In the outermost shell of an atom, *eight* electrons (or for the lightest elements *two*) constitute a stable grouping. An atom that, like sodium (2+8+1), has *one* electron in the shell farthest out easily gives off this one electron and forms a monovalent ion, like Na^+. If an atom has *seven* electrons in the outermost shell, such as for instance

---

[1] Facts for this section have been collected from refs [40.1], [40.2], [40.3] and [40.4].

chlorine (2+8+7), this number is readily completed to eight and a stable chloride ion Cl^- is formed. Carbon (2+4) and silicon (2+8+4) are situated in the middle of the periodic table. Since both of them have four valence electrons, they might formally be expected to form tetravalent positive or negative ions. Such ion formation is however not probable. Instead, *covalent* bonding occurs, in which other atoms like hydrogen or oxygen or neighboring atoms of the same element take part. The carbon atom is thus the main atom for organic chemistry. The number of possible compounds is nearly unlimited, all the way from methane CH_4 to organic molecules of vast complexity. In straight and branched hydrocarbon chains, the coordination number is four throughout. As a covalent bond consists of two electrons, a stable situation with an eight-electron group is attained in that way. Silicate chemistry has similar features. The special electron configurations for the two elements have made them to bridge-builders in one great chemistry section each: organic chemistry and silicate chemistry.

40.3.2
A Simple and Elegant Architecture

More than 90% of the earth's crust consists of silicate minerals. Feldspars constitute 60%, amphiboles, pyroxenes and olivines together 17%, and quartz 12%. Of all the known minerals, more than one-third are silicates. The principles for the building of silicates were unknown until X-ray diffraction made structural determination possible. *Max von Laue* (1879–1960) in Germany discovered that a crystal could be used as a grating for the deflection of X-rays. This rendered him the Nobel Prize for physics in 1914. *William Bragg* (1862–1942) was a British physicist. After service in professorial positions in Adelaide (Australia), Leeds and London, he became manager for the Royal Institution in 1923. He developed a diffractometer for X-ray examination of crystals. His son *Lawrence Bragg* (1890–1971) was also manager for the Royal Institution during the period 1954–1965. They used X-ray diffractometry for the study of silicates. It is said that the work done in this field by the Braggs, father and son , "transformed a chemical puzzle to a system of simple and beautiful architecture". This architecture will be treated in this chapter. For the methodology with crystal investigations, father and son together received the Nobel Prize for physics in 1915.

The percentage of oxygen in the earth's crust is 92% by volume. Oxygen ions have a considerably greater size than ions of other common elements, as is illustrated in Table 40.1 and Figure 40.1.

Table 40.1 Ionic radii of elements in the earth's crust coordination number CN is 4. For Ca CN is 6.

Element	O	Si	Al	Fe	Mg	Ca	Na
Ionic radius Å	1.24	0.40	0.53	0.77	0.71	1.14	1.13

Several silicates can thus be seen as arrangements of close-packed oxygen atoms with other, more electropositive, atoms of smaller size in holes as interstitials. These

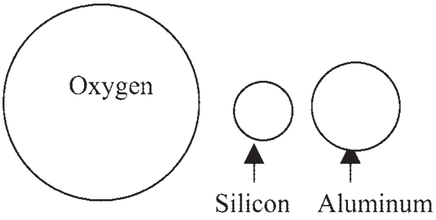

Figure 40.1 Relative ion sizes.

small atoms may be silicon, aluminum, magnesium, iron, manganese, calcium, sodium and so on. The ratio $r_{Si}/r_O = 0.40/1.24 = 0.32$. A ratio between 0.225 and 0.414 favors a tetrahedral coordination [40.5]. Thus every silicon atom surrounds itself with four oxygen atoms. Figure 40.2 shows the tetrahedral coordination of an SiO_4 group.

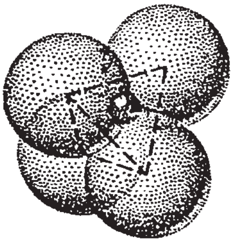

Figure 40.2 The tetrahedral coordination in an SiO_4 group. A small Si atom lies at the center of the tetrahedron, with four big oxygen atoms at the corners.

The SiO_4 group is, unlike CH_4, not electrically neutral but is 4-valent negative. Combination with metal ions is necessary for electroneutrality. Then ionic crystals are formed, of which the silicate minerals are built up. The binding cation is often Ca^{2+}, Mg^{2+}, or Fe^{2+}, but can also be a complex aluminum ion with oxygen or fluorine that is 4-valent positive: $(Al_2O)^{4+}$ or $(Al_2F_2)^{4+}$. Aluminum may also substitute for silicon in some silicate ions. SiO_4^{4-} is then changed to AlO_4^{5-}. To compensate for this, an additional cationic charge is needed.

If the oxygen supply is sufficient to add four oxygen atoms to every silicon, *nesosilicates* of the type $ZrSiO_4$ are formed. If not – if there is a deficiency of oxygen – linkage of tetrahedra by the sharing of common oxygen atoms in chains, rings, strips, sheets, etc., occurs. Then *sorosilicates*, *inosilicates*, *phyllosilicates* and *tectosilicates* are formed according to Table 40.2.

Table 40.2 Classification of silicate types depending on the supply of oxygen

Number of atoms per formula unit		O/Si	Structure model	Silicate Designation	Greek background to the designation
Oxygen	Silicon				
4	1	4	Isolated SiO_4 tetrahedra	Nesosilicate	*Nesos*, island
7	2	3.5	Linkage of two SiO_4 tetrahedra by the sharing of one oxygen	Sorosilicate	*Soros*, group or *Soror*, sister.
9	3	3	Linkage of the SiO_4 tetrahedra in rings	Cyclosilicate	*Kyklos*, ring or circle
12	4	3			
18	6	3			
3	1	3	hedra into linear chains, Linkage of the SiO_4 tetra- double chains or bands	Inosilicate	*Inos*, fiber
5	2	2.5	Sharing of three of the four oxygen atoms in each tetrahedron with neighboring tetrahedra, to form flat sheets	Phyllosilicate	*Phyllos*, sheet
2	1	2	Sharing of all four oxygen atoms of the SiO_4 tetrahedra with neighboring tetrahedra	Tectosilicate	*Tektos*, framework
6	3	2			

40.3.3
Nesosilicates

The basic principle for the structural chemistry of silicates is, as mentioned, that every silicon atom is surrounded by four oxygen atoms. If the supply of oxygen atoms is sufficient, so that the O/Si ratio is 4, isolated SiO_4 tetrahedra are formed, according to Figure 40.3[2]. The designation in this case should be "nesosilicate" and not "orthosilicate", used earlier. The latter gives no information about the structure.

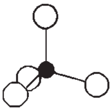

Figure 40.3 A nesosilicate ion; O/Si=4.

Mineral examples of nesosilicates are given in Table 40.3.

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[2] In this and the following figures, the silicon atoms are drawn as black circles, and the oxygen atoms as slightly larger white circles. The symbols do not represent the relative atomic sizes correctly, but the bonding directions are correct.

Table 40.3 Examples of nesosilicate minerals

Mineral	Formula	Shape and type	Appearance
Zircon (hyacinth)	$ZrSiO_4$ (Figure M30)	Tetragonal prisms. Accessory mineral in igneous rocks, crystalline limestones, schists, and gneisses	Various colors. The colorless varieties provide exceptionally brilliant gemstones
Olivine	$(Mg,Fe)_2SiO_4$ (Figure M55)	An orthorhombic mineral. It consists of the isomorphous solid-solution series *forsterite* Mg_2SiO_4 to *fayalite* Fe_2SiO_4	Rounded grains with an olive-green, grayish-green, or brown color. Transparent olivine is an appreciated gemstone
Garnet[a)] – almandine – andradite – uvarovite	 $Fe_3Al_2(SiO_4)_3$ $Ca_3Fe_2(SiO_4)_3$ $Ca_3Cr_2(SiO_4)_3$	Crystallizes in the cubic system, sometimes with so many plane surfaces that the garnets seem to be round	Garnet is a brittle mineral, having a variety of colors, dark red being the most common. Ca-rich garnets are sometimes green. Transparent garnet is used as a precious stone
Kyanite[b)] (disthene)	Al_2OSiO_4	A triclinic mineral that occurs in long, thin, bladed crystals	The color is blue or light-green
Andalusite [b)c)] brown,	Al_2OSiO_4	Orthorhombic mineral; occurs in thick, nearly square prisms in schists and gneisses	The color varies between yellow, green, red, or gray
Topaz	$Al_2F_2SiO_4$ (Figure M54)	An orthorhombic mineral that occurs as prismatic crystals and as rounded water-worn pebbles	The color is white or lightly colored. A transparent topaz is used as a gemstone

a) Garnet is a group of minerals of formula $A_3B_2(SiO_4)_3$, where A = Ca, Mg, Fe^{2+}, Mn^{2+}, and B = Al, Fe^{3+}, Mn^{3+}, V^{3+}, Cr. In Chapter 17 Rare Earth Metals we met the neodymium-doped yttrium–aluminum garnet as the important YAG laser material, $Y_3Al_5O_{12}$. It is a garnet besides the general garnet definition.

b) In Al_2OSiO_4 the O/Si ratio is 5, but only four oxygen atoms are coordinated by silicon. The commonly used way of writing the formula as Al_2SiO_5 hides the fact that the minerals are nesosilicates.

c) During World War II andalusite was used – because of the lack of bauxite – as a source for aluminum.

40.3.4
Sorosilicates

If the actual mineral does not have a sufficient supply of oxygen atoms (thus if O/Si<4), the mineral "economizes" on oxygen by letting two silicon atoms share one oxygen atom. In this way the tetrahedral coordination can be retained. The simplest case arises if O/Si=3.5. Two hypothetical nesosilicate ions, which cannot be formed due to lack of oxygen, combine to a double tetrahedron, a sorosilicate ion (see Figure 40.4).

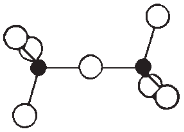

Figure 40.4 A sorosilicate ion. The silicon atom to the left "owns" alone the three oxygen atoms to the left and has a half share in the middle oxygen atom. This implies that every silicon atom binds on average to 3.5 oxygen atoms; O/Si=3.5.

As mineral examples, hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, thortveitite $Sc_2Si_2O_7$ (Figure M56), described in Chapter 17, and epidote (Figure M57) may be mentioned.

40.3.5
Cyclosilicates

For still more limited oxygen supply, expressed by O/Si=3, rings are formed with the general formula $[(SiO_3)^{2-}]_n$, according to Figure 40.5.

An example of a cyclosilicate is *beryl* $Be_3Al_2Si_6O_{18}$ (Figure M58). It usually occurs in green, bluish-green, yellow or pink hexagonal prisms. Transparent and colored gem varieties include emerald, aquamarine, heliodor and golden beryl. In the *tourmaline*

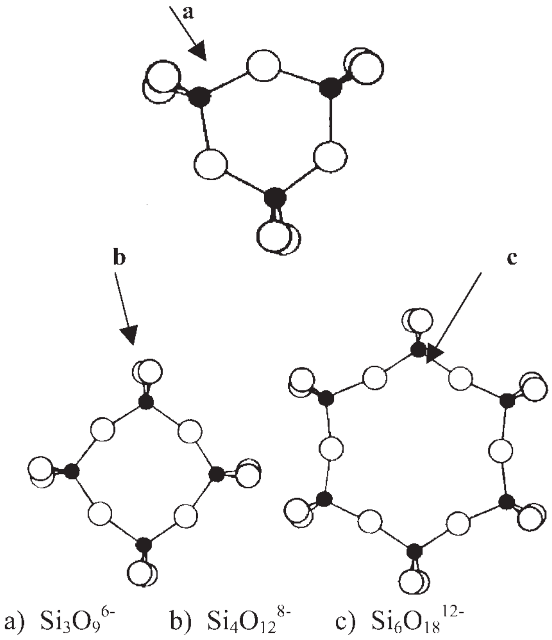

Figure 40.5 Cyclosilicates, silicate ions in ring form. One single silicon atom "owns" alone two oxygen atoms and has a half share in two others. Thus every silicon atom coordinates on average 2+2·0.5=3 oxygen atoms; O/Si=3.

group of minerals, also cyclosilicates, the anionic group $(BO_3)Si_6O_{18}$ is coupled to varying cations, such as Na, Li, Ca, Mg, Fe, Mn, Al, and minor amounts of others, resulting in varying colors of species with special names (Figure M59).

Earlier, all silicates with anions of the type SiO_3^{2-} were called "metasilicates". This designation ought to be avoided, as it does not give any information about the structure.

40.3.6
Inosilicates – Chain and Band Structures

40.3.6.1 Inosilicates as Chains

Some silicates are characterized by the linkage of the SiO_4-tetrahedra into linear chains by sharing of oxygen atoms (see Figure 40.6). The formula is $(SiO_3^{2-})_n$ as in the cyclosilicate case. *Spodumen* $LiAlSi_2O_6$ and *jadeite* $NaAlSi_2O_6$ belong to the inosilicates with chains. The *pyroxenes*, a group of dark rock-forming silicate minerals, also have chain structure.

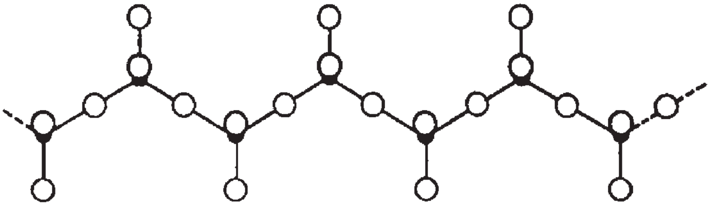

Figure 40.6 Inosilicate with chain structure. An arbitrary silicon atom "owns" alone two oxygen atoms and has a half share in two others; O/Si=3.

These minerals have the general formula $ABSi_2O_6$, where A = Ca, Na, Mg, Fe^{2+}, and B = Mg, Fe^{2+}, Fe^{3+}, Cr, Mn, Al, with silicon sometimes replaced in part by aluminum. Pyroxenes may crystallize in the orthorhombic or monoclinic systems and occur as short, stout prismatic crystals. Specific mineral examples from the pyroxene group are *augite* $(Mg,Fe,Ca)SiO_3$ and *hedenbergite* $CaFe(SiO_3)_2$ (Figure M60).

40.3.6.2 Inosilicates as Bands

If the chains are combined to double chains by further sharing of oxygen atoms (Figure 40.7), the formula becomes $(Si_4O_{11})^{6-}$ with the O/Si ratio becoming 2.75.

The minerals in the *amphibole group* are of this type. Different substitutions may make the formulas very complicated and sometimes formally deviating from O/Si=2.75. Specific mineral examples are *hornblende* $NaCa_2(Mg,Fe)_4Al_3Si_6O_{22} \cdot (OH)_2$ (Figure M61) and *actinolite* (asbestos of amphibole type) $Ca_2(Mg,Fe)_5(OH \cdot Si_4O_{11})_2$ (Figure M62).

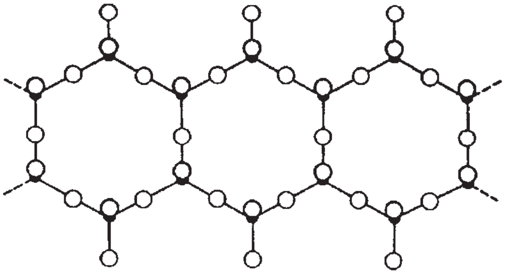

Figure 40.7 Inosilicate with band structure. Every second silicon atom "owns" alone two and has a half share in two other oxygen atoms, thus in total 3. On the other hand, the remaining silicon atoms (also every second) "owns" alone one but has a half share in three, thus in total 2.5. The average for every silicon atom will be 2.75 oxygen atoms; O/Si=2.75.

40.3.7
Phyllosilicates – Flat Sheets With Infinite Extent

If the oxygen supply is even more restricted so that the O/Si ratio becomes less than 2.75, a more extensive coordination of SiO_4 tetrahedra has to occur. If band is laid to band in one plane, a layer ion with "infinite" extent is formed (Figure 40.8). The gross formula will be $(Si_2O_5^{2-})_n$. Layers of this type are present in mica and clay minerals. Hydroxides of different types, according to Table 40.4, also crystallize as layers and combine with the silicate ion $(Si_2O_5)^{2-}$ to double and triple layers in many minerals.

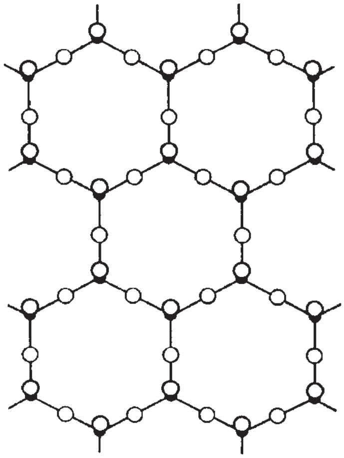

Figure 40.8 Silicate ion $(Si_2O_5^{2-})_n$ with extension in one plane; O/Si=2.5.

Table 40.4 Hydroxide layers that combine with phyllosilicate layers in mica and clay minerals

Layer type	Formula
A	$Al(OH)_3$
B	$Mg(OH)_2$
C	$Mg_2Al(OH)_6^+$

Possible layer combinations are shown in Figure 40.9 and described in Table 40.5, which also gives some mineral examples.

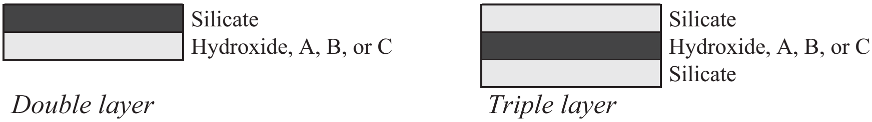

Figure 40.9 Schematic of layer combinations.

Table 40.5 Examples of phyllosilicate minerals

Mineral	Formula	Layer combinations	Appearance
Kaolinite	$Al_2(OH)_4Si_2O_5$ (Figure M64)	Type A + silicate layer on one side	White to yellow. The principal component of porcelain clay
Serpentine	$Mg_3(OH)_4Si_2O_5$	Type B + silicate layer on one side[a)]	Serpentines are commonly greenish yellow and have a greasy or silky luster and a slightly soapy feel
Talc	$Mg_3(OH)_2(Si_2O_5)_2$	Type B + silicate on both sides	Very soft, light green or yellow mineral with a soapy or greasy feel. Can be cut with a knife
Pyrophyllite	$Al_2(OH)_2(Si_2O_5)_2$	Type A + silicate on both sides[b)]	The mineral occurs foliated or in compact masses The color is gray to brown
Muscovite (white mica)	$KAl_2(OH)_2 \cdot (AlSi_3O_{10})$ (Figure M63)	Type A + silicate on both sides. A substituted pyrophyllite[c)]	A colorless to yellowish mineral. Can easily be split to thin, transparent sheets
Biotite (black mica)	$K(Mg,Fe)_3(OH)_2 \cdot (AlSi_3O_{10})$	Type B + silicate on both sides. Substituted talc[d)]	A black, brown, or dark green, foliated mineral, more common than muscovite[e)]
Chlorite (a mineral group)	$(Mg,Fe)_5Al(OH)_8 \cdot (AlSi_3)O_{10}$ (formula for clinochlore)	Type C + silicate on both sides. The hydroxide has reacted with talc[f)]	The blackish green minerals within this group cleave into thin flakes like those of mica but not so elastic
Montmorillonite (a clay mineral)	Hydrated (Al,Mg,Na,Ca) silicate	A special A-type between two silicate layers[g)]	Very fine-grained mineral, white, gray, or brown[h)]
Vermiculite	$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot nH_2O$ (Figure M65)	Closely related to montmorillonite	Yellow to brown mineral[i)]

[a)] A fibrous, silky, greenish serpentine is called chrysotile. It is an important type of asbestos, serpentine asbestos. This is not to be confused with actinolite asbestos (an inosilicate).

[b)] The mineral is used as a filler in paper and rubber as well as a lubricant and for isolator purposes within electrical technology.

▶

40.3.8
Tectosilicates – A Three-Dimensional Network

Tectosilicates are characterized by a complete three-dimensional network, in which all four oxygen atoms of the SiO_4-tetrahedra are linked to neighboring tetrahedra.

The mineral quartz SiO_2 (Figure M52) belongs to this group. Quartz is one of the most common minerals in the earth's crust. The white, opaque quartzite, consisting chiefly of quartz grains, is widely spread. Quartz is also the commonest gangue mineral, forming the major proportion of most sands. It has a widespread distribution in granite and gneiss. Colorless, transparent quartz, rock crystal, is a valued gemstone. Also esteemed are transparent colored quartz grades, smoky quartz (brown), citrine (yellow) and amethyst (violet). Hydrated silica, $SiO_2 \cdot nH_2O$ is known as the gemstone opal.

Among the tectosilicates the O/Si ratio is 2. When Al partly replaces Si, the silicate anion becomes more complicated, such as for instance $[AlSi_3O_8]^-$. This ion complex is an essential part of the *feldspar minerals*, the most widespread of any mineral group. They constitute 60% of the earth's crust. Feldspars have no color of their own and are often nearly white. They may however be colored due to impurities. On decomposition, feldspars yield kaolinite and clay minerals.

Plagioclase is a group of feldspars forming a complete series from albite $NaAlSi_3O_8$ (Ab) to anorthite $CaAl_2Si_2O_8$ (An). Members of the series are, with increasing anorthite content (% An, in parentheses), *albite* (An 0–10), *oligoclase* (An 10–30), *andesine* (An 30–50), *labradorite* (An 50–70), *bytownite* (An 70–90) and *anorthite* (An 90–100).

Tectosilicate mineral examples are collected in Table 40.6.

▶ **c)** In the silicate layers Si^{4+} has partly been replaced by Al^{3+}. The electroneutrality has been restored by addition of K^+ into the hydroxide layer.

d) In the silicate layers Si^{4+} has partly been replaced by Al^{3+}. Building K^+ into the hydroxide layer has restored the electroneutrality. In addition Mg^{2+} has partly been replaced by Fe^{2+}.

e) When the black mica, biotite, weathers, its content of metals is partly leached out. The brownish-black color is changed, sometimes to yellow, shining like gold. "Cat gold" has been formed. This disparaging designation is also used for the beautiful yellow cubes of pyrite (Figure M74).

f) Chlorite is a transformation product of biotite. Mg^{2+} has partly been substituted by Fe^{2+} and Si^{4+} by Al^{3+}.

g) Deficiencies in charge are balanced by the presence of calcium and sodium.

h) Montmorillonite easily absorbs water between the layers and because of that it has a tendency to swell. This may cause landslip, and extensive reinforcement work may be necessary in tunnel building. The mineral is the chief constituent of bentonite, used as a binding agent in molds for metal casting. Another use is as a binder in pelletizing of iron ore and as a sealing material in the building industry. The use of bentonite for storage of highly radioactive nuclear fuel in rock shelters has also been discussed.

i) Water between the layers generates a steam pressure on heating to about 300°C. The mineral exfoliates and expands to wormlike particles. Hence the mineral name, taken from the Latin word *vermiculare*. Vermiculite is used in light concrete and as insulating material.

Table 40.6 Examples of tectosilicate minerals

Mineral	Formula	Crystal form and habit[a)]	Appearance
Quartz	SiO_2 (Figure M52)	Hexagonal/trigonal	Opaque, white. Colorless transparent, with different colors
Albite (sodium feldspar)	$NaAlSi_3O_8$	Triclinic. Plates and rods. A lamellar, leaf-like variety of albite is called *cleavelandite*	A colorless or milky-white mineral
Orthoclase[b)] (common feldspar)	$KAlSi_3O_8$ (Figure M66)	Monoclinic. Grains are tabular and have near-parallel orientation. Blunted prisms	A reddish, cream-yellow, or gray mineral. If green, it is called *amazonstone* or *amazonite*. If opalescent, it is called *moonstone*
Microcline (potassium feldspar)	$KAlSi_3O_8$ (Figure M67)	Triclinic. Oblique blunted crystals	White to gray, brick red. If green, it is called *amazonite* or *amazonstone*
Anorthite (calcium feldspar)	$CaAl_2Si_2O_8$	Triclinic. Parallelepipedic prisms	Grayish, greenish, or reddish white

a) Habit is a general term for the outward appearance of a mineral or rock.

b) The name of this feldspar mineral is taken from the Greek words *orthos* (right) and *klas* (to break), describing its two dominant cleavage planes at right angles. This is a diagnostic mark useful to distinguish orthoclase from plagioclase in general.

40.3.9
Solidification of Molten Rocks and Formation of the Earth

When a silicate melts, e.g. when a volcanic magma solidifies, or even during the original formation of the mantle and crust of the earth[3)], the various silicates crystallize in order of their melting points, the nesosilicates first. That may be olivine $(Mg,Fe)_2SiO_4$. When the chain-form pyroxenes (inosilicates) solidify, also in an early stage, magnesium and iron become components of the solid phase. This can explain the dark color of the rocks in the upper mantle and the lower parts of the crust. *Basalt* is an example. It is the most common of all volcanic rocks and constitutes the crust under the oceans. It is a gray- or even black-colored igneous[4)] rock, composed chiefly of pyroxene and plagioclase and with a high content of iron and magnesium.

Phyllosilicates and tectosilicates (e.g. quartz and feldspar) dominate the upper parts of the crust. We meet them there as for instance *granite*, a gray or red rock in light nuances, containing quartz and feldspar (with inclusions of dark mica).

Some rare elements in the silicate melt are *compatible* with the main elements in the solidified phase due to similarity regarding ion size and charge. In the crystals

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[3)] Compare section 4.4.2 in chapter 4.

[4)] “Igneous” is the designation for a rock or a mineral that has solidified from molten material. The other two classes are “metamorphic” and “sedimentary”.

they take the positions of the related atoms and follow the solidified phase. Because of that they are very much scattered in the crust, present with low contents. One example of this is gallium, which follows aluminum.

Other rare elements are *incompatible* with the main elements in the solidified silicate melt. Ion radius and charge differ too much. These elements will be enriched in the melt, remaining when the silicates gradually solidify. They will be found in the coarse-grained pegmatites, rich in rare earths and minerals containing such elements as lithium, niobium and tantalum.

40.4
Silicon – A Key Material in Modern Technology

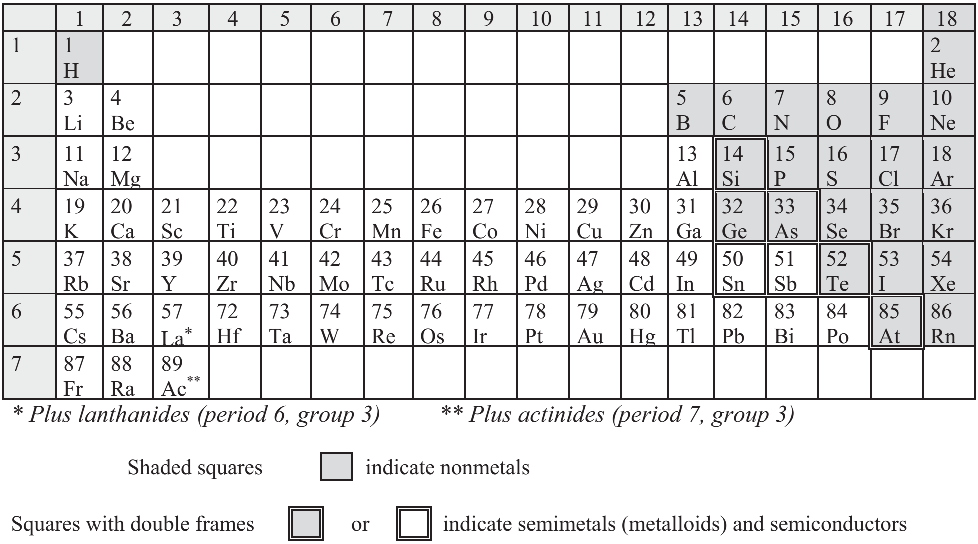
40.4.1
Our Need for Amplification

Many instruments in modern society produce and/or receive weak electrical signals. To be useful to us, their information has to be output through loudspeakers and on the screens of TV sets, computers and oscilloscopes. To make this possible, the weak incoming signals have to be *amplified* in such a way that the outgoing signal not only becomes stronger but also correctly reproduces the character of the incoming signal. In the earlier days of radio, electron tubes were used for amplification. A heated cathode emitted electrons, which migrated to the positively charged counter-electrode, the anode. In 1906 the triode was invented, a tube with a grid between cathode and anode. A small voltage change on the grid could be transformed to a big change in the electron current to the anode and a great voltage change over the resistance in series with the anode. The triode could thus amplify weak signals. Electron tubes were later developed into tetrodes, pentodes and so on.

But the amplifying tubes took up a lot of space. In the 1930s and 1940s radio sets were big, bulky boxes. Portable radio sets were unthinkable. Electron tubes were also used for the first computers. The early computers filled great rooms and yet their capabilities were insignificant compared to modern portable computers. A technological revolution came with a big change – a revolution linked to materials science and to two elements, first germanium and then silicon.

40.4.2
Metal or Nonmetal?

The elements are broadly divided into *metals* and *nonmetals*. The typical properties of a metal are strength, elasticity and ductility, as well as good conductivity of heat and electricity. Nonmetals, shaded in Figure 40.10, are hydrogen and the elements (gases and solids) to the right of the periodic table. The borderline between metals and nonmetals is however not sharp. Some elements, for instance tin, have both metallic and nonmetallic crystalline forms, and some elements are on the limit regarding con-



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac**															

** Plus lanthanides (period 6, group 3)* *** Plus actinides (period 7, group 3)*

Shaded squares ▨ indicate nonmetals

Squares with double frames ▨ or ☐ indicate semimetals (metalloids) and semiconductors

Figure 40.10 Metals, nonmetals and semi-metals in the periodic table.

ductivity. These are designated *metalloids* (meaning similar to metals) or *semi-metals*. They have been marked with double frames in the figure.

40.4.3
Conductors and Semiconductors – Another Principle of Division

According to the *band theory* for elements, the valence electrons are found in a *valence band*. If this is only partly filled with electrons, there are occupied and unoccupied levels (with small energy differences) within the valence band. A small electrical potential difference applied across the crystal excites electrons from the highest (regarding energy) filled levels to unfilled levels immediately above. The unfilled valence band is also a *conduction band*, according to Figure 40.11a. This explains the ability of metals to conduct electricity.

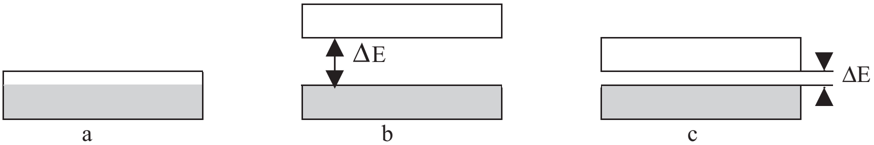


Figure 40.11 Conductors, isolators and semiconductors in the band theory. (a) The partly filled valence band serves as a conduction band. (b) In an isolator a large energy gap separates the valence band from the conduction band. (c) In a semiconductor the valence band is filled and the conduction band is empty. The energy gap between the two is small.

In an insulator (Figure 40.11b) the valence band is filled with electrons and a large energy gap, ΔE, separates the valence and conduction bands.

A semiconductor is characterized by the fact that transition across the gap between valence and conduction bands is possible after a small external energy contribution (Figure 40.11c). The greater this contribution is, in the form of thermal energy, the more electrons move to the conduction band. This is why the conductivity of semiconductors increases with temperature.

The insulator diamond has a band gap energy of 5.5 eV, while silicon has 1.1 meV and germanium 0.7 meV. Germanium loses its semiconductor characteristics at 100°C, compared to 200°C for silicon.

Besides the elements germanium and silicon, some compounds have semiconductor properties. Important ones are the phosphides, arsenides and antimonides of gallium and indium, thus GaP, GaAs, GaSb, InP, InAs and InSb. It is notable that elements in group 14 (Si, Ge) have semiconductor properties but also compounds of elements from both sides of group 14 (Ga group 13, P group 15, etc.). Semiconductors have become very important in technology. Much of modern electronics is dependent on semiconductor materials.

Some semiconductors have a fixed (and small) energy gap ΔE between valence and conduction bands. These are called intrinsic *semiconductors*. In others it is possible to influence the energy gap between the bands. In these types, the *extrinsic semiconductors*, impurities are added by *doping*. If silicon is doped with phosphorus, the P atom is called a *donor atom*. It uses four of its five valence electrons to bind silicon, and the fifth electron can easily move to the conduction band. Such silicon is thus called an *n-type semiconductor* ("n" for negative). On the other hand, If silicon is doped with boron (with three valence electrons), the B atoms may accept electrons from the valence band itself and positive holes are created. The doping agent in this case is called an *acceptor atom*. As the conductivity now is based on the migration of positive holes, this semiconductor is called a *p-type conductor*.

Doping is achieved by ion implantation in a vacuum chamber at very low pressure (10^{-4}–10^{-5} torr; 0.013–0.0013 Pa). The material intended for the doping is formed as ions (e.g. boron ions) in a plasma. The ions are then accelerated in a potential gradient column. Electrostatic and magnetic lenses form the ion beam and scan it over the surface of the material (for instance silicon) to be doped. The depth of ion penetration may be 0.1–1 µm.

40.4.4

Silicon Disks From Silicon Valley and Integrated Circuits from Taiwan

Silicon is an immensely important element in modern electronics. The invention of the transistor is treated in Chapter 41 Germanium. Silicon, utilized in connection with transistors, must be extremely pure and, in addition, monocrystalline. This makes great demands on the manufacturing technique. A conventional, polycrystalline material consists of a great number of grains. If the crystallization from a melt is adjusted so that one single grain is formed, a monocrystalline material is obtained.

In that case there are no grain boundaries. That is very important for electrical components.

A "silicon metal" (Figure M53) with 98% Si is manufactured by reduction of quartz with coke in an electric furnace. It is chlorinated to $SiCl_4$, which is purified by fractional distillation and reduced with zinc.

Silicon for transistor purposes needs further purification. In the beginning *zone melting* was utilized (Figure 40.12). A rod of the element (already very pure) is supported horizontally through a series of high-frequency coils. A thin section is melted in every coil. The surface tension prevents the melt from flowing away. The rod is slowly pushed through the coils at a rate of 10–250 mm/h. Pure material is crystallized in the direction of motion while any impurities concentrate in the melt, and are moved backwards to the end of the rod (the left in the figure). After a great number of passages, up to 50, the rod has been made pure and monocrystalline. Demand for a degree of purity, expressed as one contaminant atom in 10^8 base element atoms, can be fulfilled.

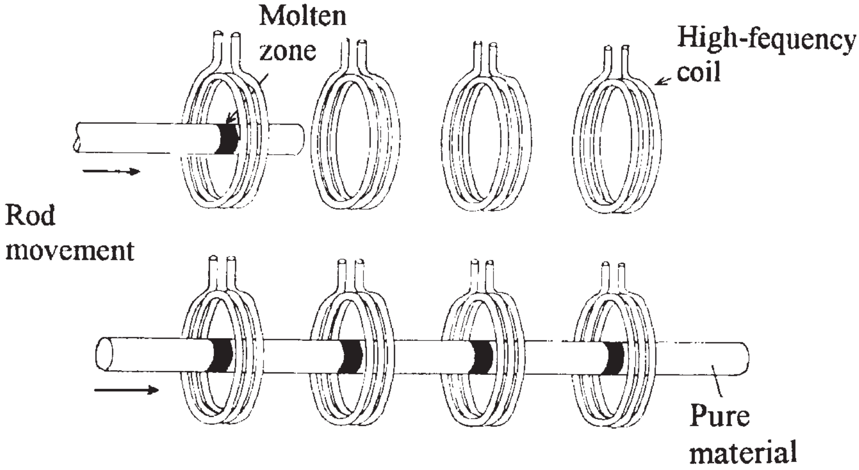


Figure 40.12 Zone melting for the purification of metals. (From G. Hägg, General and Inorganic Chemistry (Allmän och Oorganisk Kemi), 9th edition, Almqvist och Wiksell, Uppsala, 1988.)

A more modern manufacturing process is the following. The metallurgical "silicon metal" is finely ground and reacted with hydrochloric acid at 300°C in a fluidized bed. Trichlorosilane $SiHCl_3$ is formed, but also chlorides of the impurities, iron, calcium, aluminum and titanium. The silicon chloride is distilled off at +32°C, the chlorides of the impurities at much higher temperatures. By double distillation a very pure trichlorosilane is obtained. At 1150°C this compound is passed over a rod of pure silicon in a hydrogen gas atmosphere. $SiHCl_3$ will be decomposed. The process continues for more than 200 hours and a thick layer of fine-grained silicon is deposited on the silicon rod. Its diameter will have grown from 8 to 190 mm. This silicon is polycrystalline. It has to be transformed to a monocrystalline modification in order to make it suitable for semiconductor components. The material is transferred to a quartz crucible, which is placed in a crucible of graphite. The latter is heated inductively and the silicon in the quartz crucible melts.

Single crystals of silicon are grown in a process known as the Czochralski process (Figure 40.13). A thin seed crystal is lowered into the melt. While being rotated it is slowly pulled out from the melt, at a rate of 1 mm/min. In this process a single crystal is formed. The diameter of the rod increases up to 150 mm. Thin disks, *wafers*, are cut by a diamond saw from the rods. The wafers are polished on one or both sides and *chips* are taken out. These are small rectangular semiconductor plates with an edge length of 5–15 mm. By a sophisticated plating and etching technique, *integrated circuits* (ICs) are manufactured.

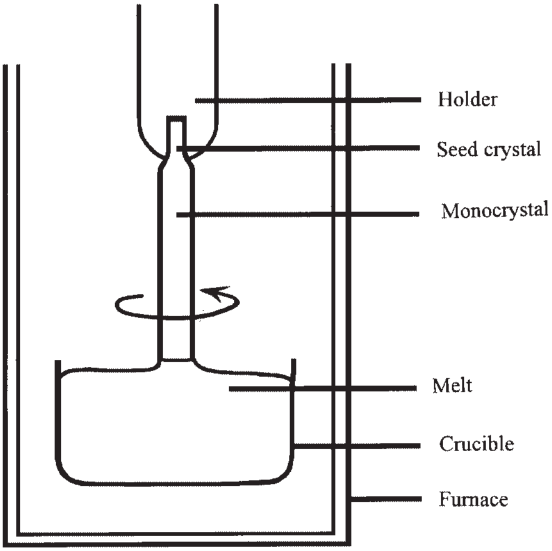


Figure 40.13 The Czochralski process for producing silicon single crystals.

In complete integrated circuits a great number of components – transistors, diodes, resistors and capacitors – interact. They are now used in mini-calculators, computers and mobile phones as well as in automobile and airplane electronics. The IC technique has made the enormous growth of the modern electronics industry possible.

> The history of the integrated circuit is in fact a contemporary history, which began about 1950 when the electron tube was replaced by the transistor, as described in Chapter 41 Germanium. The need for conventional connecting of wires set a limit to how small the device could be made. Could new possibilities be found? In 1958 *Jack S. Kilby* (born 1923) got the idea that all parts

> of a circuit, transistor, capacitors and resistors, could be made of semiconductor material. Kilby, then working with Texas Instruments, built a working model and applied for a patent. In 1959 *Robert Noyce* (1927–1990) had similar, but even more advanced, ideas when he worked with electronics development at Fairchild Semiconductor Company in California. He thought of a whole circuit that could be made on a single chip. He connected the components with circuits, which had been etched out in a metal layer, vaporized on the surface of the semiconductor. Today, both these men are acknowledged as having independently brought the technical development into new and fascinating areas.

In 2000 Jack S. Kilby got the Nobel Prize for physics together with Zhores I. Alferov and Herbert Kraemer. At that time Noyce was not alive. He had unexpectedly died of a heart attack ten years earlier at the age of 62.

The production of wafers is concentrated in the hi-tech countries of the world, the USA (Silicon Valley) and Japan. IC production, however, is mainly located in the countries of Southeast Asia. This results from the time when these countries still were low-wage markets, but nowadays they keep the production due to skill and efficiency.

40.5
Other Applications for Silicon

Silicon is not just only an IT element. Several other industries rely on silicon:

- manufacture of cement is based on a special calcium silicate;
- glass-making is based on sand, thus on silicon oxide;
- ferrosilicon for the steel industry is based on quartz and coke.

The use of silicon is very diversified, and here a few examples will be mentioned.

- Heating quartz and coke to 3000°C in an electric furnace produces silicon carbide SiC, carborundum. This rather impure product is ground and classified into different grain size groups. It is extremely hard and is used as an abrasive as powders, sandpaper and pastes for grinding, lapping and polishing applications. Pure silicon carbide is used for more sophisticated purposes as X-ray mirrors and high-temperature transistors.
- Quartz is a piezoelectric material, which vibrates when a voltage is applied. Quartz crystals became used as a time standard with the first quartz clock in 1927. Quartz crystals for watches have been mass-produced since the 1970s. The cut and shape of the actual quartz crystal determine the frequency of the quartz oscillator.
- Water glass, sodium silicate, is produced by fusing sodium carbonate with sand at high temperature or by heating sodium hydroxide with sand under pressure. The product, dissolved in water, is water glass. It was earlier used as an agent for preserving eggs (the pores in the eggshell are filled with silicate, preventing the entry

of air). It has detergent properties and is used in laundries. Due to its adhesive properties, it can be used as cement for glass, pottery and stoneware.

- Elemental silicon of metallurgical grade (98–99% Si) is used as an alloying element for aluminum intended for casting. In steel metallurgy a product, ferrosilicon, with 45–75% silicon is used partly for deoxidation purposes, partly for alloying of steels with silicon.
- "Silicon metal" of the highest degree of purity is used in solar cells, a new ecofriendly energy source. Sunlight can be converted to electricity in thin-film photovoltaic modules of silicon deposited on titanium dioxide. Another method is to use a wafer, composed of a layer of silicon doped with arsenic (an n-type semiconductor) combined with a layer doped with boron (a p-type semiconductor). When exposed to sunlight electrons flow between the p- and n-layers and thus an electric current is generated.
- Silicones are synthetic polymers with chains of alternating silicon and oxygen atoms (Figure 40.14). Each silicon atom has two groups (denoted R) attached to it, which can be organic. If all these Rs are methyl groups, the compound is called polydimethylsilicone (PDMS), the most common silicone. It may contain thousands of units, but by varying the chain length the viscosity of the corresponding silicone oil can be regulated. Crosslinking of the chains produces silicone rubber (elastomer). Mixed with boric acid $B(OH)_3$ polydimethylsilicone gives a pliable substance, which can be formed to any shape.

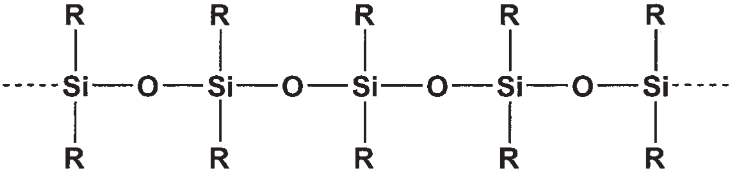


Figure 40.14 The structure of a silicone polymer.

- Silicone oils and rubber are used for many purposes. The oils can be cooled to low temperatures without becoming viscous but can also be used as high-temperature lubricants. Silicone oils are also used in cosmetics and hair conditioners, giving skin and hair a silky feeling. Silicone rubbers have a good chemical resistance and are used for caulking purposes, as for instance as putty for sealing around windows and pipes, especially in kitchens and bathrooms. Due to their thermal stability, silicones are in fact also utilized for heat-resistant tiles on the bottom of the Space Shuttles. Silicones have in recent years found some medical uses as breast implants.

40.6
Silicon in the Environment

Silicon and silicon compounds, sand and minerals, are non-toxic and yet very dangerous.

40.6.1
Silicosis and Asbestosis

Prolonged and extensive exposure to some crystalline silicates (quartz, tridymite and cristobalite) and to silicates with a fiber structure (asbestos) cause the serious diseases *silicosis* and *asbestosis*.

When workers inhale crystalline silica (dust), scars are developed around trapped silica particles in the lungs. For the silicosis victim, breathing becomes difficult and there is also a high risk of developing tuberculosis.

In the past, asbestos was added to a variety of products to provide heat insulation and fire resistance. It could have been for building and furnace insulation, brake pads and linings and even for components in the homes such as hair-driers and toasters. Airborne, inhaled asbestos needles can remain in the lungs for a long period of time, causing severe health problems that do not appear until many years later. Workers who manufacture or use asbestos products and have high exposures to asbestos are often affected with asbestosis. It is known that smokers exposed to asbestos have a much greater chance of developing lung cancer than just from smoking alone.

Use of asbestos has been banned but asbestos removal is a hazardous process. If done improperly it increases the health risks to those exposed.

40.6.2
Essential for Some Species

The silicon in biology is derived from amorphous $Si(OH)_4$ and no organic chemistry is involved. How silica moves in living systems is unclear, and many plants seem to have special uptake mechanisms.

For some species, such as for instance sponges and diatoms, silica is essential as they use it for their skeletons. In fact there seems to be a direct control from DNA in building of silica frameworks in organisms of this type. In the case of the stinging nettle, extra strength is supplied by the incorporation of amorphous silica

The element silicon has also been proved important for bone growth in animals. For humans it is probably essential in connective tissue and skin. Cereals in the daily diet are the main silicon source.

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41
Germanium

41.1 Ge
Facts about Germanium

41.1.1 Ge
The Element

Symbol:	Ge
Atomic number:	32
Atomic weight:	72.61
Ground state electron configuration:	[Ar]$3d^{10}4s^24p^2$
Crystal structure:	Cubic, diamond structure with *a* = 5.66 Å

41.1.2 Ge
Discovery and Occurrence

Discovery: The element germanium was discovered in 1886 by C. A. Winkler in Freiberg, Germany. Mendeleev had predicted the existence of the element in 1871 and called it eka-silicon.

Most important mineral: Germanite $Cu_3(Ge,Ga,Fe)S_4$ (Figure M68).
Renierite $Cu_3(Ge,Zn,Fe)S_4$
Argyrodite $GeS_2 \cdot 4Ag_2S$
Germanium occurs finely dispersed in many other minerals and is also present in coal.

Ranking in order of abundance in earth crust:	55
Mean content in earth crust:	1.5 ppm (g/tonne)
Mean content in oceans:	$5 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

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41.1.3 Ge
Chemical Characterization

Germanium is an important semiconductor material. The development of the germanium transistor opened the door to countless applications in solid-state electronics. Today silicon has taken over the role as the main transistor element but germanium is very much used in other advanced applications, such as for instance fiber optics and solar cells.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ge^{II} as in GeS, GeF_2 and GeF_3^-	$Ge(g) \rightarrow Ge^+(g) + e^-$	762	$Ge(g) + e^- \rightarrow Ge^-(g)$
Ge^{IV} as in GeO_2 and K_2GeF_6	$Ge^+(g) \rightarrow Ge^{2+}(g) + e^-$	1537	–119
	$Ge^{2+}(g) \rightarrow Ge^{3+}(g) + e^-$	3302	
	$Ge^{3+}(g) \rightarrow Ge^{4+}(g) + e^-$	4411	
	$Ge^{4+}(g) \rightarrow Ge^{5+}(g) + e^-$	9020	

Standard reduction potential:	$Ge^{4+}(aq) + 2e^- \rightarrow Ge^{2+}(aq)$	$E^0 = 0.00$ V
	$Ge^{2+}(aq) + 2e^- \rightarrow Ge(s)$	$E^0 = +0.245$ V
Electronegativity (Pauling):	2.01	
Radii of atoms and ions:	Atomic:	125 pm
(WebElements™)	Covalent:	122 pm
	Ge^{2+} (6-coordinate, octahedral):	87 pm
	Ge^{4+} (6-coordinate, octahedral):	67 pm
	Ge^{4+} (4-coordinate, tetrahedral):	53 pm

41.1.4 Ge
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
5323 kg m^{-3} 5.32 g cm^{-3}	13.64 cm^3	1211.5 K 938.3 °C	3106 K 2833 °C	322 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**273 K**	**373 K**	**573 K**	**973 K**
113	67	47	29	18

Coefficient of linear expansion K^{-1}

100 K	**293 K**	**500 K**	**800 K**
$2.4 \cdot 10^{-6}$	$5.7 \cdot 10^{-6}$	$6.5 \cdot 10^{-6}$	$7.2 \cdot 10^{-6}$

Resistivity nΩm

78 K	**298 K**	**373 K**	**573 K**	**973 K**	**1473 K**
–	$46 \cdot 10^7$	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-1.33 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
81 GPa	31 GPa	70 GPa	0.31

41.1.5 Ge
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	31.8 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	334 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	375 $kJmol^{-1}$
Entropy S^0 at 298 K	31.09 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	13.8	23.35	25.4	26.9	27.6	27.6

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Ge+O_2 \rightarrow GeO_2$	–520	–480	–390	–292	–

41.1.6 Ge
Nuclear Properties and X-ray

Isotope range, natural and artificial	61–85

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{70}Ge	Stable	21.23	0+	–
^{72}Ge	Stable	27.66	0+	–
^{73}Ge	Stable	7.73	9/2+	–0.8795
^{74}Ge	Stable	35.94	0+	–
^{76}Ge	Stable	7.44	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{73}Ge
Reference compound	$Ge(CH_3)_4+C_6D_6$
Frequency MHz (^1H = 100 MHz)	3.488
Receptivity D^P relative to ^1H = 1.00	$1.09 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	0.624
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-0.936 \cdot 10^7$
Nuclear quadropole moment, barn	–0.173

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
31	Ga	9.231
32	Ge	9.856
33	As	10.509

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	68.2
17.37 keV ($MoK\alpha_2$)	61.9

Neutron absorption	**Thermal neutron capture cross section**	2.3 barns

41.2
The Discovery of Germanium

In Zschopenthal, near Freiberg in Erzgebirge, cobalt deposits were well known. Kurt Winkler had built up a plant for production of *Zaffer* (or *Safflor*) by roasting of cobalt ore and sand together. This product had extensive use for blue coloring of glass. Herr Winkler was a well-educated chemist and metallurgist, who had studied in Sweden under Berzelius and Sefström. Inspired by his teachers, he had set up a good laboratory in connection with his industry. His son *Clemens Alexander Winkler* (1838–1904) grew up in an environment that created interest in minerals and metals, but also in nature with animals and plants. His father had been an eminent teacher. Clemens was admitted to the Bergakademie Freiberg as a student in 1857. From the beginning he had more knowledge about analytical chemistry than was being taught. This perhaps explains why, in spite of an active participation in student life, he was able to make remarkable progress in the studies of geology and metallurgy and other important subjects at the academy. In off-duty hours he contributed to his own living costs by making and selling nickel and cobalt metal. His talent and enthusiasm were observed and appreciated, and at the age of 35 he was appointed to be professor of chemical technology and analytical chemistry at the Freiberg Academy.

In 1885 a new mineral was discovered in the Himmelfürst mine near Freiberg. It contained silver and was named *argyrodite*. Professor Winkler was requested to make a careful analysis of the new mineral. He found repeatedly 75% silver and 18% sulfur; but 7% was missing. His hunt for this 7% became the pursuit of an elusive shadow. He fused the sample with soda, leached the melt with water, and examined the insoluble matter. No unknown substance was present there. The filtrate was acidified with hydrochloric acid. With hydrogen sulfide, small amounts of arsenic and antimony were precipitated. The 7% missed now *had to be* in the filtrate. He added more hydrochloric acid. Free sulfur but no sulfides precipitated. It was filtered off and the solution was evaporated to dryness. The residue was sodium chloride! Nothing more. The professor of analytical chemistry became confused. His own students were often assigned the task of doing mineral analyses – to determine their contents of CaO, FeO, MnO, SiO_2 and so on. They summed up afterwards, and very seldom was a sum between 99% and 100% obtained, because they were so inexperienced. But their deviations were never as big as 7%. Professor Winkler, recognized as a skilful analyzer, toiled at the problem for months. At the beginning of February 1886 he filtered off the sulfur precipitate after hydrochloric acid addition and was left yet again with the clear solution in which the unknown substance must be hidden. He had lost count of the number of times he had done this! In desperation he added hydrochloric acid in large excess. A huge surprise! A heavy white precipitate was formed. It was the chloride of the element he searched for. After filtering, he dissolved it in ammonia and precipitated it again with hydrochloric acid in excess. The dried chloride was treated with hydrogen gas under heat. A gray metal powder was formed and a new element discovered. Winkler named it *germanium* after his native country. The laboratory in which the discovery was made is shown in Figure 41.1.

Figure 41.1 Clemens Winkler's laboratory at Bergakademie Freiberg [41.1].

The news of Winkler's discovery spread quickly in Europe and also reached Mendeleev. In 1871 he had foreseen that an element between silicon and tin awaited discovery. He and other prominent chemists in Europe thought that Winkler had found eka-silicon. Thus within a period of 15 years three of the Russian prophet's predictions had been fulfilled, eka-aluminum in 1875, eka-boron in 1879 and eka-silicon in 1886. In the nationalistic manner of the actual time they had all been named after home countries or regions: gallium (discovered in France), scandium (discovered in Sweden) and germanium (discovered in Germany).

Before the end of the discovery year, Winkler received a letter from Mendeleev offering congratulations on his discovery. Later the two scientists, nearly the same age, also met in Freiberg (Figure 41.2) and they maintained friendly contacts throughout their lives.

Figure 41.2 Dmitri Mendeleev (1834–1907) and Clemens Winkler (1838–1904), in the Bergakademie Freiberg [41.1].

The following is a possible dialogue between the two learned gentlemen[1].

Mendeleev: When you found the new element, a large debate arose among the chemists in all Europe. That you really had filled in the empty space between silicon and tin was however soon accepted. Different name proposals for the new element were also put forward. Your own decision, germanium, I supported from the beginning. In all the excitement I could however not find any explanation for why you had such great difficulties in your analytical work. My dear Herr doctor Winkler, tell me about the seven percent which disappeared at your first examinations of the mineral from the Himmelfürst mine.

Winkler: Professor Mendeleev, you must understand that it is a great honor for me to be allowed to sit here conversing with you. After having built up the framework for the elements on earth, you informed us about the eka-elements, not yet discovered, and situated in empty places of your system. Impressively you also described the properties of these, then unknown, elements. After that, three common chemists, Lecoq de Boisbaudran in Paris, Nilson in Uppsala and I myself in little Freiberg, filled in the gaps. We are no prophets, as you are, but we worked hard and had a very good guidance of your predictions, when we determined atomic weights and other properties for the new elements.

Mendeleev: Well, well ... But what about the seven percent?

Winkler: You had foreseen that the tetrachloride should have a boiling point below 100°C. I missed that. One reason was that I in fact did not know that I was hunting your eka-silicon. The occurrence of a possible new element in a sulfide mineral made me suppose a metal like antimony or bismuth. By the way, did you not describe such an element in your textbook of chemistry in 1891? An element below tellurium in your system. Perhaps it will be discovered some day, even if it does not occur in our lifetime. Anyhow, in my filtrate in January 1886 I had eka-silicon in a hydrochloric acid solution. I evaporated to dryness to take care of the seven percent. But they were lost. And now I know the reason. The boiling point of germanium tetrachloride is 83°C. Thus the compound was vaporized and went up in smoke.

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[1] This conversation is not reproduced from some literature source, but is a fictitious dialog formulated by the present author.

Mendeleev: Hmm ... Interesting. The end of this story is in any case really good. With your laborious analysis, you found my eka-silicon. I thank you and congratulate you!

Winkler: I am really glad that our Bergakademie Freiberg for the second time took a place in the history of the discovery of the elements. As you certainly remember, Reich and Richter discovered the element indium here in 1863.

41.3
Occurrence and Manufacture

Germanium is widely distributed in both oxide and sulfide minerals but almost never found in high concentrations. There is some enrichment in zinc ores and in coal. Special minerals are the reddish-gray *germanite* (Figure M68) and the steel-gray *argyrodite*. Industrial germanium is obtained mainly as a byproduct of zinc ore processing, but a copper deposit, at Apex, Utah, USA, has such a high germanium content (600 ppm) that the mine has been reopened for the winning of germanium (and gallium).

Germanium is commercially available as:

- germanium tetrachloride $GeCl_4$
- germanium dioxide GeO_2
- metal ingots and rods
- semiconductor-grade germanium.

The first production step is pyrometallurgical treatment of leach residues or roasting products from zinc ore processing. The impure zinc oxide is reduced with coke or carbon monoxide. In this process, germanium, cadmium, indium and thallium, which usually follow zinc, are reduced to the metallic state. They vaporize and are separated by fractional condensation. The germanium fraction is transformed to the tetrachloride by treatment with hydrochloric acid.

Germanium oxide GeO_2 is prepared by hydrolyzing the chloride with high-purity water:

$$GeCl_4 + 2H_2O \rightarrow GeO_2 + 4HCl$$

The oxide is reduced with hydrogen gas at 650°C and the metal powder is melted at 1100°C. Small germanium ingots are cast as rods in a protective gas atmosphere. Semiconductor-grade germanium is produced by the zone melting technique, as described in Chapter 40 Silicon.

After the burning of coal, germanium is found in the ash and fly ash. The ashes are mixed with soda, copper oxide, carbon powder and slag former. On heating, a molten metal, containing germanium, is obtained. The metal is treated in a dilute solution of iron(III) chloride, into which chlorine gas is passed. The metal is dissolved.

After adding hydrochloric acid in excess (as Winkler did), germanium chloride precipitates. It can be separated and transformed to the oxide and metal.

41.4
Properties and Uses

Germanium is a hard, grayish white element with metallic luster but without the ductility that is typical for most metals. It has the same crystal structure as diamond and is hard and brittle. Chemically, it has many similarities with silicon. Physically, it is mainly characterized by its semiconducting properties. Curiously enough the metal is transparent to infrared radiation of wavelengths 2–16 μm.

The development of the germanium transistor opened the door to countless applications in solid-state electronics. Today the biggest uses of germanium are for fiber optics (50% of world consumption), as polymerization catalysts (25%), for infrared optics (15%) and in solar cell applications (5%). For special purposes, e.g. phosphors and chemotherapy, the utilization is another 5% [41.2]. The world market supply was about 100 tonne in 2001, of which recycling accounted for 30 tonne.

41.4.1
The Transistor – The Greatest Invention of the 20th Century?

Before 1947 there was almost no use for germanium. It was one of several strange metals, known only by a few specialists. Yet the story of its discovery was curious, with some factors of excitement. But, after all that, of what use was it? Then, in December 1947, the transistor was invented and the situation changed dramatically. Germanium became an extremely important element, and its minerals and compounds were sought everywhere.

John Bardeen (1908–1991) worked from 1945 to 1951 at Bell Telephone Laboratories. During this time he discovered the transistor effect together with *Walter H. Brattain* (1902–1987). They worked in a group managed by *William B. Shockley* (1910–1989). When studying how electrons acted on a semiconductor surface, they placed two gold point contacts less than 1 mm apart. Signals coming in through one gold contact left the other, considerably magnified. They had found a power amplification of the same type as was known for electron tubes. The three scientists shared the 1956 Nobel Prize for physics2) for their investigations on semiconductors and the discovery of the transistor effect.

After the discovery Shockley developed a basic transistor theory. Practically he replaced (in 1951) the point contact with a junction system. The bipolar junction transistor may consist of three layers, farthest out emitter and collector of p-type (compare chapter 40 Silicon) and between them a base layer of n-type (pnp transistor). The

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2) Bardeen got a further Nobel Prize. He and two colleagues, L. N. Cooper and J. R. Schrieffer, proposed in 1957 the first successful explanation of superconductivity, which had been a puzzle since its discovery in 1908. For that they were awarded the Nobel Prize for physics in 1972.

boundary between each layer forms a junction, which only allows current to flow from p to n (compare Chapter 40 Silicon). A small current through the base–emitter junction causes a much greater current to flow between the collector and emitter. Therefore, small changes in the voltage of the base cause large changes in the voltage drop across the collector resistance, making this type of transistor an effective amplifier. The transistor is utilized both as a single component and as a building block in integrated circuits, containing millions of transistors.

The effect was obvious for the people of the 1950s. Everybody had to have these new, light transistor radios – in their cars, house trailers, weekend cottages and sailing boats. (In fact, there were so many that they introduced "non-stop pop" on bathing beaches, to the detriment of rest and peace!) On the other hand, from that time the radio has become a powerful and easily accessible tool for information and education, not least in developing countries.

Germanium's time of prosperity as the main element of electronics was short. In the 1960s silicon took over as the principal semiconductor material, and transistors of this element now constitute the integrated circuits in modern electronics and computer technology. For the germanium manufacturers, however, new possibilities opened up.

41.4.2
Infrared Optics

Lenses and windows of germanium are transparent to infrared radiation. At room temperature or slightly higher, all specimens emit heat radiation, and still more is emitted by living organisms and engines in operation. Germanium is about as transparent to this radiation as glass is to visible light. A tank hidden in dense fog, or an unconscious man in a smoke-filled house, both can be observed through the infrared radiation that they emit. The optics, lenses of germanium, focuses the radiation onto a detector, often cadmium telluride. The information is transformed to a picture on a screen, visible to the eye. In some modern automobiles, germanium has been utilized for night-vision systems.

41.4.3
Fiber Optics and Other Communications Networks

In fiber optics communications networks, optical fibers transport a great amount of information. Their capacity is 80 times larger than for a conventional coaxial cable. In the receivers of the fiber optic system, semiconductors decode the light signals and convert them into electronic signals. For this purpose germanium is very much utilized and the demand has increased through the development of broadband technology. In wireless telecommunications newly developed silicon–germanium chips substitute for gallium arsenide. SiGe microchips, small, fast and cheap, are expected to be very much utilized for third-generation mobile phones.

41.4.4
Polymerization Catalysts

PET bottles, which we meet in the self-service store, are manufactured of the plastic polyethylene terephthalate (hence the designation PET). Germanium oxide is used as a catalyst when this compound is synthesized from ethylene glycol and terephthalic acid. GeO_2 has, for environmental reasons, replaced the earlier used catalyst antimony oxide. New types of plastics are also expected to utilize germanium oxide as catalyst for their formation.

41.5
Germanium in the Environment

Germanium is not essential for life, nor does it present any threat to the environment. Its compounds have very low solubility and low concentrations in natural waters.

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42
Tin

42.1 Sn
Facts about Tin

42.1.1 Sn
The Element

Symbol:	Sn
Atomic number:	50
Atomic weight:	118.71
Ground state electron configuration:	$[Kr]4d^{10}5s^25p^2$
Crystal structure:	Tetragonal β-Sn (white) with a = b = 5.83 Å, c = 3.18 Å Cubic α-Sn (gray; diamond structure) with a = 6.49 Å β-Sn is stable above 13 °C, α-Sn below

42.1.2 Sn
Discovery and Occurrence

Discovery: The element tin was known to ancient civilizations and tin utensils were produced before 2000 BC. The metal was too soft for tool purposes but early metallurgists made the great discovery that soft copper, alloyed with still softer tin, gave the hard alloy bronze, the basis for the Bronze Age.

Most important mineral: Cassiterite, tinstone SnO_2 (Figure M69).
Stannite, tin pyrites Cu_2FeSnS_4

Ranking in order of abundance in earth crust:	51
Mean content in earth crust:	2.3 ppm (g/tonne)
Mean content in oceans:	$4 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	0.2 ppm
Content in a man's body (weight 70 kg):	14 mg

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42.1.3 Sn

Chemical Characterization

Tin is ordinarily a silver-white metal but below 13 °C it may change into a non-ductile form, known as gray tin ("tin pest"). Tin has been used as a protective coating for copper vessels and it is important in the production of common alloys, especially bronze (tin and copper). Some organic tin compounds, such as for instance tributyltin TBT, mixed into marine paints prevent the growth of algae and other organisms on the hulls of ships. Consequently it results in decrease of the vessel's friction in the water and lower energy consumption. This positive effect is however a result of the toxicity of TBT to the organisms. In 1998 the International Maritime Organization adopted a resolution to phase out the use of the substance.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
Sn^{II} as in $SnBr_2$,	$Sn(g) \rightarrow Sn^+(g) + e^-$	709	$Sn(g) + e^- \rightarrow Sn^-(g)$
and $Sn_3(OH)_2OSO_4$	$Sn^+(g) \rightarrow Sn^{2+}(g) + e^-$	1412	–116
Sn^{IV} as in SnO_2 and $SnCl_4$	$Sn^{2+}(g) \rightarrow Sn^{3+}(g) + e^-$	2943	
	$Sn^{3+}(g) \rightarrow Sn^{4+}(g) + e^-$	3930	
	$Sn^{4+}(g) \rightarrow Sn^{5+}(g) + e^-$	7456	

Standard reduction potential:	$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	$E^0 = +0.154$ V
	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$E^0 = -0.137$ V

Electronegativity (Pauling): 1.96

Radii of atoms and ions:	Atomic:	125 pm
(WebElements™)	Covalent:	122 pm
	Sn^{4+} (4-coordinate, tetrahedral):	69 pm
	Sn^{4+} (6-coordinate, octahedral):	83 pm
	Sn^{4+} (8-coordinate):	95 pm

42.1.4 Sn
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
7310 kg m^{-3} (white) 7.31 g cm^{-3} 5770 kg m^{-3} (gray) 5.77 g cm^{-3}	16.24 cm^3 (white) 20.57 cm^3 (gray)	505.1 K 231.9 °C	2543 K 2270 °C	227 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
76	68	63	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$16.5 \cdot 10^{-6}$	$22 \cdot 10^{-6}$	$27.2 \cdot 10^{-6}$	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
21	115	158	500	600	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+0.33 \cdot 10^{-9}$ m^3kg^{-1} (white) $-4.0 \cdot 10^{-9}$ m^3kg^{-1} (gray)
Magnetic characterization	White tin is paramagnetic (as susceptibility is positive) Gray tin is diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
50 GPa	19 GPa	45 GPa	0.32

42.1.5 Sn
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	7.20 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	290 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	302 $kJmol^{-1}$
Entropy S^0 at 298 K	51.55 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	22.2	26.99	28.7	27.9	28.9	29.6

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$Sn+O_2 \rightarrow SnO_2$	–520	–478	–373	–269	–

42.1.6 Sn
Nuclear Properties and X-ray

Isotope range, natural and artificial 100–134

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{112}Sn	Stable	0.97	0+	–
^{114}Sn	Stable	0.65	0+	–
^{115}Sn	Stable	0.34	1/2+	–0.9188
^{116}Sn	Stable	14.53	0+	–
^{117}Sn	Stable	7.68	1/2+	–1.001
^{118}Sn	Stable	24.23	0+	–
^{119}Sn	Stable	8.59	1/2+	–1.047
^{120}Sn	Stable	32.59	0+	–
^{122}Sn	Stable	4.63	0+	–
^{124}Sn	Stable	5.79	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{115}Sn	^{117}Sn	^{119}Sn
Reference compound	$Sn(CH_3)_4$		
Frequency MHz (^1H = 100 MHz)	32.719	35.632	37.291
Receptivity D^P relative to ^1H = 1.00	$1.21 \cdot 10^{-4}$	$35.4 \cdot 10^{-4}$	$45.3 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	0.694	20.2	25.9
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-8.801 \cdot 10^7$	$-9.589 \cdot 10^7$	$-10.032 \cdot 10^7$
Nuclear quadropole moment, barn	–	–	–

Characteristic X-radiation **Z**	 **Element**	 **Kα_2 keV**
49	In	24.002
50	Sn	25.044
51	Sb	26.110

X-ray radiation absorbed by the element **Incoming radiation energy**	 **Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	248
17.37 keV (MoKα_2)	31.4

Neutron absorption	**Thermal neutron capture cross section**	0.63 barns

42.2
Tin in History

Tin is one of the oldest metals used by humans. Along with gold, silver, mercury, copper and iron, it was known already in antiquity. The significance of tin was originally connected with the tremendous importance of bronze in history. It was a real technological leap when – perhaps accidentally – it was found that the hard alloy bronze was formed on mixing soft copper, not at all suitable for weapons and tools, with the still softer metal tin. Due to its properties, bronze became so important that its name was used as the designation for a whole historical period, the *Bronze Age*. The civilizations of ancient times, in Egypt, Mesopotamia, Greece, China and South America, in fact owe a debt of gratitude to the unpromising gray metal tin. The beginning of the Bronze Age is considered to have been about 3000 BC in Mesopotamia, Egypt and Thailand, while the period began at about 1600 BC in Northern Europe. In the early days of these epochs, however, bronze was not made by melting together copper (from copper ores) and tin (from tin ores). Instead, it was probably the case that special copper ores had been found, from which the desirable "hard copper" was obtained. It happened with no knowledge about the composition of the actual ore and its tin content. Later, about 1000 BC, a proper alloy of copper with tin metal became used, as shown in Chapter 7 Copper (see Figure 7.1).

Knowledge about early winning and use of tin is fragmentary. Sparse manufacture of tin objects is reported from very old times, yet a finger ring and a pilgrim's cup, made of pure tin and dated 1500 BC, have been found in Egypt. The legendary islands *Cassiterides* could have been the source of the tin ore, and the metal was said to have been bought in the likewise magical *Tartessos*. Speculations have been expressed that the islands are the Isles of Scilly southwest of Land's End, Cornwall, UK. Archeological studies have shown that Tartessos possibly was situated in the delta of the river Guadalquivir in the south of Spain. In the markets of this town, gold, silver, tin ore (cassiterite) and tin metal were being sold as early as 2000 BC. The town is considered to be identified with *Tarshis* in the Old Testament, a town with which King Solomon had business relations:

> The king had a fleet of ships plying to Tarshis with Hiram's men; once every three years this fleet of merchantmen came home, bringing gold and silver, ivory apes, and monkeys. (2 Chronicles 9:21)

No notice was obviously taken of tin. Perhaps the metal, which resembled silver without being silver, was not worth mentioning alongside apes and monkeys. It is surprising that silver was mentioned. In the passage before (verse 20) it is said:

> All Solomon's drinking vessels were of gold ... Silver was reckoned of no value in the days of Solomon.

Herodotos (484–425 BC), the major Hellenistic historian, wrote in his *Historiai* that he had not heard of the islands called the Cassiterides and that he had not even obtained an eyewitness description of a sea beyond Europe:

> Nevertheless tin and amber seem to come to us from the ends of the earth.

Julius Caesar wrote in his *Commentaries on the War in Gaul* that tin was produced in Britannia. During the first century of our chronology, tin was *plumbum album* (white lead), while lead was *plumbum nigrum* (black lead). Tin articles had by now become common. Pliny also described the use of tin coating of copper pots as corrosion protection.

In the Middle Ages tin deposits were discovered in Bavaria, Saxony and Bohemia and tin mines were established. The tinstone from the German *Erzgebirge* ("ore mountains") was reduced and tin metal produced. A great industry grew up in order to produce tinplate. This was the raw material for cauldrons, tankards, plates, and tea and coffee pots. In the 18th century these goods were very well known and were exported all over Europe. The tinplate was exported to many countries. When it reached the UK, the Welsh began to tin-coat hot rolled sheet iron with tin from Cornwall.

Due to its appearance, resembling silver, and its good formability, tin became more and more used as a material for utility goods and ornaments. From the 14th century tin objects were common in religious ceremonies. In households of the European upper classes, tin became an important material. Hundreds of tin pitchers, dishes and plates are today on view as specimens in museums, old churches and castles. After a peak in manufacture at the turn of the century, after 1800 the number of pewterers decreased and production was concentrated on tools for households and hospitals. During the 20th century tin again came into vogue for, among other things, vases and candlesticks.

When the Europeans colonized South and Central America they were surprised not only at the Indians' knowledge of gold, silver and platinum but also that tin metal was well known and used, even as coins. In the 17th century *Father A. A. Barba* visited tin mines in Bolivia, which originally were worked by the Inca Indians but in his time were mined by the Spaniards. Father Barba said that "in my parish of San Bernardo, where I am at present the incumbent, rich tin mines are situated, quite near the church". This priest, A. A. Barba, wrote the first book about American metallurgy, *El Arte de los Metales*, the first edition of which was published in Madrid in 1640 [42.1].

42.3
Tin, Stannum, Cassiterite – Why These Names?

The name for the element tin seems to be Anglo-Saxon: in the German language *Zinn*, in Swedish *tenn*, in English *tin*. It is thought that the word derives its origin from an old word *ten* for a metal rod. In the French language the same word form was used from the beginning. In the 13th century tin was called *tain*, which nowadays is *étain*. The Romans used many names for tin, *plumbum album* (white lead), *plumbum candidum* (shining lead), as well as *stagnum* and *stannum*. The latter designation may be derived from the Sanskrit word *stan* (meaning “hard”). In modern Italian the name is *stagno*, in Spanish *estaño*. When Berzelius accomplished his great remodeling of the chemical language in 1812–1813, he utilized the Latin word *stannum* for the chemical designation *Sn*. The Greek name for the metal is *kassiteros*, which gave rise to the scientific word *cassiterite* for the mineral tinstone.

42.4
Tin in Cornwall, UK

Cornwall is a peninsula and a county in southwest England. Its region farthest out is Land’s End. The Isles of Scilly, 45 km beyond Land’s End, also belong to the county. As mentioned above, these islands are assumed to have been the *Cassiterides*, from which tin was collected and shipped to the early Mediterranean countries. This may perhaps be legend and myth. But it is a historical fact that the rich tin ore deposits in mainland Cornwall brought this region into contact with the Mediterranean world during the Bronze Age. Excavations made in the 20th century have shown that mining for tin has occurred in Cornwall for at least 2000 years. The Carthaginians and Romans developed the tin trade in the last century BC and Cornwall was incorporated in the Roman province Britannia. Already during the first centuries of our chronology the significance of Cornish tin for the Roman Empire decreased as more adjacent deposits were discovered in Spain. In Cornwall mining continued for a long time. The increased use of tin in Central and Northern Europe was, besides German tin, to a great extent based on cassiterite from Cornwall.

In Cornwall various minerals and ores are present according to Figure 42.1. In the tin ore veins of the granite massif, the content of SnO_2 is 1–2%. The ore has been mined down to a depth of 1000 m. Nowadays, the ore has run out and tin mining with its 2000 years’ duration has come to an end.

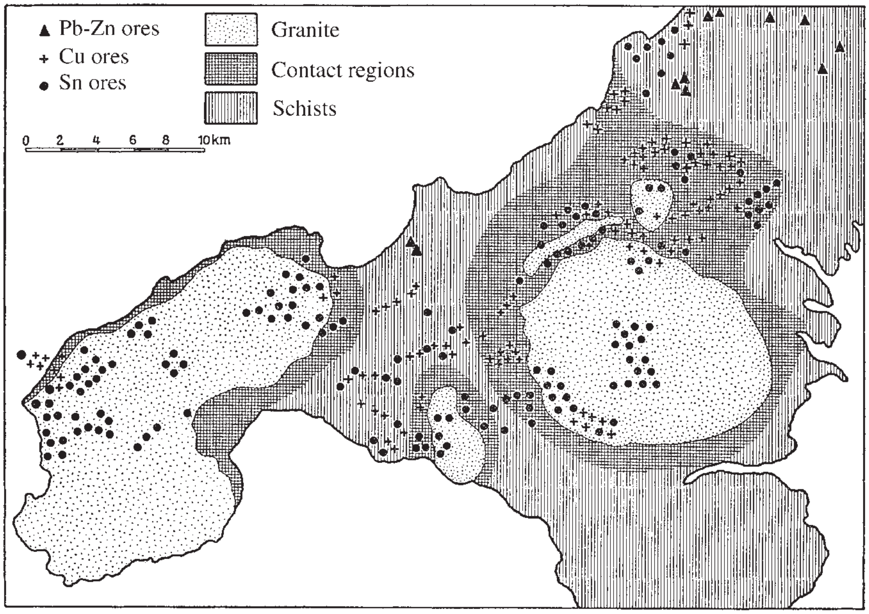

Figure 42.1 Ore deposits in the west of Cornwall [42.2]. Observe that the tin deposits are concentrated in the granite areas.

42.5
Tin Minerals and Ores in the World

The most important tin mineral and the principal ore of tin is *cassiterite*. It is a brown or black, shiny, tetragonal mineral with the formula SnO_2, also called tinstone (Figure M69). Another mineral is *stannite* (tin pyrites or bell-metal ore), Cu_2FeSnS_4. It is a steel gray or iron-black tetragonal mineral with a metallic luster. It usually occurs associated with cassiterite.

During magmatic processes tin remains in the melt and after solidification is found among the pegmatites. Weathering, especially in tropical climatic conditions, dissolves feldspars and mica, while tinstone stays undissolved together with quartz. The density difference between these two minerals is considerable, and quartz is transported away. The heavier cassiterite is enriched in the residue. This is the reason why alluvial deposits, *placers*, are the most important in modern winning of tin. It is also the background to the many deposits in the equatorial belt (Figure 42.2).

The tin reserves of the world are estimated to 8 million tonnes, concentrated in the coastal areas of Southeast Asia and in South America. Important tin ore producers are China, Indonesia, Peru, Brazil, Bolivia, Australia, according to Table 42.1. In 2001 the total world production (counted as tin) was 220 000 tonnes.

The distribution of tin production among countries has changed. In 1990 Brazil and China had the top positions and produced about 40 000 tonnes each. In 2001 Chi-

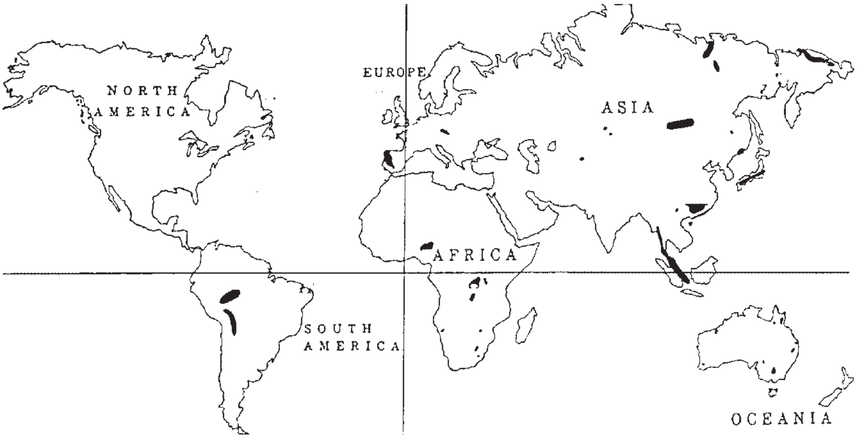

Figure 42.2 Regions of the world with large tin deposits. (Reprinted from Swedish Geological Service, Report SGU PM 1991:5. With permission.)

Table 42.1 Tin production in mines (counted as tin) in the year 2001

Country	Production tonnes	Percentage of total production	Country	Production tonnes	Percentage of total production
China	79 000	35,6	Malaysia	5000	2,3
Indonesia	51 000	23,0	Russia	4500	2,0
Peru	38 200	17,2	Vietnam	3500	1,6
Brazil	14 000	6,3	Thailand	2500	1,1
Bolivia	12 500	5,6	Portugal	1200	0,5
Australia	9600	4,3	Other countries	1000	0,5
			Total	222 000	100,0

Source: ref. [42.3].

na was first with 79 000 tonnes, while Brazil with 14 000 tonnes had moved back to fourth position. In South America the Bolivian deposits are situated in the western part of the country, in the so-called tin belt. Underground mining leads to higher costs than in open cut mines as in Brazil or dredging offshore as in Southeast Asia. Yet the tin winning of Bolivia lives on. The old mine in Potosi, worked since the 16th century and originally a silver mine, is now a well-known tin mine. Bolivian production has however decreased (17 000 tonnes in 1990 compared to 12 500 tonnes in 2001). Its neighbor, Peru, has increased tin production considerably from 5000 tonnes in 1990 to 38 000 tonnes in 2001 and 71 000 tonnes in 2002.

Indonesia has very large tin reserves, situated on islands in the straits between Sumatra and Borneo. Thailand is also an important tin country. The winning of tinstone was often a small family business, and the work was very hard and dirty, partly because of lack of technical facilities, and partly because the ore is of placer type and has to be washed for winning of the cassiterite. In the 1980s there were about 200 tin mines in the country. In the 1990s the number had decreased to 100, and by 1997 to 22. The amount of tin winning has also diminished. In connection with Thai tin winning, niobium and tantalum are also obtained.

The largest underground tin mine in the world is *Rension*, Tasmania, Australia. In 1997, 692 000 tonnes of tin ore were worked there, giving – after ore dressing – 16 000 tonnes of concentrate with 53% tin.

42.6
Manufacture of Tin Metal

Enriched cassiterite ore, tin oxide concentrate, is heated with coke to about 1200°C in an electric furnace. This temperature is very high compared to the melting temperature of metallic tin, 231°C. It is used in order to obtain a fluid slag. Part of the tin will go into the slag as tin silicate and has to be reduced in a second stage. Crude tin metal is refined by different methods, finally by electrolysis and, if necessary, also with vacuum treatment and zone melting.

Tin is to some extent recycled from tinned steel. One method is dissolution in an aqueous solution of sodium hydroxide and sodium nitrate. The tin is dissolved without attacking the steel. Tin is precipitated from the solution by electrolysis.

The world tin metal production was 290 000 tonnes in 2001, of which 92% was primary, thus reduced from enriched tin ore. China produced the largest quantity (32% of the total). Other large producing countries were Indonesia (17%), Peru (13%), Malaysia (11%), Thailand (7%) and Brazil (5%). The United States also had a 5% share, totally based on secondary production.

42.7
Uses of Tin

Manufacturing of bronze was once the principal use of tin. This is no longer the case. Only 10% of all tin is utilized for bronze. The use of tin in different alloys is treated in other chapters according to Table 42.2.

Wood's metal consists of bismuth, lead, tin and cadmium. It has a melting range between 50 and 80°C. *Rose's metal*, an alloy of bismuth, lead and tin, melts at about 100°C. It takes its name from the German chemist and pharmacist *Valentin Rose Sr.* (1736–1771). Tin is used as one component in *bell metal*, a type of bronze. The use of tin in ornaments and household articles has been treated above in connection with tin in history.

Soldering is an extensive tin application. Alloys of tin and lead are still used, but lead has to be avoided if the component will be in contact with foodstuff. For soldering of copper radiators, tin alloys are used. Aluminum components are difficult to solder

Table 42.2 Tin alloys that have been covered in other chapters

Alloy	Composition	Treated in chapter	
		No.	Name
Bronze	Copper, tin	7	Copper
Wood's metal	Bismuth, lead, tin, cadmium	46	Arsenic, Antimony and Bismuth: bismuth section
Rose's metal	Bismuth, lead, tin	46	Arsenic, Antimony and Bismuth: bismuth section
Britannia metal	Antimony, copper, tin	46	Arsenic, Antimony and Bismuth: antimony section
Type metal	Lead, antimony, tin	43	Lead

due to the passive layer of aluminum oxide on the metal surface. By tinning the aluminum becomes solderable.

One very important alloy for *machine bearings* is Babbitt metal, invented by the American Isaac Babbitt (1799–1862). In present-day usage the term is applied to a whole class of silver-white bearing metals or "white metals". They are composed primarily of tin, antimony and copper, such as for instance 90% Sn, 6% Sb and 3% Cu. This alloy is used in situations with sliding contact under pressure. Its bearing properties are favored by the fact that hard components of the type CuSn and SbSn are formed and embedded in the soft tin matrix.

Tin is used in *coatings for steel containers* intended for food and drinks. Earlier the tinning was made by a hot dip technique, but nowadays it is done electrolytically. In Europe 38 billion metal cans were produced in 2001, 20 billions of aluminum and 18 billions of tinned steel. They were mainly used for soft drinks and beer.

Within the glass industry there is an odd use of tin. In order to make window glass perfectly plane, the molten glass is allowed to float out over and solidify on molten tin. The product is called float glass, and the technique is called the Pilkington process. About 300 tonnes of tin is used in such a melt.

Electrically conductive tin coatings on glass have been used for panel lighting and for frost-free windshields.

42.8
Tin Cry and Tin Pest

When molten tin solidifies, a modification called β-tin is formed. This common tin is a silvery-white, malleable metal with a tetragonal structure. It has large grains (crystallites), which rub against each other when a rod of tin is bent. The sound generated is known as *tin cry*.

The fact that the interior of metals may emit sound is utilized in a modern method for materials testing, called *acoustic emission* (AE). When cracks are initiated in a structure under stress, a rapid release of energy occurs and high-frequency elastic waves are generated. Their "sound" is generally not detectable by ear. Tin cry is an exception. Instead piezoelectric sensors are used, which record the acoustic emission and transform it to optical signals. In this way it is possible to "hear" an incipient crack formation in the material of, for instance, nuclear reactors.

β-Tin is stable down to +13°C. If the metal is kept below this temperature for a long time, the transition to α-tin occurs. It has the diamond structure and lacks metallic ductility. Once started, the transformation takes place rather rapidly. The gray α-tin has a low density (5.77 g/cm^3 compared to 7.31 for β) and thus the metal expands and crumbles to a powder at the transformation. The phenomenon is known as *tin pest* or *tin disease* or *tin plague*. The conversion was first noted on organ pipes in European cathedrals, where it was thought to be the devil's work. It has been said that soldiers in Napoleon's army in 1812 had tin buttons in their uniforms. After spending a long, cold time in Russia, the buttons would have disintegrated due to tin pest. If true, it would have been a bad omen. Perhaps it is only a myth, as the historians tell us that the soldiers had buttons of bone and the officers of brass.

42.9
Modern Tinning

A thin coating of tin (5–15 μm) provides solderability to aluminum as well as corrosion protection to copper and nickel. This is not the case for tin-plated steel in an ordinary atmosphere. Inside a tin can the steel is however protected as long as the atmosphere is oxygen-free. We observe that the inside of the sealed can is not attacked even after a long storage of food in it, while the emptied can, exposed to the environment, rusts immediately. This plating in the steel mill is the largest application for the electrodeposition of tin. In the electronics industry many surfaces requiring solderability are also tin-coated.

Both alkaline and acid electrolytes are used for tin plating. A bath containing sulfuric acid and tin(II) sulfate is very much used because of its ease of operation. A number of organic additives improve brightening and leveling. Tin(II) tetrafluoroborate baths are capable of operation at higher current densities and because of that are utilized for continuous tinning of wire, strip and sheet.

42.10
Tin in the Environment

Tin oxide has low solubility in water and consequently the tin contents in rivers and oceans are very low. Tin is also unlike its neighbors in the periodic table, cadmium and lead, regarding affinity for sulfur. For these reasons, tin is looked upon as a non-toxic metal, and so has been safely used on the inside of all our foodstuff cans.

Some organic tin compounds are different, however. Tributyl-tin $(C_4H_9)_3SnOCO \cdot CH_3$ (TBT) mixed into marine paints prevents the growth of algae and other organisms on the hulls of ships. Consequently it decreases the vessel's friction through the water and lowers energy consumption. This positive effect is however the result of TBT toxicity to marine organisms. The substance also affects mussels and oysters, showing dwarfism. Certain types of fish are also influenced in a negative way. Since 1990 there has been a ban on using paint containing TBT on boats shorter than 25 m. TBT has however continued to be used in paints for larger ships. In 1998 the International Maritime Organization adopted a resolution to phase out the substance. Trace amounts of TBT can now be found in almost all the world's harbors.

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43
Lead

43.1 Pb
Facts about Lead

43.1.1 Pb
The Element

Symbol:	Pb
Atomic number:	82
Atomic weight:	207.2
Ground state electron configuration:	$[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$
Crystal structure:	Cubic fcc with a = 4.95 Å

43.1.2 Pb
Discovery and Occurrence

Discovery: Known since antiquity and used before 4000 BC.

Most important mineral: Galena, lead glance PbS (Figure M70)

Ranking in order of abundance in earth crust:	36
Mean content in earth crust:	14 ppm (g/tonne)
Mean content in oceans:	$3 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	400 years
Mean content in an adult human body:	1.7 ppm
Content in a man's body (weight 70 kg):	119 mg

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43.1.3 Pb
Chemical Characterization

Lead was one of the first known metals. It is however toxic and avoided for environmental reasons. Lead taken internally in any form is accumulated in the body and gives symptoms of lead poisoning. Children are especially at risk because lead can reduce intelligence, and cause hearing problems. In spite of that, lead is still used so much that its tonnage is number five among the metals. Only iron, copper, aluminum and zinc are used more. Large quantities of lead are used in batteries and for sheathing of electrical cables. Bearing alloys have to withstand sliding contacts under pressure. For this purpose lead–tin bronzes (copper–tin alloys with 10–20% lead) are used. Because of its high density and nuclear properties, lead is used extensively as protective shielding for X-ray apparatus and equipment containing radioactive substances. White lead, basic lead carbonate, has been used for over 2000 years as a white pigment. Lead chromate or chrome yellow ($PbCrO_4$) is a crystalline powder used as a yellow pigment. Because of the risk of poisoning, lead-based paints are however avoided. Tetraethyl lead $Pb(C_2H_5)_4$ (TEL) was added to gasoline to prevent premature detonation in internal combustion engines. This antiknock compound was a significant contributor to air pollution. The development of new, lead-free petrol and new engine designs have eliminated the need for antiknocking additives, and TEL is being phased out.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**	
Pb^{II} as in PbO, $PbSO_4$, and $PbCrO_4$	$Pb(g) \rightarrow Pb^+(g) + e^-$	716	$Pb(g) + e^- \rightarrow Pb^-(g)$	−35.1
Pb^{IV} as in PbO_2 and $Pb(C_2H_5)_4$	$Pb^+(g) \rightarrow Pb^{2+}(g) + e^-$	1450.5		
Pb^{II} and Pb^{IV} as in Pb_3O_4	$Pb^{2+}(g) \rightarrow Pb^{3+}(g) + e^-$	3081.5		
	$Pb^{3+}(g) \rightarrow Pb^{4+}(g) + e^-$	4083		
	$Pb^{4+}(g) \rightarrow Pb^{5+}(g) + e^-$	6640		

Standard reduction potential:	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ $E^0 = +1.69$ V $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $E^0 = -0.125$	
Electronegativity (Pauling):	2.33	
Radii of atoms and ions: (WebElements™)	Atomic:	180 pm
	Covalent:	145 pm
	Van der Waals	202
	Pb^{2+} (6-coordinate, octahedral):	133 pm
	Pb^{2+} (8-coordinate):	143 pm
	Pb^{4+} (4-coordinate, tetrahedral):	79 pm
	Pb^{4+} (6-coordinate, octahedral):	91.5 pm
	Pb^{4+} (8-coordinate):	108 pm

43.1.4 Pb

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
11 345 kg m^{-3} 11.35 g cm^{-3}	18.26 cm^3	600.7 K 327.5 °C	2022 K 1749 °C	128 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
37	36	34	32	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$25.6 \cdot 10^{-6}$	$28.9 \cdot 10^{-6}$	$33.3 \cdot 10^{-6}$	–

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
47	192	270	500	1080	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-1.39 \cdot 10^{-9}$ m^3kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
16 GPa	5.6 GPa	37 GPa	0.44

43.1.5 Pb
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	4.77 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	178 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	195 $kJmol^{-1}$
Entropy S^0 at 298 K	64.81 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	24.4	26.44	29.7	29.4	28.6	29.4

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$2Pb+O_2 \rightarrow 2PbO$	–376	–333	–236	–152	–
$3/2Pb+O_2 \rightarrow 1/2Pb_3O_4$	–301	–259	–169	–	–

43.1.6 Pb
Nuclear Properties and X-ray

Isotope range, natural and artificial	181–215

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{206}Pb	Stable	24.1	0+	–	–	–	–
^{207}Pb	Stable	22.1	1/2-	0.5881	–	–	–
^{208}Pb	Stable	52.4	0+	–	–	–	–
^{204}Pb	Active	1.4	0+	–	$1.4 \cdot 10^{17}$ y	–	–
^{210}Pb	Active	0.0	0+	–	22.3 y	β^-	0.064 MeV
^{214}Pb	Active	0.0	0+	–	26.8 m	β^-	1.024 MeV

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{207}Pb
Reference compound	$Pb(CH_3)_4$
Frequency MHz (^1H = 100 MHz)	20.921
Receptivity D^P relative to ^1H = 1.00	$2.01 \cdot 10^{-3}$
Receptivity D^C relative to ^{13}C = 1.00	11.5
Magnetogyric ratio, $radT^{-1}s^{-1}$	$5.580 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
81	Tl	70.832
82	Pb	72.804
83	Bi	74.815

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	227
17.37 keV ($MoK\alpha_2$)	123

Neutron absorption	Thermal neutron capture cross section	0.175 barns

43.2
Lead in History

43.2.1
From Time Immemorial

Lead is one of the oldest metals that mankind has used. It was known in Egypt already by 4000 BC and described in very old documents. In Babylonia, lead plates were used to write upon with metal pens. The early use of lead has its background in the special properties of the metal:

- It is easy to reduce from its own ores.
- It often occurs together with silver and is a by-product of silver winning.
- It is easily fusible.
- It is soft and formable.
- It is heavy.

43.2.2
Plumbum and Mólybdos

In Rome *plumbum* was the word for soft metals with low melting points. *Plumbum candidum* or *plumbum album* was tin, and *plumbum nigrum* was lead. Probably *plumbum* is related to the Greek word μολυβδος (*molybdos*). Both these names are said to be derived from Sanskrit. How the Greek word happened to give its name to the metal molybdenum, discovered in Sweden in 1781, is described in Chapter 25 Molybdenum. The old Germanic word *blio* (*bliw*) and the German word *Blei* are derivable from the Indo-European word "bhli" (shining, shiny). The English *lead* is probably borrowed from a Celtic word *luaide*, of unknown origin.

Because of its high density, lead played a special role for the alchemists. They believed lead to be the oldest metal and easily converted into gold. They had many names for it, among others *plumbago*. Many designations were also secret.

Hekataios was a Greek historian and geographer from Miletos, living about 500 BC. After extensive travels he described the geography and ethnography of Europe, Egypt and Asia. He told that the Phoenicians, with their large merchant vessels, collected lead from a town called Molybdine (the lead town) in Spain, situated beyond Tartessos, mentioned in Chapter 42 Tin. There was a further lead town, Molybdana, located on the lead island Plumbaria. The Greeks themselves were also able – even in Hekataios' time – to win lead from domestic lead deposits. They also knew the products *litharge* PbO, *white lead* (a basic lead carbonate) $Pb_3(OH)_2(CO_3)_2$ and *red lead* Pb_3O_4.

During the important silver winning connected with the Greek mines at Laurion and the Roman mines in Spain, lead was removed from silver by the cupellation process, described in Chapter 6 Silver. The lead passed into the slag, which was stored on the "slag mountains". In both Laurion and the Spanish Cartagena, the lead content of the slag was 6–12%. In late Roman time the slags were worked for lead.

The toxicity of lead made it suitable as a surface coating for vessels in the Mediterranean Sea. Lead prevented the growth of algae and other organisms on the hulls of ships. It was also observed in Roman history.

> *Hiero*, an officer under the Greek adventurer Pyrrhos, executed a military coup in Syracuse about 275 BC. In 265 BC he won a decisive victory over a pirate empire that had caused much suffering to the citizens of Syracuse. As a result, his grateful subjects proclaimed Hiero King of Syracuse. The newly chosen king had been aware of the importance of large, quick and safe vessels in the naval war, and he built a giant ship *Alexandreia* in 264 BC. The hull was covered with thin lead plate below the waterline. It was in the time of the First Punic War, in which Carthage and Syracuse were initially allied against Rome. Hiero however changed his position and decided that it would be wiser to be an ally of Rome than of Carthage. With his lead-covered ship he provided supplies and grain to the Romans while the Romans and Carthaginians were busy fighting each other.

43.2.3
Lead in Water Pipes and Kitchen Pans

In Roman lead manufacturing, the raw material was the slag from the manufacture of silver, mentioned above. In the Hoovers' translation[1] of Agricola's *De Re Metallica* [43.1], the manufacture of small litharge tubes with "the Roman method" is described in Figure 43.1. This lead oxide, litharge, could easily be reduced to lead metal for production of lead tubes and household utensils.

The big cities in all parts of the Roman Empire had a great demand for water. The citizens used water not only for drinking and cooking but also for public conveniences, for thermal baths and for fountains. Aqueducts had to be built to transport these enormous quantities of water. Lead tubes were used for branch pipes. In fact the Romans made lead into a metal for everyday use.

The manufacture of lead tubes was a manifestation of the Roman system and regulations. Molten lead was cast into plates with the length of 3 m and a thickness of

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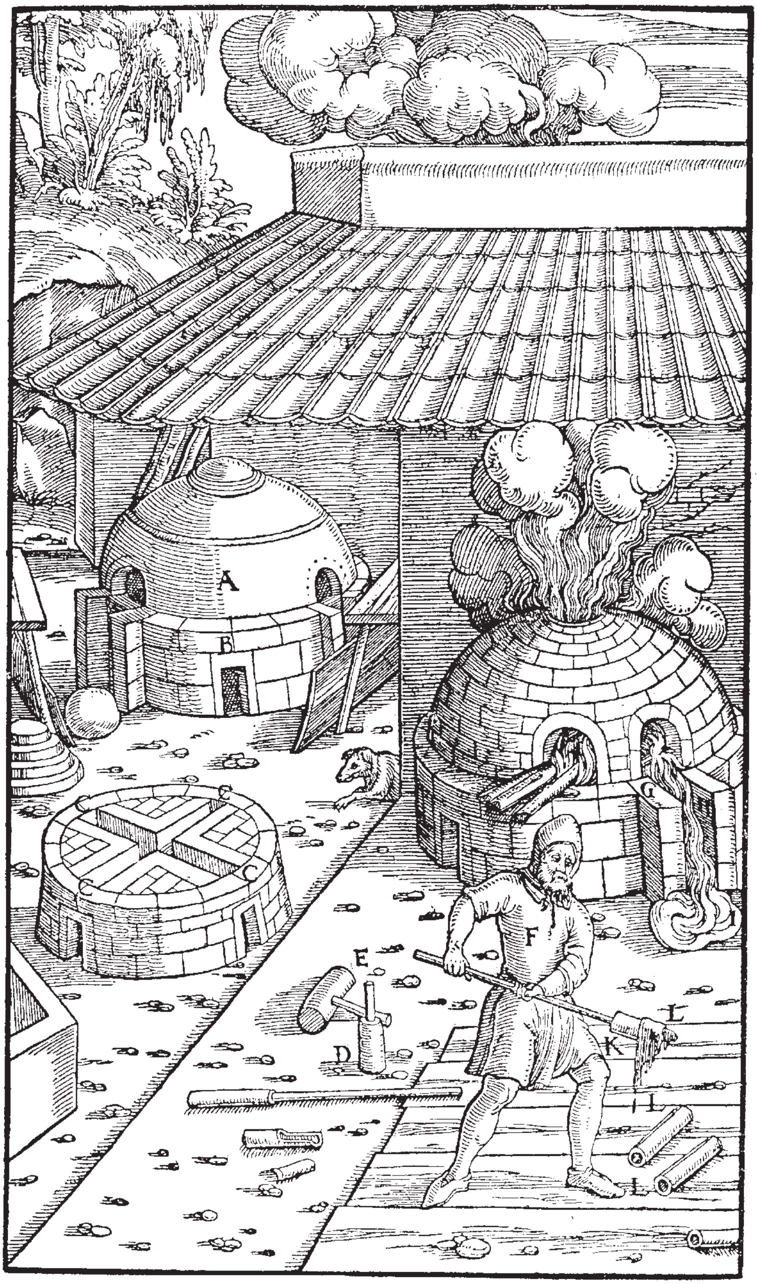
[1] A translation into English in 1912 by Herbert C. Hoover, mining engineer, and his wife Lou, geologist. In 1929 Herbert Hoover became the 31st President of the United States.



A—Chamber of the furnace. B—Its bed. C—Passages. D—Rammer. E—Mallet. F—Artificer making tubes from litharge according to the Roman method. G—Channel. H—Litharge. I—Lower crucible or hearth. K—Stick. L—Tubes.

Figure 43.1 The manufacture of lead oxide, litharge, in connection with the separation of lead and silver [43.1].

5–7 mm. Ten different plate widths were used for ten “standardized” tube sizes. The greatest and the smallest tube dimensions are shown in Table 43.1.

Table 43.1 Two standardized Roman lead tubes

Tube type	Plate width		Inner diameter of tube	Weight of tube
	inch[a)]	mm	mm	kg
100	100	1856	550	393
5	5	93	25	20

Source: cited from Gmelin Blei PbAl, p. 27.
a) Roman inches.

The plate was bent in its longitudinal direction over a mandrel (Figure 43.2a) and the forming was completed to a pear-shaped section (Figure 43.2b). Along the joint were laid two rows of moist clay, which were scraped away from the edges of the plates in order to expose clean metal. The clay was heated to dryness and hardness with glowing charcoal. Thus a mould was formed along the full length of the tube, into which liquid lead was poured. When solidified, a welded tube was obtained and ready for use.

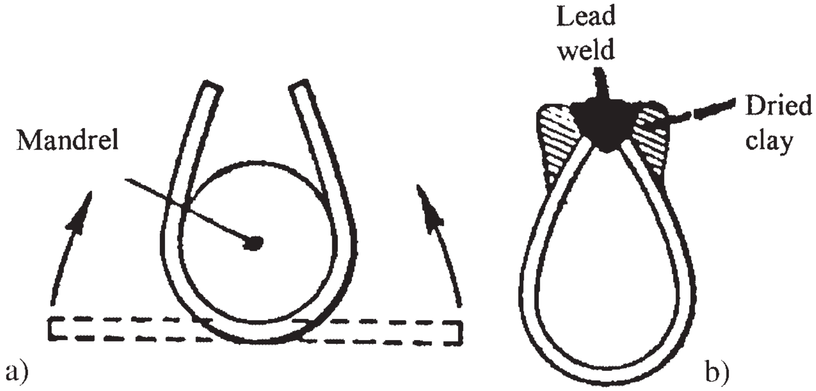


Figure 43.2 Roman manufacturing process of lead tubes for water.

The connection of tube to tube was made simply by putting one tube into the widened end of another and sealing the joint with molten lead. An outlet from a container to a local consumer was made according to Figure 43.3. A bronze tube through the container wall was combined with and soldered to a lead tube, widened at one end.

In Roman households, containers of copper or lead were used for boiling the juice out of grapes before the fermentation process. Lead pans were preferred because juice and wine got a better taste. At the excavations in Pompeii, containers, perma-

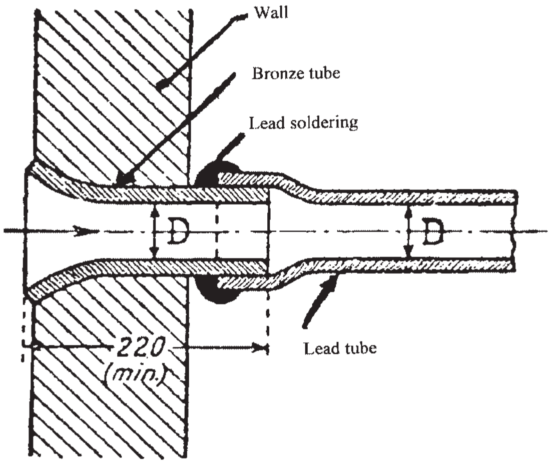


Figure 43.3 An outlet from a container to a local consumer.

nently built into the fireplace, were found. They were used for preparing aromatic wines and other hot drinks and soups. Pliny noticed that lead pans in reality could not be placed in open fires, because they melt. He added, however, that a pan does not melt if it is filled with a liquid. With certain astonishment he had observed that a copper coin, dropped into the liquid, leads to melting and formation of a hole just where the coin lies on the lead bottom.

43.2.4
Lead in the Armed Services

The catapult was a weapon for throwing large stones, burning fragments and so on against an enemy. Roman armies also utilized heavy lead shot in their catapults. It struck terror into enemy armies, still using stones in their missiles. Caesar mentions this in his description of the war against the Gallic tribes, 58–50 BC.

43.2.5
A Champion of the Environment in Antiquity

During the cupellation process, a great part of the lead was vaporized. In our present time we understand that this must have been unhealthy. Socrates also wrote that many people in the area around Laurion were sick. Roman engineers did not, however, pay any attention to warnings about the adverse influence of lead on health. Pliny, who was an ardent advocate of utilizing lead in water systems, supported them. One of his contemporaries, *Marcus Vitruvius Pollio*, was evidently of the opposite opinion. He was active as an architect in Rome during the decades BC. He is well known for his work, *De architectura libri decem*, dedicated to an un-named emperor, assumed to be Augustus. This great work (ten books about architecture, as its name implies) has had a profound influence on the understanding of ancient classical architecture until modern times. Vitruvius appears in his writing almost as a modern environmentalist and made this proclamation to people building water systems with lead tubes:

> Water conducted through earthen pipes is more wholesome than that through lead; indeed that conveyed in lead must be injurious because from it white lead is obtained, and this is said to be injurious to the human system. Hence, if what is generated from it is pernicious, there can be no doubt that itself cannot be a wholesome body.
>
> This may be verified by observing the workers in lead, who are of a pallid color; for in casting lead, the fumes from it fixing on the different members, and daily burning them, destroy the vigor of the blood; water should therefore on no account be conducted in leaden pipes if we are desirous that it should be wholesome. That the flavour of that conveyed in earthen pipes is better, is shown at our daily meals, for all those whose tables are furnished with silver vessels, nevertheless use those made of earth, from the purity of the flavor being preserved in them [43.2].

The powerful Roman Empire had to provide cities and garrisons with water. Lead was an ideal metal for that. It was available in abundance, and it was easy to manufacture and form using well-known techniques. The arguments of the environmentalists remained unheeded.

The leading families in Rome, being relatively wealthy, could afford to install lead-borne water in their homes and to have cooking utensils of lead. But that "advantage" was the cause of high infant mortality, mental retardation and sterility. In the analysis by historians of the decline and fall of the Roman Empire, *general lead poisoning* is a factor that should perhaps be taken into account.

43.2.6
Historical Lead Deposits

All the time up to the Middle Ages lead was a by-product in the working of silver ores. In the period AD 700–1200 mines were opened in the present Germany (Rhineland, Harz and Saxony), the present Poland (Silesia) and the present Czech Republic (Bohemia). The ores were mainly lead ores, but the mines were called silver mines. Lead, produced from these deposits, can now be found in decorative fixtures, roofs, pipes and windows in castles and cathedrals all over Europe.

In the USA the first lead mines were opened in 1621 and new deposits were found as settlement spread westwards. In the 19th century many great lead ore finds were made in different parts of the world, in Mexico and Australia among other countries. The breakthrough in the 1920s of the ore dressing technique by flotation made it possible to separate the different minerals in complex ores. This increased the number of workable lead deposits.

In Sweden a silver-rich lead ore was mined in Sala from the beginning of the 16th century but lead was not taken care of until the middle of the 18th century. Today Sweden is the largest lead producer in Europe, mainly due to the great deposit in Laisvall in the north of the country. Mining there began in 1943.

43.3
The Geology of Lead

43.3.1
The Mineral Galena

Galena PbS is the most important ore mineral of lead and an important source of silver. Galena occurs in limestone, dolomite and sandstone as dissemination in veins. Its crystals are cubic or octahedral. The mineral is bluish-gray, soft and heavy and has a shiny metallic luster. It is also called lead glance (Figure M70).

43.3.2
Lead Ores

Lead ores are mainly mined for lead, zinc and silver. They include, besides galena, also sphalerite ZnS, often also pyrite FeS_2 and/or pyrrhotite Fe_6S_7. Some notes about various lead ores are given in Table 43.2. The three first mentioned types account for the major part of lead production in the world.

Table 43.2 Some geological notes about important lead ores

Type of deposit and process of formation	Composition	Occurrence and examples
Massive sulfides, exhalites, formed by volcanogenic processes. Deposition has occurred on sea bottom	The ore often contains 1–1.5% Pb, 4–5% Zn and up to 30% Cu; furthermore, Ag 200 g/tonne and Au 3 g/tonne. Pyrite and/or pyrrhotite are also present	Hellyer in Australia. The Skelleftå deposits in Sweden
Sediments formed by the exhalation of hydrothermal fluids, rich in metals, onto the sea floor	The ores are composed of pyrite and/or pyrrhotite. They may contain ca. 4% Pb and 7 % Zn. The Cu content is low, less than 1%. Ag ca. 50 g/tonne	Some of the greatest lead deposits are of this type: Broken Hill and Mount Isa in Australia
Ore formed in water but in small depths. The ore mineral is found in contraction fissures in dolomite and limestone deposits	The ores are conglomerates pyrite and chalcopyrite, containing galena and sphalerite. The content of Pb+Zn is 3–10%. The amount of noble metals is low	West Fork, Sweet-water, Doe Runs in the Mississippi Valley. The ore type is also found in the Cracow region, Poland
Ores of sandstone type. Metals have been leached out from the bedrock and have been transported of the groundwater to quartzitic sandstones	Galena has been formed in a reducing environment. The ore analysis may be 2–5% Pb, 0.2–0.8% Zn, Ag 1–20 g/tonne	Bou-Sellam in Morocco. Laisvall in Sweden

Table 43.2 (continued)

Type of deposit and process of formation	Composition	Occurrence and examples
Hydrothermal solutions, containing lead and zinc, have come into contact with limestone or dolomite. The dissolved ions have reacted with the original rock and replaced some components in it	The ores are complex, containing many different minerals. Galena and sphalerite make them workable from an economic point of view. Due to the method of formation, the ores are found in different permeable structures in the rock	Cerro de Pasco in Peru. Tiontik, Gilman and Leadville in USA. Tsumeb in Namibia. Garpenberg in Sweden
The ore minerals occur in vein systems in different rocks	Coarse crystals of the minerals pyrite, chalcopyrite, galena, sphalerite and noble metals. The content of Pb+Zn is 10–30%	Taxco in Mexico. Freiberg in Germany. Coeur d'Alene in USA

43.4
World Production of Lead in Mines

Mining of lead is found in more than 40 countries. However, production is more concentrated than what this figure indicates, because 12 countries according to Table 43.3 account for about 90% of the world's production. The reserves are estimated at 64 000 ktonne (world total) of which Australia has 15 000 and China and the United States 9000 ktonne each.

Table 43.3 Lead ore production in mines (counted as lead) in the year 2001

Country	Production thousand tonnes	Percentage of total production	Country	Production thousand tonnes	Percentage of total production
Australia	714	23.18	Morocco	83	2.69
China	600	19.48	Korea North	70	2.27
United States	466	15.13	Poland	60	1.95
Peru	271	8.80	South Africa	51	1.66
Canada	149	4.85	Spain	49.5	1.62
Mexico	135	4.38	Other countries	336.5	10.91
Sweden	95	3.08			
			Total	3080	100

Source: ref. [43.3].

43.5
The Manufacture of Lead Metal

The ore is crushed and ground and separated into various mineral concentrates by flotation. The complex lead–zinc ores have played an important role in the development of the flotation technique. A lead concentrate with perhaps 77% Pb is roasted to oxide, in general on a sinter band, a process in which sulfur is removed as sulfur dioxide. Limestone is added for slag formation and the sinter is reduced by coke in a shaft furnace. An alternative method is to use a rotating converter furnace, from which the sulfur dioxide can be used for sulfuric acid production. This is good for the environment and good for the economics of the process.

Lead ores, except those from the Mississippi Valley, are an important source of silver. Silver is collected in the crude lead and removed in the refining process, as also are other metals such as copper, arsenic, antimony, bismuth, zinc, cadmium, nickel, tin, gold and platinum. The refining of lead is complex and a number of processes and techniques are involved. There are two methodologies utilized: one is electrolysis, in which the crude lead is anodically dissolved and precipitated on cathodes; the other is pyrometallurgical, including cupellation or distillation processes. Lead is sold as *refined lead* with a purity of 99.99%.

Besides this *primary lead* (manufactured from ore), *secondary lead* (remelted lead scrap) is of increased importance, based as it is mainly on the recycling of batteries from cars. At the beginning of the 1990s the total annual lead production in the world was 5.5 million tonnes, of which 2 million tonnes (thus 36%) were secondary. In 2001 the corresponding figures were 6.5 million tonnes (total), 2.8 million tonnes (secondary) and 43%. In some countries the share of the total lead production attributed to secondary lead is very high, as is shown in Table 43.4.

Table 43.4 Produced lead metal and share of secondary lead in some countries in the year 2001

Country	Total thousand tonnes	Secondary thousand tonnes	Secondary percentage of total
United States	1390	1100	79.1
China	1180	100	8.5
Germany	374	142	38.0
United Kingdom	366	163	44.5
Australia	303	33	10.9
Japan	302	175	57.9
Canada	283	137	48.4
France	238	142	59.7
Italy	203	121	59.6
Korea South	180	10	5.5
Mexico	150	10	6.7
India	94	20	21.3
Sweden	82	45	54.9
Korea North	75	5	6.7
Other countries	1250	–[a]	–[a]
World total	6470	2790[b]	43.1

Source: ref. [43.3].

a) Many reported values are undifferentiated regarding secondary/primary lead.

b) Some 245 thousand tonnes are undifferentiated.

43.6
Lead Is Still Used

Lead is toxic and is avoided where possible for environmental reasons. In spite of that, it is still used so much that, counted in tonnes, it is number five among the metals. Only iron, copper, aluminum and zinc are used more. There are in fact applications for which it is difficult to replace lead metal. In all applications where lead is utilized, careful supervision of the environmental circumstances is necessary.

43.6.1
Lead in Crystal Glass

If soda is replaced by potassium carbonate in glass manufacture and lead oxide is added, the light refraction properties of the glass are improved. The *whole crystal glass* contains at least 24% lead oxide, while the *semi-crystal glass* has at least 10% in all of lead, potassium and zinc oxides. Some characteristic physical properties of the different glass types are shown in Table 43.5.

Lead glass has been appreciated as crystal glass due to its refraction, brightness and weight. The glass is also used for optical applications, as well as for cathode ray tubes

Table 43.5 Physical properties of lead glass compared to other glass types

Glass type	Density g/cm³	Refractive index	Coefficient of thermal expansion
Soda glass 14% Na_2O, 10% CaO	2.5	1.5	8.5×10^{-6}
Borosilicate glass 12% B_2O_3, 2.5% Al_2O_3	2.35	1.45	4×10^{-6}
Lead glass, whole crystal 30% PbO, 13% K_2O	2.9	1.6	10×10^{-6}

in TV sets and for fluorescent tubes. Due to the ability of lead to absorb X-ray radiation, lead glass is also used in glass for radiation protection.

Environmental objections have been met with the argument that lead is so fixed in the glass structure that no dangerous lead leakage occurs into drinks of juice or wine. On the other hand, severe environmental objections can be raised against the use of lead oxide in the high-temperature manufacturing process for crystal glass. Alternatives are being developed [43.4]. Potassium, barium, strontium and zinc have been tested as lead alternatives for semi-crystal optical glass, used also for fluorescent tubes and light bulbs. In cathode ray tubes zirconium addition has been examined. All these glass alternatives, however, are more difficult to process.

For whole crystal glass no alternative seems to be possible as the international quality systems specify a lead oxide content of 24% or more. Until these specifications are changed, the manufacture of glass with high lead levels will continue.

43.6.2
Metallic Lead

Elements with high atomic weights are especially suitable as absorbers for X-rays and gamma radiation. For that reason, lead has an important use as protection against radiation in laboratories and hospitals in which X-ray methods are utilized, and lead protection is used in the nuclear industry. Lead foils are used, for similar reasons, for packing of radioactive preparations and X-ray films.

Electrical cables were earlier sheathed mainly with lead. Nowadays sheathing is made with plastic, at least for cables above ground. For subterranean and submarine cables, the demand for good corrosion resistance has however made lead necessary. This lead is often alloyed with about 1% antimony.

The noise-absorbing ability of lead has been observed by architects. Thin lead foils in interior hotel walls and in office walls make small wall thickness possible, with corresponding increase of the floor space. Lead has also been tested as a shock absorber for buildings in earthquake regions.

Molten lead has a very good heat transfer ability and is used in the continuous heat treatment process for the manufacture of high-carbon steel wire. This process demands a very rapid heating from room temperature to 450°C (tempering after hardening) and a very quick cooling from 900°C to 550°C (so-called *lead patenting*). The latter is shown in Figure 43.4. The wire passes through a bath of molten lead. Because of the environmental problems with lead, the wire industry has made every effort to find an alternative for the lead patenting process.

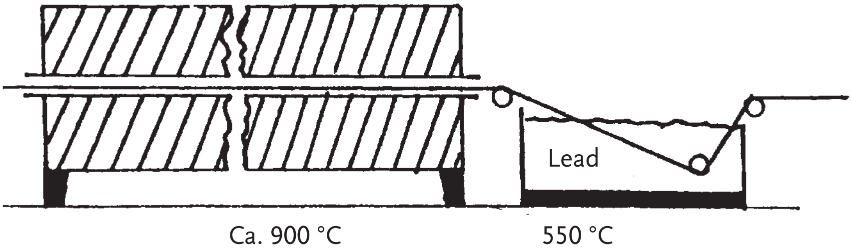


Figure 43.4 So-called patenting of steel wire with high carbon content, 0.5–1% C. This heat treatment gives the steel a proper structure for further drawing and is used for the manufacture of spring wire, rope wire and cord wire for steel radial tires.

43.6.3
Lead in Alloys

Bearing alloys have to withstand sliding contacts under pressure. Three lead–tin bronzes are used for this purpose:

- CuPb10Sn with 10% Pb, 10% Sn (and 80% Cu);
- CuPb15Sn with 15% Pb, 8% Sn, 1% Ni (and 76% Cu);
- CuPb20Sn with 20% Pb, 4% Sn, 2% Ni (and 74% Cu).

Lead is also a component in some steel and brass types:

- free cutting steel with 0.3% Pb and 0.2% S;
- brass with good machinability due to a lead content of 1–3%.

Lead improves machinability during turning, drilling and milling due to the fact that it stays undissolved as small “islands” in the metal structure. The lead islands become fracture positions, the chips break easily and balls of long chips are avoided. This makes faster machining possible in modern automatic machines.

Alloying with antimony can strengthen the soft lead metal. Lead alloys with 2–11% antimony are called *hard lead*.

The high density of lead has been the reason for its use in *ammunition*. Lead shot is not made of pure lead but of lead alloyed with 1–8% antimony. The shot is produced by dropping the molten alloy through holes in a pan. Often old mines are utilized to let the lead alloy “rain” a long distance to form drops. A small arsenic content in the alloy influences the surface tension and improves the roundness of the shot. The use of lead shot for bird shooting has been very much criticized. Birds, especially ducks, that have escaped hunting mistake the shot left behind for grains of corn or pebbles. The shot will accumulate in the crop, giving rise to lead poisoning. For that reason, bird shooting with lead shot is banned in regions with low water levels. The use of lead rifle bullets has caused an accumulation of lead in the embankments of the shooting ranges and leakage of lead into the groundwater. An alternative for rifles is bullets made of copper. It has been difficult to develop alternatives for lead shot with sufficient weight and formability. Steel shot is used, and bismuth and tungsten have both been tested.

Type metal was an alloy with low melting point that was utilized to make the type for printing. The composition may be 81% lead, 15.5% antimony and 3.5% tin. The molten alloy expands on solidification and thus fills the moulds very well. This gives the type sharp edges. The technique has entirely been replaced by new printing methods.

43.6.4
Lead in Accumulators

43.6.4.1 Primary and Secondary Cells

A galvanic cell, in which chemical energy is transformed to electrical energy, is called a *primary cell*. It has two electrodes at different potentials. The original primary cell was the voltaic pile in the year 1800. It contained copper and zinc electrodes in contact with intermediate disks of cloth, soaked in brine or acidified water. Another primary cell, used very much also nowadays, is the Leclanché cell, described by Georges Leclanché (1839–1882). The two electrodes are carbon and zinc, with an ammonium chloride electrolyte. The carbon electrode is mixed with manganese dioxide. This cell is the common flashlight battery. Primary cells are discharged in use but not recharged.

The lead battery of the Planté type (1860) and the nickel–cadmium battery are *secondary cells*, accumulators or storage batteries. They are charged with electrical energy from the beginning and are discharged during use. Then they are recharged and used again. Utilization of nickel–lanthanum alloys and lithium materials has made higher energy densities possible. For vehicles and their starting–lighting–ignition (SLI) functions, the lead accumulator has retained its dominant position.

43.6.4.2 The Largest Lead User

After World War I, demand for lead increased considerably as motorized vehicles, automobiles and trucks had to be equipped with batteries for SLI. In addition, terne metal for gasoline tanks increased lead consumption. Terne metal is made of steel sheet, coated on both sides with a terne alloy, 80% lead and 20% tin.

In the lead accumulator the electrode plates are lead grids, filled initially with a paste of lead oxide PbO. They are placed in an electrolyte of dilute sulfuric acid. One electrode plate is marked “plus”, the other “minus”. The battery is charged with DC current from a rectifier. In this process the plus plate is connected to the positive pole of the rectifier, the minus plate to its negative pole. On the plus plate the lead oxide is changed to lead dioxide PbO_2, and on the minus plate metallic lead is formed. Between these plates, the voltage is 2 V. Six cells, connected in series, thus give the 12 V we know from the automobile lead battery. When the battery is used, as for instance to start the car, the following reactions occur:

- at the plus plates
  $PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$
- at the minus plates
  $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

The electrons move in the outer connection from the minus to the plus pole and do their job to actuate the starter motor.

Lead sulfate is formed on both types of plates and sulfuric acid is consumed. The density of the sulfuric acid can thus indicate the charge/discharge condition. In a charged battery the electrolyte density is 1.2–1.3 g/cm^3. The operation of a lead accumulator is disturbed by contamination by certain elements in the electrolyte, especially chlorides, iron, manganese and platinum. Because of that, replenishment of electrolyte must always occur with ion-free water.

In normal motor operation the generator of the engine recharges the battery continuously. A completely discharged battery has to be charged from a rectifier. The reactions above then occur in the opposite direction, from right to left.

The reliability of the lead accumulator has widened its field of application. In industries with large daily variations regarding consumption of electrical energy, lead accumulators can be used for energy storage. Various vehicles, such as forklift trucks and baggage trucks, utilize lead batteries. Emergency sources of energy in hospitals and in large telephone and computer installations are also equipped with lead batteries.

Worn-out lead batteries are nowadays collected to a great extent and the lead is recycled. This is the main source for secondary lead manufacture.

43.6.5
Tetraethyl Lead for Knocking Protection – A Use That Is Disappearing

A conventional car engine (an Otto engine) has two valves per cylinder, one inlet valve and one exhaust valve. In the intake stroke the air–fuel mixture is sucked into the cylinder by the piston sliding downward. In the next stroke the piston is sliding upward and compresses the mixture. In the upper position the mixture is ignited and the burning mixture expands, moving the piston back. Finally the burned gas is ejected through the exhaust valve. In modern car engines, the mixture of petrol vapor and air is compressed before it is sparked, in order to get the maximum energy out of the burning fuel. When the fuel burns, a flame front is assumed to advance from the spark plug in an orderly fashion. Radiation from the flame may raise the temperature of the unburnt mixture and initiate a sudden detonation. The engine is “knocking”. Branched hydrocarbons resist this pre-ignition better than unbranched ones. Fuel mixtures are given *octane ratings*, depending on their knocking tendency. A special, branched hydrocarbon, an isomer of octane, is given the octane rating 100. A real petrol mixture may have a low octane rating and a high tendency for knocking. Adding of tetraethyl lead $Pb(C_2H_5)_4$ (TEL) improves the fuel. It decomposes at the flame front and leaves a fog of lead oxide dust, which reflects much of the heat back into the burnt gas. Consequently, high compression ratios can be tolerated. The lead released from car exhausts is however dispersed into the environment, causing health problems. An additional problem is that catalytic converters – for removal of carbon monoxide CO, nitrogen oxides NO_x and unburned hydrocarbons $(CH)_n$ – are poisoned if leaded petrol is used. The catalyst and its function is treated in Chapter 32 Platinum Metals.

The development of new, lead-free petrol and new engine designs have eliminated the need for anti-knocking additives, and TEL is being phased out. This has led to an obvious improvement of the environment. The exhaust fumes are free of lead and have very much reduced contents of CO, NO_x and $(CH)_n$ due to the catalytic action. In modern engines, with a great number of valves in each cylinder, the flame front advances properly. High compression can be used without risk of knocking (Figure 43.5).

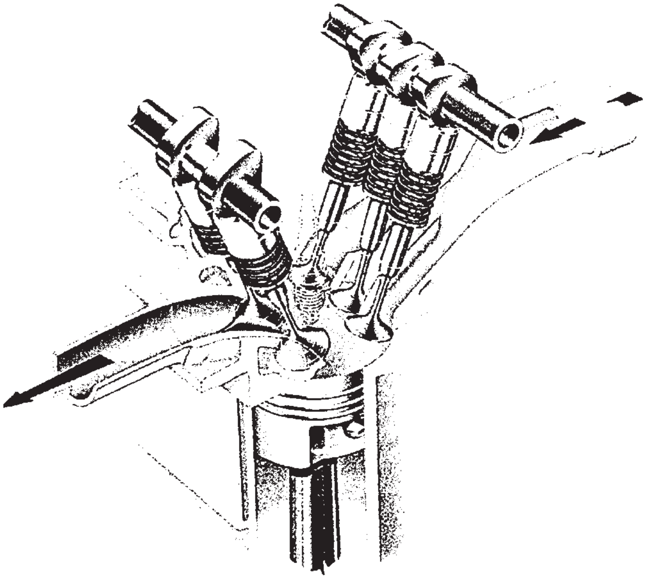


Figure 43.5 A recently developed engine with five valves in each cylinder. The engine can work with high compression without knocking, even if lead is not added to the petrol.

43.6.6
Paints – With and Without Lead

White lead, the basic carbonate, $Pb_3(CO_3)_2(OH)_2$, was a commonly used pigment for paints. It is no longer used indoors. It has also been replaced for outdoor painting of window frames. The toxicity of lead can be observed in this application. Nowadays, when white lead is avoided, black mildew stains soon develop on frames, which the older paint prevented, as the mould fungus was poisoned by the lead. *Red lead* Pb_3O_4 is still used as an orange-red pigment for outdoor painting and as an anticorrosive agent for steel constructions.

43.6.7
Environmental Actions Achieve Results

Figure 43.6 shows how the use of lead for storage batteries increased during the 20 year period from 1975 to 1994. This indicates a raised use of automobiles and other vehicles. In spite of that the usage of lead in many other applications has decreased as a result of environmental pressure. This is clearly manifested in the reduced shares of lead in petrol and in sheathed cables. Environmental actions have not resulted in decreased lead consumption but rather in a changed pattern, exemplified by the fact that, of all the lead used in the USA in 2001, 96% was for storage batteries.

43.7
Why Is Lead an Environmental Problem?

Of the heavy metals, lead, cadmium, tin and iron, the first two are toxic, the last two are not. We accept tin as a metal coating in contact with foodstuffs, and iron is even vital for human beings and mammals. The difference is due to the fact that lead and cadmium are markedly chalcophilic[2] (occur as sulfides in nature) while tin and iron are lithophilic (occur mainly as oxides in nature). Like all chalcophilic elements, lead has a strong tendency to bind sulfur. That is the reason for its toxicity.

Lead that is taken up by an organism will combine strongly with the hydrogen sulfide groups HS^- in enzymes. This disturbs their vital functions. In these and other connections, lead competes with essential elements, such as calcium, zinc and copper. It also causes anemia as it inhibits the synthesis of iron-containing heme, giving rise to a deficiency of hemoglobin in the blood. This causes tiredness and weakness, as already Vitruvius Pollio had observed, two thousand years ago (see section 43.2.5). For children, permanent exposure can lead to impairment of learning and to behavior disturbances. Lead uptake occurs mainly through the lungs but lead from tetraethyl lead can also pass through the skin. The residence time of lead in the body is very long. Present-day treatment of lead poisoning includes treatment with EDTA.

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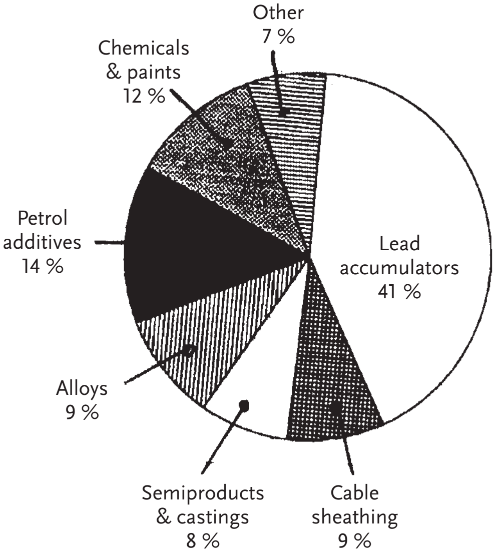
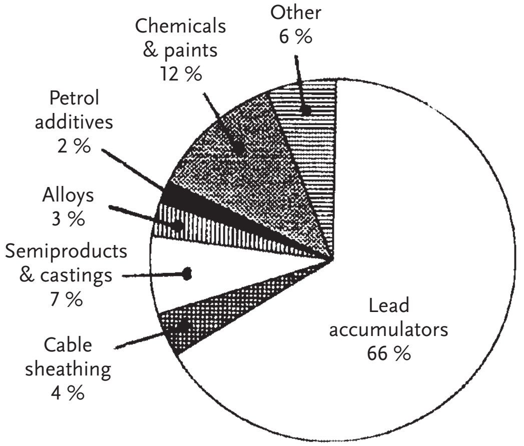
[2] For more about chalcophilic and lithophilic elements, see Chapter 4 Geochemistry.



a) Consumption in 1975 by product, in total 3100 tonnes of lead



b) Consumption in 1994 by product, in total 4500 tonnes of lead

Figure 43.6 The use of lead for different purposes in the West in 1975 and 1994. The increase in the share of lead for accumulators is obviously due to the increased total number of vehicles. In spite of that, lead in petrol has decreased remarkably. These two trends have continued over the turn of the century. In the USA the share of lead was 96% for storage batteries in 2001. Source: Geological Survey of Sweden PM 1995: 5 with permission.

This molecule forms a stable chelate complex with lead, which is excreted in the urine.

For people working with molten lead, as in the continuous heat treatment of steel (see Figure 43.4), it is mainly not the vapors from the molten metal that are dangerous. Much more severe is the health risk arising from lead oxide, formed on the liquid metal surface at high temperature. If it is ingested with food, snuff or cigarettes, the blood lead content increases considerably. Thus personal care is of great importance. Nail-biters are not allowed to be operators at a lead furnace. As mentioned above, the steel wire industry makes great efforts to find alternatives to the lead patenting process.

Different environmental aspects of lead are given in ref. [43.4].

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43.3 Gerald Smith, Lead chapter in US Geological Survey Mineral Commodity Summaries 2002, pp. 94–95, and Lead chapter in US Geological Survey Minerals Yearbook 2001, Vol. I, Metals and Minerals, pp. 44.1–44.10, http://minerals.usgs.gov/minerals/pubs/commodity/lead

43.4 Nordic Councils of Ministers, *Lead Review*, January 2003, http://www.norden.org/miljoe/uk/NMR_Lead.pdf

44
Nitrogen

44.1 N
Facts about Nitrogen

44.1.1 N
The Element

Symbol:	N
Atomic number:	7
Atomic weight:	14.01
Ground state electron configuration:	[He]$2s^22p^3$
Crystal structure:	Hexagonal hcp with $a = 3.86$ Å, $c = 6.27$ Å. (From 35 K to mp.) Below 35 K the structure is cubic with $a = 5.64$ Å.

44.1.2 N
Discovery and Occurrence

Discovery: Daniel Rutherford in Scotland discovered nitrogen in 1772. Scheele, Priestley and Cavendish discovered the element independently at about the same time.

Important raw materials: The atmosphere with 78% nitrogen by volume.
Sodium nitrate $NaNO_3$ (Chile saltpeter).

Ranking in order of abundance in earth crust:	34–35
Mean content in earth crust:	19 ppm (g/tonne)
Mean content in oceans:	0.5 ppm (g/tonne)
Residence time in oceans:	$2 \cdot 10^6$ years
Mean content in an adult human body:	$2.6 \cdot 10^4$ ppm = 2.6%
Content in a man's body (weight 70 kg):	1.8 kg

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44.1.3 N
Chemical Characterization

Nitrogen is a colorless, odorless and non-toxic gas. Most of the nitrogen used in the chemical industry is obtained by the fractional distillation of liquid air. It is then used to synthesize ammonia. From ammonia, a wide variety of important chemical products are prepared, including fertilizers, nitric acid, urea, hydrazine and amines. Nitrogen is an important element in plant nutrition but atmospheric nitrogen is too inert to be absorbed by vegetation. Certain bacteria in the soil convert nitrogen to nitrate that can be utilized by the plants, a process called nitrogen fixation. Nitrogen in proteins is an important constituent of animal tissue.

Oxidation states:

Oxides of nitrogen with N^{I} as in N_2O, N^{II} as in NO, N^{III} as in N_2O_3, N^{IV} as in NO_2 and N^{V} as in N_2O_5

Nitrogen hydrides with N^{-III} as in NH_3 (ammonia), N^{-II} as in N_2H_4 (hydrazine) and N^{-I} as in NH_2OH (hydroxylamine). In hydrazoic acid HN_3 and with salts azides N_3^-, nitrogen has formally the oxidation state –1/3 (mean).

Ionic nitrides with N^{-III} as in Li_3N, AlN, and Mg_3N_2;

Covalent nitrides as BN and P_3N_5;

Interstitial nitrides as TiN and VN

Ionization energy (kJ mol^{-1}):

$N(g) \rightarrow N^+(g) + e^-$	1402
$N^+(g) \rightarrow N^{2+}(g) + e^-$	2856
$N^{2+}(g) \rightarrow N^{3+}(g) + e^-$	4578
$N^{3+}(g) \rightarrow N^{4+}(g) + e^-$	7475
$N^{4+}(g) \rightarrow N^{5+}(g) + e^-$	9445
$N^{5+}(g) \rightarrow N^{6+}(g) + e^-$	53 267

Electron affinity (kJ mol^{-1}):

$N(g) + e^- \rightarrow N^-(g)$
+7

Standard reduction potential:		
	$NO_2(g) + H^+(aq) + e^- \rightarrow HNO_2\ (aq)$	$E^0 = +1.07$ V
	$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$	$E^0 = +0.94$ V
	$HNO_2(aq) + H^+ + e^- \rightarrow NO(g) + H_2O(l)$	$E^0 = +0.996$ V
	$N_2(g) + 4H_2O(l) + 4e^- \rightarrow 4OH^- + N_2H_4(aq)$; [alkaline solution]	$E^0 = -1.16$ V

Electronegativity (Pauling): 3.04

Radii of atoms and ions: (WebElements™)		
	Atomic:	65 pm
	Covalent:	75 pm
	Van der Waals	155 pm
	N^{3-} (4-coordinate, tetrahedral):	132 pm
	N^{3+} (6-coordinate, octahedral):	30 pm
	N^{5+} (6-coordinate, octahedral):	27 pm

44.1.4 N
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
1.2506 kg m^{-3} 1.25 g/l	0.97	63.29 K –209.86 °C	77.4 K –195.8 °C	1040 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

73 K	173 K	273 K	373 K	1273 K
–	0.0159	0.024	0.0309	0.074

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K)

a	b	c
28.58	$3.77 \cdot 10^{-3}$	$-0.50 \cdot 10^5$

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.4 (278–287 K)

Solubility in water m^3 gas at STP per m^3 water

273 K	293 K	313 K	333 K	353 K	373 K
0.0235	0.0156	0.0118	0.0103	0.0096	0.0095

Mass magnetic susceptibility χ_{mass} at 293 K	$-5.4 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	diamagnetic (as susceptibility is negative)
Critical point:	T_c 126.3 K T_p 3.40 MPa

44.1.5 N
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	0.719 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	5.58 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	473 $kJmol^{-1}$
Entropy S^0 at 298 K	191.6 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
29.10	29.12	30.11	32.70	35.97	36.61

44.1.6 N
Nuclear Properties and X-ray

Isotope range, natural and artificial	11–22

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{14}N	Stable	99.63	1+	0.4038
^{15}N	Stable	0.37	1/2–	–0.2832

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{14}N	^{15}N
Reference compound	$CH_3NO_2 + C_6D_6$	
Frequency MHz (^1H = 100 MHz)	7.226	10.137
Receptivity D^P relative to ^1H = 1.00	$1.00 \cdot 10^{-3}$	$3.82 \cdot 10^{-6}$
Receptivity D^C relative to ^{13}C = 1.00	5.73	0.0218
Magnetogyric ratio, radT^{-1}s^{-1}	$1.934 \cdot 10^7$	$-2.713 \cdot 10^7$
Nuclear quadropole moment, barn	0.020	–

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
6	C	0.277
7	N	0.393
8	O	0.525

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	7.48
17.37 keV ($MoK\alpha_2$)	0.853

Neutron absorption	**Thermal neutron capture cross section**	2.00 barns

44.2
Discovery of Nitrogen

44.2.1
Who Discovered Nitrogen?

Joseph Black (1728–1799) was a professor of chemistry in Edinburgh and Glasgow. His large contributions to the development of chemistry and physics, and his discovery of magnesium, have been described in Chapter 14 Magnesium and Calcium. In his textbook *Lectures on the Elements of Chemistry*, Vol. 2, edited posthumously in 1803, he mentions the work of both Carl Wilhelm Scheele and Daniel Rutherford (Black's own student in Edinburgh) in the discovery of nitrogen.

In fact two (or even three) further pretenders to the "throne" of priority should be mentioned. In March 1772 Joseph Priestley read a paper[1] to the Royal Society in London and mentioned the work of Henry Cavendish:

> ... the Honorable Mr. Cavendish had accounted for experiments in which he had led common air through a red-hot iron tube, filled with charcoal. Fixed air (carbon dioxide) had been formed. After absorbing that gas in soaps of ley the reduced air volume not only extinguishes flames but is also noxious to animals.

Priestley also accounts for other experiments, to all appearances his own:

> If common air is heated over a metal, instead of charcoal, the gas does not make limewater turbid. When the gas volume is measured (over mercury) before and after the high temperature reaction, the volume diminishing is 1/5. The air residue, after burning, is somewhat lighter than common air.

Even Leonardo da Vinci (1452–1519) had found that air is made up of different components. Air is consumed at breathing and burning, but not totally. He also clearly described the similarity between burning and breathing:

> Where a flame cannot burn an animal cannot breathe and live.

In Uppsala, Scheele let flies, shut in a glass jar, consume oxygen and die. In England, Cavendish, Rutherford and Priestley performed corresponding experiments. Especially well known were Priestley's experiments with mice. The scientists were on the same track, but Scheele in Sweden worked independently of his English colleagues[2]. It was clarified that when the animal had died the air volume had decreased somewhat. The gas residue lost more of its volume when the carbon dioxide was removed by alkali. A burning candle was extinguished in this gas residue and the wick

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[1] Observations on different kinds of air, *Phil. Trans.* 62 (1772) 147–256.

[2] Biographical information about Cavendish is given in Chapter 9 Hydrogen, about Scheele in Chapter 27 Manganese, and about Priestley in Chapter 47 Oxygen.

stopped glowing immediately. The interpretation of the results was made in the spirit of the phlogiston theory:

> Poisonous air is air saturated with phlogiston.

So it is impossible to give a single person priority in the discovery of nitrogen. The history of its discovery should be summarized as follows. Air, which was *one* element in antiquity, remained as a uniform substance in the public consciousness up to the middle of the 18th century (Leonardo was an exception in this as in many other respects). The fact that air is composed of two different elements, nitrogen and oxygen, was elucidated by several scientists at the beginning of the 1770s. It seems wise to agree with Mary Weeks, saying that Daniel Rutherford discovered nitrogen in 1772, with the addition that Scheele, Priestley and Cavendish discovered it independently at about the same time.

44.2.2
Daniel Rutherford in Edinburgh

Sir Walter Scott, the author of *Ivanhoe* and other historical novels, was born in 1771. In his autobiography (1808) he described, with pride, that his mother's half-brother, Daniel Rutherford, was professor of botany at the University of Edinburgh and that he, in his thesis in 1772, had submitted conclusive proofs for the existence of a new gas. The celebrated novelist wrote in the retrospective portrait of his life that his uncle had been one of the best chemists in Europe.

Daniel Rutherford, born in 1749, was a contemporary of Carl Wilhelm Scheele, but in many respects the opposite of his Swedish colleague. Scheele was the incomparable chemist and experimentalist but did not have a broad general education. Rutherford, on the other hand, with classical education and manner, was very interested in English literature and Scottish history. Perhaps he exerted an influence on the future author. He had however studied chemistry with Professor Joseph Black (the discoverer of magnesium) in Edinburgh. There was one interest that Rutherford and Scheele did have in common, namely the investigation of the chemistry of gases. Professor Black himself had observed that, when a substance burns in air, and the carbon dioxide formed (fixed air) had been absorbed in caustic soda, a certain part of the original air remains. He commissioned Daniel Rutherford to make a detailed investigation of this gas residue as part of a planned thesis for a doctorate in medicine [44.1]. In his dissertation Rutherford describes *mephitic air* and means primarily "fixed air" (carbon dioxide) obtained after burning carbon in air. He notes that this mephitic air can be obtained from limestone by calcination or by dissolving it in acid. Mephitic air is fatal to animals, extinguishes fire and flame, and is attracted with great affinity by quicklime and alkaline salts. In this part of the dissertation no discovery of the new gas, nitrogen, can be tracked. However he reports another finding, expressed by his statement that:

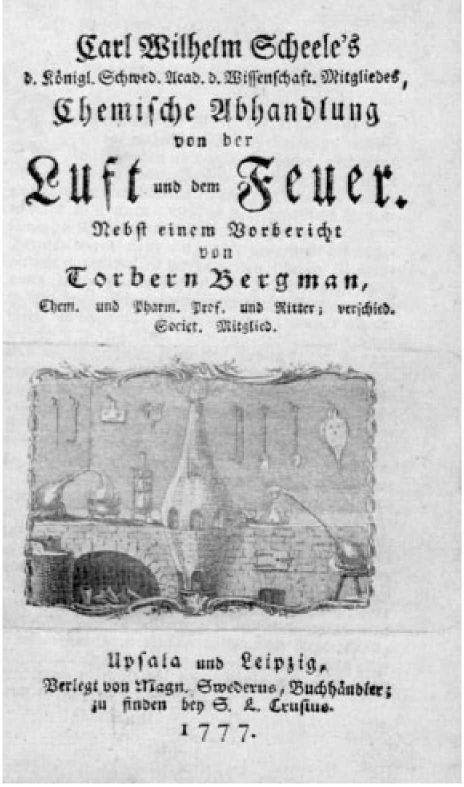
> … by the respiration of animals, wholesome and good air not only becomes in part mephitic, but it also suffers another singular change. For, after all the mephitic air has been separated and removed from it by means of caustic lye,

> still what remains does not become in any way more wholesome; for although it produces no precipitate in lime-water it extinguishes both flame and life no less than before ... From these things it follows that malignant air is composed of atmospheric air united with phlogiston and, as it were, saturated.

Obviously Rutherford had come to the opinion that common air is composed of one substance (oxygen) that can take part in combustion reactions by absorbing phlogiston from the burning carbon or metal, and a second substance (malignant air, nitrogen) that is saturated with phlogiston and thus is incapable of supporting burning and breathing. It is thus correct to say that he was one of the discoverers of the element nitrogen.

44.2.3
Air and Fire

Carl Wilhelm Scheele was obsessed by the idea to expose the secret of the air. He published his great work *Chemische Abhandlung von der Luft und dem Feuer* (*Air and Fire*) in German in Uppsala and Leipzig in 1777, in English in 1780, and in French in 1781. Its title page is shown in Figure 44.1.



Carl Wilhelm Scheele's
d. Königl. Schwed. Acad. d. Wiſſenſchaft. Mitgliedes,
Chemiſche Abhandlung
von der
Luft und dem Feuer.
Nebſt einem Vorbericht
von
Torbern Bergman,
Chem. und Pharm. Prof. und Ritter; verſchied.
Societ. Mitglied.

Upſala und Leipzig,
Verlegt von Magn. Swederus, Buchhändler;
zu finden bey S. L. Cruſius.
1777.

Figure 44.1 The title page of Scheele's large publication *Air and Fire*.

The first edition had been delayed. Probably in 1772 he had already succeeded in separating the two components of air, nitrogen and oxygen. He placed flies in a closed jar and arranged fairly acceptable terms for the poor creatures by also installing a paper smeared with honey. But anyhow, after two days the flies had died. One fourth of the air had been transformed to carbon dioxide. When this gas was removed by limewater, a residue of nitrogen or "rotten air" remained. This proved that the air contains one substance, oxygen or "flame air", essential for breathing. No doubt Scheele has to be given priority, even if divided, for the discovery of both nitrogen and oxygen.

Scheele's pioneering work was a great achievement, even more so because of the very primitive equipment available in his laboratory (Figure 44.2). For his experiments with gases, ox bladders and common bottles were utilized.

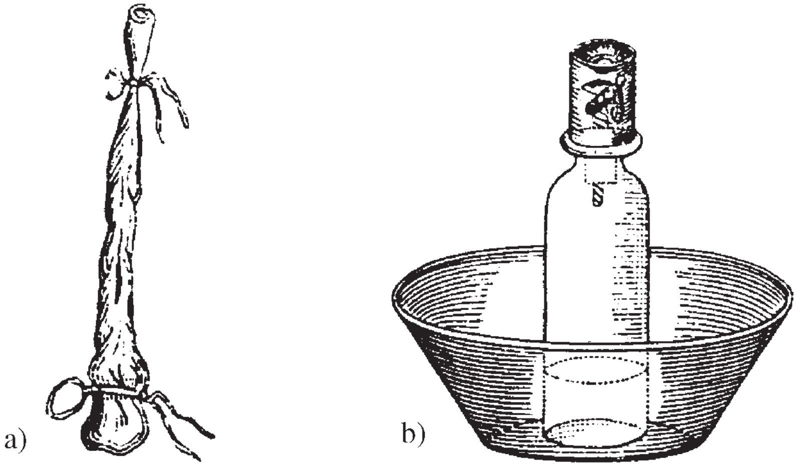


Figure 44.2 Simple scientific equipment available in the 18th century. (a) Scheele's carbon dioxide apparatus. (b) Flies show that it is impossible to breathe in "rotten air". (From Scheele's *Air and Fire*.)

44.3
Occurrence of Nitrogen

44.3.1
Nitrogen in Aquatic Ecosystems

In the oceans, nitrates, nitrites and ammonium compounds are utilized as nutritive salts for plankton. As a result the surface layers of the seas are often lacking in nitrogen compounds. At depth the contents of these compounds are higher, maybe 0.3–0.5 ppm. If the nitrogen content of the surface layer increases, the production of plankton also increases, which can give rise to a disturbing algal "bloom". Augmentations of this type occur after the disturbance of water bodies by storms, resulting in deep water moving upward to the surface layer.

Another and more severe cause of algal blooms is the supplying of nitrates and ammonium salts leached from surrounding areas under cultivation. The reactive nitrogen ought to be retained in the nitrogen cycle from earth to crops, to animals, to human beings and back to earth. However, great quantities of nitrogen leach out and escape, causing eutrophication and damage to aquatic, terrestrial and marine ecosystems due to lack of oxygen, especially in coastal regions. It is estimated that only one-quarter to one-third of the nitrogen applied as fertilizer is actually absorbed by crops. Significant costs are associated with such inefficient use, and the American Association for the Advancement of Science (AAAS) recently paid attention to the problem in an international conference. The conference theme was "Meeting the nitrogen management challenge: Arresting the nitrogen cascade", and new strategies and opportunities for improved nitrogen management were treated [44.2].

44.3.2
Saltpeter – Potassium and Sodium

Potassium nitrate KNO_3, saltpeter, was won in very small quantities from the soil under farmers' cattle barns. From this "nitrous" earth, mixed up with the animals' urine, limited amounts of saltpeter were prepared as described in Chapter 11 Sodium and Potassium. The material was reserved for the manufacture of gunpowder and became of strategic importance. Nowadays potassium nitrate can be manufactured from sodium nitrate, Chile saltpeter. The mineral saltpeter is also found as crusts on the surfaces of rocks and as a component of surface soil in various desert regions of the world.

The discovery of deposits of sodium nitrate $NaNO_3$ in Chile became of enormous importance for satisfying the world's need for fertilizers and explosives. It got the name *Chile saltpeter* but is found as an impure nitrate rock or gravel in arid regions of Chile, Peru, Argentina and Bolivia. The Spanish had already found the deposits in the 16th century. From a sandstone a salt could be leached out with water, a salt that was identified as sodium nitrate. At first very primitive methods were used to win the white, crystalline sodium nitrate. The sandstone was crushed and treated with water in leather sacks. The clear solution was heated in copper pots over an open fire until water was evaporated and sodium nitrate crystals formed. At the beginning of the 1800s, when its very positive effect as a fertilizer had been revealed and well known, the production was industrialized and concentrated to the Chilean provinces Tarapaca and Antofagasta. In the middle of the century tens of thousands of tonnes of the product were exported annually. In 1917 an export maximum of three million tonnes was reached, and by then it had become clear that reserves were limited. The population of the world continued to increase and there were many mouths to feed. Shortage of saltpeter would cause a global food crisis. The availability of nitrogenous fertilizers was a must.

44.3.3
An Inexhaustible Store of Nitrogen

The percentage of nitrogen in air is 78% by volume, which means that the natural nitrogen resources of the atmosphere are immense, an estimated $4 \cdot 10^{15}$ tonnes! There was really not a shortage, as long as atmospheric nitrogen could be assimilated.

So chemists had something to think about and were confronted with a gigantic problem: the conversion of atmospheric nitrogen into chemically useful compounds.

44.4
The Great Demand for Soluble Nitrogen

44.4.1
Birkeland and Eyde Set Fire to the Incombustible

Kristian Birkeland (1867–1917) was a professor of physics in Oslo and became well known for investigations of the relations between geomagnetism and the aurora borealis. Obviously he covered a broad field of interest, as his name is also connected with the very first method of manufacturing nitric acid from atmospheric nitrogen. The technique is known as the *Birkeland–Eyde process*.

Samuel Eyde (1866–1940) was a civil engineer and became a prominent industrialist, founder of the large Norwegian company Norsk Hydro.

Birkeland and Eyde together developed a method for combining nitrogen and oxygen from the air to nitrogen oxides in an electric arc. When these oxides were allowed to react with water, nitric acid was formed. With lime or ammonia, the acid gave calcium nitrate and ammonium nitrate, respectively, both known as Norway saltpeter. Technically the process functioned well, but the consumption of electrical energy was too large, even for the Norwegians with the cheapest energy prices in the world! The technique is no longer utilized industrially.

44.4.2
Calcium Cyanamide

Countries with higher costs for electrical energy than Norway needed alternative methods for transforming atmospheric nitrogen to chemically useful compounds. It was found that, on heating limestone and carbon in a nitrogen atmosphere, calcium carbide was formed, which combined with nitrogen to *calcium cyanamide*, $CaNCN$. This could be used as such as a fertilizer. Moisture in the soil transformed the cyanamide to lime and free cyanamide H_2NCN, which was changed by microorganisms into urea and ammonia. Calcium cyanamide came to play an essential role in increasing agricultural productivity (and also for the manufacture of gunpowder and explosives). The world production of calcium cyanamide was one million tonnes at the beginning of the 1960s but has since decreased considerably. The product is however still used as a raw material for different advanced chemical products such as melamine (for the production of formaldehyde resins).

44.4.3
Technology Imitates Nature

Nitrogen fixation by enzymes transforms atmospheric nitrogen to ammonia and urea. Would it not be possible to imitate this by finding a catalyst for transforming nitrogen to ammonia? And with moderate energy costs. This was in fact a challenge for a real enthusiast within physical chemistry!

Fritz Haber (1868–1934) was a professor at the University of Technology in Karlsruhe in Germany. In 1908 he began to study the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

and found that the main difficulty was that the reaction did not go to completion but was reversible and stayed in an equilibrium position. The NH_3 initially produced was spontaneously decomposed back to H_2 and N_2. To achieve a high yield of ammonia required:

- a temperature of 400°C;
- a catalyst to reach the equilibrium position in a short time;
- a pressure of about 200 atm (20.3 MPa), as the reaction occurs with decreasing volume and is thus favored by high pressure.

In 1911 Haber became the manager of the newly established Kaiser-Wilhelm Institut für Physikalische Chemie. Work on developing a large-scale manufacturing process continued in cooperation with *Carl Bosch* (1874–1940) at Badische Anilin- und Sodafabrik. Haber's catalysts in the research work, osmium and uranium, had to be replaced by pure iron containing additives that were more easily available and cheaper. The method was industrialized in 1913, resulting in a workable technique, which made ammonia available for use in industry and agriculture. This new method allowed chemical fertilizers to be mass-produced without using Chile saltpeter. In 1913 the plant produced 30 000 kg of NH_3 per day. The capacity of a modern ammonia plant is about 50 times greater.

The development of the Haber–Bosch process was one of the most challenging engineering efforts ever, and is considered to be one of the greatest achievements in the field of technology. It rendered the increased production of foodstuffs possible for an ever-increasing population. As a "bonus", the technology also allowed the mass production of explosives, not only for building work but also for war.

In 1933 Haber was ordered to discharge all Jewish workers at the Institute, but was offered to stay on as manager, although he himself was of Jewish descent. He refused, gave up his position and moved to England. He was employed at the Cavendish Laboratory but died in 1934. The Kaiser-Wilhelm Institut für Physikalische Chemie nowadays bears the name *Fritz-Haber-Institut*.

Haber was awarded the Nobel Prize for chemistry in 1918, and Carl Bosch in 1931.

44.5
Uses of Nitrogen and Nitrogen Products

44.5.1
Nitrogen Gas and Liquid Nitrogen

Liquid nitrogen is produced by distillation of liquid air. As this process has been so very important for the production of liquid oxygen for the modern steel industry, the availability for liquid nitrogen has increased. The separation is possible due to the different boiling points of the components in air, according to Table 44.1

Table 44.1 Boiling points of the components of air

Gas	Boiling point °C
Neon	–246,1
Nitrogen	–195,8
Argon	–185,9
Oxygen	–183,0
Krypton	–152,9
Xenon	–107,1

The largest consumption of nitrogen is, without doubt, for ammonia production in the Haber–Bosch process. In addition liquid nitrogen is an important refrigerant for deep-freezing of foodstuffs and biological specimens and preparations. Its low price and wide availability have meant that there has been great interest in liquid nitrogen in connection with the development of new superconductors, based on special ceramics (Chapter 17, Rare Earth Metals).

The fact that nitrogen gas is inert makes it usable in various applications, such as:

- protection gas in heat treatments in order to prevent metals from oxidation;
- protective environment in the manufacture of nylon and polyester in order to avoid contact between the oxygen in the air and polymer melts;
- fill gas for electric bulbs;
- fill gas for silos in order to avoid explosions.

As a protection gas for stainless steels during heat treatment (1050°C), a mixture of 75% hydrogen and 25% nitrogen is very much used. It is prepared by cracking of ammonia at 900°C and atmospheric pressure with a nickel catalyst present. The process thus compels the Haber synthesis to go backwards.

44.5.2
Ammonia and Nitrogen Oxides

Ammonia production in the world is presently as large as 110 million tonnes per year. The product is stored as a liquid at a pressure of 100 atm (10.1 MPa) and a temperature of –35.5°C. Ammonia is the base material for the manufacture of nitrogen oxides and various industrial products. Nitrogen oxides have a number of applications. N_2O is used in medicine, as it has anesthetic properties (laughing gas). N_2O_4 is used as an oxidizer in rocket fuel. From ammonia, nitric acid is manufactured by oxidation with air at about 800°C. Different types of catalysts, e.g. platinum, may be used. NO_2, formed in the oxidation, is reacted with water to HNO_3 and NO. The technique is called the Ostwald process.

Ammonia and nitrates are the main components in artificial fertilizers.

44.5.3
Fertilizers

When a crop is grown year after year in the same ground, the soil may become exhausted of some specific nutrient(s). If so, fertilizers must be added. Nitrogen, present in immense quantities in the atmosphere, cannot be utilized in this gaseous form by plants in general. Some plants – the legume family – can however utilize bacteria and obtain nitrogen from the air through a process called nitrogen fixation. For other plant types it is necessary to add soluble nitrogen by means of fertilizers. Besides nitrogen, phosphorous and potassium are regularly added. A complete fertilizer is a mixture containing all three elements. In some countries it is called NPK (N for nitrogen, P for phosphorus and K for potassium). In other countries the fertilizer mixture is characterized by three figures, e.g. 6–9–8, meaning 6% nitrogen, 9% phosphorus (calculated as P_2O_5) and 8% potassium (as K_2O).

Some other essential elements such as boron, copper and manganese sometimes need to be added too.

44.5.3.1 Synthetic Nitrogen Fertilizers

Nitrogen fertilizers contain nitrogen as nitrate, ammonia, ammonium compounds or urea. Nitrates are water-soluble and follow the movement of water in the soil. When anhydrous ammonia gas is used directly as a fertilizer, it reacts with water in the soil and changes to the ammonium ion form. When used as a fertilizer, ammonia must be injected under the soil surface.

Ammonium compounds such as ammonium phosphates, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, are good fertilizers because they supply *two* vital nutrients, nitrogen and phosphorus. During the growing season, soil microorganisms convert the ammonium ion to nitrate, which is the main form taken up by plants.

Urea $CO(NH_3)_2$ is manufactured from ammonia and carbon dioxide:

$$2NH_3 + CO_2 \rightarrow \underset{\text{urea}}{CO(NH_3)_2} + H_2O$$

Urea is an excellent fertilizer, either as a pure solid or in concentrated aqueous solutions, containing also NH_4NO_3 and/or NH_3. Enzymes and microorganisms in the soil convert the urea nitrogen to nitrate.

44.5.3.2 Natural Nitrogen Fertilizers

A cow, producing 35 kg milk per day, excretes yearly 150 kg nitrogen, 20 kg phosphorus and 80 kg potassium. Most of the nutrients from a farm are thus excreted in *manure* and remain on the farm. When returned to the soil these elements are reused to produce more feed.

Guano is another natural fertilizer. It consists of the dried excrement from seabirds The source of guano was discovered on a series of islands off the coast of Peru, which have almost no vegetation due to lack of rain. The native populations in pre-Spanish time originally used it as a fertilizer to increase crop yields. In the early 1800s the Europeans discovered guano as a valuable agricultural fertilizer.

44.5.4
Gunpowder and Explosives

In the 8th century AD it was discovered in China that an explosive mixture could be produced by combining 75% saltpeter (potassium nitrate), 10% sulfur and 15% charcoal. This gunpowder became known in Europe from the Middle Ages and was used for military applications and in mining. From the beginning the powder was utilized in fireworks and so is the case also nowadays.

A new explosive, nitroglycerin $C_3H_5(ONO_2)_3$, a highly explosive liquid, was invented about 1850 by an Italian chemist Ascanio Sobrero. Its explosive power very much exceeded that of gunpowder but the liquid exploded in a very unpredictable manner. It seemed to be too dangerous for practical use. *Alfred Nobel* (1833–1896) met the inventor in Paris, became very interested in nitroglycerin, and decided to find a method for its safe use in construction work. Experimenting in Stockholm, he found that when liquid nitroglycerin was mixed with silica powder a paste was formed that could be shaped into rods suitable for insertion into drilling holes. In 1867 he patented this material under the name of *dynamite*. For a century dynamite was the dominant explosive for mining, underground construction, road and railway work.

Ammonium nitrate NH_4NO_3 is used as a fertilizer and originally its explosive power was not known. The first Haber–Bosch equipment was built at Oppau in Ludwigshafen, Germany. In 1921 a large quantity, some 4500 tonnes, of fertilizer of ammonium nitrate type had been stored and was causing problems, because the substance had hardened to a mass that was impossible to handle and spread. In order to loosen it up, some dynamite cartridges were installed and detonated. Everything exploded, and five hundred people were killed.

In more recent times, mixtures of ammonium nitrate and fuel oil (ANFO) are generally utilized as explosives in construction work, because of their low price and absence of unhealthy nitroglycerin vapors. However they require a highly effective blasting fuse. They have also been used in terrorist attacks in the USA, such as for instance one in Oklahoma City in 1995.

An explosive used for saving lives is sodium azide NaN_3. An airbag in passenger cars contains about 200 g of this compound. On collision it explodes and the gases inflate the bag in a very short time.

44.6
Nitride Ceramics

44.6.1
Engineering Ceramics in General

Ceramics are traditional products for household articles and ornaments, often obtained by turning and sintering. On the other hand *engineering ceramics* are high-efficiency ceramic materials with special compositions and properties. In the manufacture of engineering ceramics, a carefully specified powder blend is ground and pressed to the required shape. On sintering, binding and strength are created. There are two types of sintering. In *solid-phase sintering,* the grains are in direct contact with each other and binding occurs by mutual diffusion. In *molten-phase sintering,* components are present that melt at the sintering temperature, causing more effective pore closure. Some ceramics are sintered at high temperature and atmospheric pressure, and others require *hot isostatic pressure* (HIP) treatment. This implies a pressure of 100–200 MPa (1000–2000 atm) and a temperature of 1500–1700°C. HIP treatment in a Quintus high-pressure furnace is shown in Figure 44.3.

The traditional white construction and tool ceramics have Al_2O_3 as the main component. Nowadays additions of ZrO_2 are used to improve toughness.

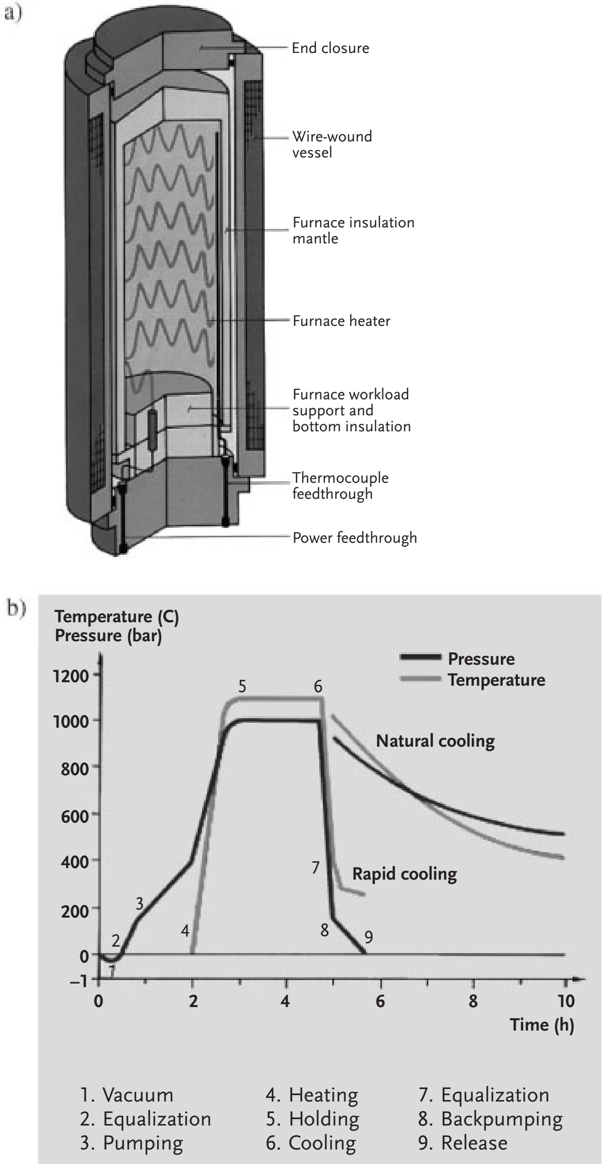


Figure 44.3 (a) The main components of the Quintus high-pressure furnace. (b) The temperature and pressure cycles in HIP treatment with natural and rapid cooling. (Reprinted with permission from ABB Pressure Systems AB, Västerås, Sweden.)

44.6.2
Special Nitride Ceramics

Two important groups of ceramics have silicon nitride Si_3N_4 as the main component. Both are characterized by better toughness than ceramics in general. The first product is *pressure-sintered silicon nitride* Si_3N_4 (Figure 44.4).

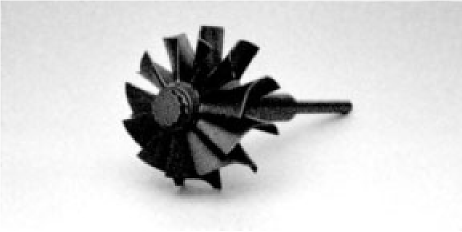


Figure 44.4 A silicon nitride component produced to its end shape. Nitride powder is encapsulated in glass and "hipped" (HIP treated). (Reprinted with permission from ABB Cerama, and ABB Pressure Systems AB, Västerås, Sweden.)

The other silicon nitride product is the more complicated *sialon*. Typical of sialons is that the composition can be selected so that a rather large liquid volume is formed in the sintering. Added yttrium oxide is dissolved in this melt. Chemical reactions occur between the molten phase and the grains of silicon nitride. In these reactions special sialon phases are crystallized. On cooling, the remaining liquid phase solidifies to a glass. Yttrium gives a glass with very good mechanical properties. The reaction formula is, schematically:

$$\underset{90\text{–}80\%}{Si_3N_4} + \underset{5\text{–}15\%}{Al_2O_3/AlN} + \underset{4\text{–}6\%}{Y_2O_3} \rightarrow \underset{\text{sialon}}{Si_{6-z}Al_zO_zN_{8-z}} + \underset{\text{yttrium glass}}{\text{Y–Si–O–N}}$$

The good mechanical properties have made it possible to use sialon ceramics in tools for machining of nickel alloys, notoriously hard to work.

44.7
We Cannot Live Without "Malignant Air" – The Biological Role of Nitrogen

Nitrogen is an essential element for life, and the human body contains about 3% by weight of nitrogen. Thus it is the fourth frequent among the elements in living organisms. Nitrogen is above all present in proteins, which consist of 16% nitrogen. All four of the bases forming the genetic code in DNA, adenine (A), guanine (G), thymine (T) and cytosine (C), contain nitrogen (Figure 44.5).

The nitrogen in the atmosphere is very inert, and the bond in N_2 is characterized by a barrier of high activation energy. The nitrogen fixation in organisms necessary

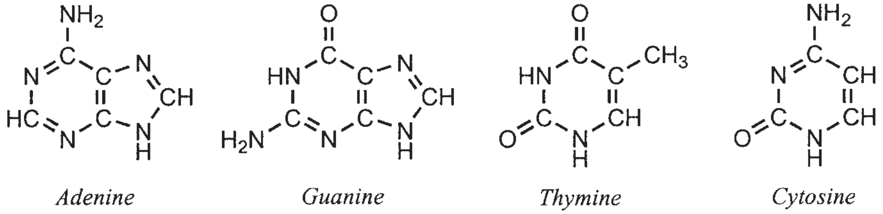


Figure 44.5 The bases adenine (A), guanine (G), thymine (T) and cytosine (C), which together with 2-deoxyribose form the nucleic acid DNA.

for life must have been a big problem. Only some special leguminous plants, such as beans, peas and alfalfa, have bacteria on their roots that convert elemental nitrogen from the air into compounds that the plant can use for making proteins. By alternating cultivation of food crops and leguminous plants, nitrogen can be conveyed into fields in a natural way.

Ammonia and nitrates are taken up more easily and are preferred, if available, as for instance in fertilizers.

Nitrates in drinking water can create problems for infants. On reduction of nitrate to organic compounds, toxic nitrite is formed as an intermediate ion. This can react with iron in hemoglobin and make it incapable of transporting oxygen in the blood. This is the so-called “blue baby syndrome”, and is a strong reason to restrict the nitrate content in drinking water.

Nitroglycerin $C_3H_5(ONO_2)_3$ is also used as a medicine in the treatment of angina pectoris. The reason is that it has the ability to widen the coronary arteries.

It has been reported [44.3] that the simple molecule NO has sophisticated biological functions. It can diffuse through membranes and is involved in the regulation of blood pressure, as it influences muscles that are outside conscious control. The activation of muscles that control the blood flow into erectile tissues is utilized in the drug Viagra.

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45
Phosphorus

45.1 P
Facts about Phosphorus

45.1.1 P
The Element

Symbol:	P
Atomic number:	15
Atomic weight:	30.97
Ground state electron configuration:	$[Ne]3s^23p^3$
Crystal structure:	White phosphorus is metastable and is hexagonal below –76.9°C. From this temperature and up to the melting point it is cubic. Red phosphorus is more stable than white but still metastable. It has a very disordered crystal structure. Black phosphorus is stable up to about 400°C and has an orthorhombic structure with $a = 3.31$ Å, $b = 10.48$ Å, $c = 4.38$ Å.

45.1.2 P
Discovery and Occurrence

Discovery: The German alchemist Hennig Brand discovered phosphorus in 1669 when carrying out experiments to prepare gold.

Most important mineral: Apatite $Ca_5[(F,Cl,OH)(PO_4)_3]$

Ranking in order of abundance in earth crust:	11
Mean content in earth crust:	1050 ppm (g/tonne)
Mean content in oceans:	0.06 ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	$1.1 \cdot 10^4$ ppm = 1.1 %
Content in a man's body (weight 70 kg):	770 g

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45.1.3 P
Chemical Characterization

Phosphorus exists in three forms, white, red and black (violet). The *white* modification is a waxy solid, very toxic and inflammable. Heated to 300–400°C without contact with air, white is transformed to the non-toxic *red* phosphorus. If white or red phosphorus is heated to 200°C at a pressure of 12 000 bar (1200 MPa), *black* phosphorus is formed. Even at low pressure it can however be obtained if red or white is heated at 350°C together with bismuth or mercury. Once formed black phosphorus is stable from low temperatures up to about 400°C. White phosphorus is prepared commercially by heating calcium phosphate with quartz and coke in an electric furnace. Most of the phosphorus produced is converted to phosphoric acid for use in making fertilizer. The element is important in plant and animal physiology and is a constituent of all animal bones, in the form of calcium phosphate.

Oxidation states:

P^{I} as in H_3PO_2
  hypophosphorous acid
  [sometimes written $H_2P(O)(OH)$]
P^{III} as in P_4O_6 and H_3PO_3
  phosphorous acid
  [sometimes written $HP(O)(OH)_2$]
P^{V} as in P_4O_{10} and H_3PO_4
  orthophosphoric acid
  [sometimes written $PO(OH)_3$]
P^{-III} as in PH_3 phosphine

Ionization energy (kJ mol^{-1}):

$P(g) \rightarrow P^{+}(g) + e^{-}$	1012
$P^{+}(g) \rightarrow P^{2+}(g) + e^{-}$	1907
$P^{2+}(g) \rightarrow P^{3+}(g) + e^{-}$	2914
$P^{3+}(g) \rightarrow P^{4+}(g) + e^{-}$	4964
$P^{4+}(g) \rightarrow P^{5+}(g) + e^{-}$	6274
$P^{5+}(g) \rightarrow P^{6+}(g) + e^{-}$	21 267

Electron affinity (kJ mol^{-1}):

$P(g) + e^{-} \rightarrow P^{-}(g)$
–72

Standard reduction potential:

$H_3PO_4(aq) + 2H^{+}(aq) + 2e^{-} \rightarrow H_3PO_3(aq) + H_2O(l)$	$E^0 = -0.276$ V
$H_3PO_3(aq) + 3H^{+}(aq) + 3e^{-} \rightarrow P(s) + 3H_2O(l)$	$E^0 = -0.502$ V

Electronegativity (Pauling): 2.19

Radii of atoms and ions:
(WebElements™)

Atomic:	100 pm
Covalent:	106 pm
Van der Waals	180 pm
P^{3+} (6-coordinate, octahedral):	58 pm
P^{5+} (4-coordinate, tetrahedral):	31 pm
P^{5+} (6-coordinate, octahedral):	52 pm

45.1.4 P
Physical Properties

Density	Molar volume	Melting point
1820 kg m^{-3} (white) 1.82 g cm^{-3} 2340 kg m^{-3} (red) 2.34 g/cm^3	17.01 cm^3 (white) 13.24 cm^3 (red)	317.3 K (white) 44.15 °C 863 K (red; triple point; 43 atm.) 590 °C 883 K (black) 610 °C

Boiling point	Specific heat c_p at 298 K
553.7 K (white) 280.5 °C 704 K (red; sublimation point) 431 °C	769 J K^{-1} kg^{-1} (white) 685 J K^{-1} kg^{-1} (red)

Thermal conductivity Wm^{-1}K^{-1}

173 K	273 K	298 K	573 K	973 K
– (white)	0.25	0.235	–	–
20 (black)	13	12	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
– (white)	$125 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	298 K	373 K	573 K	973 K	1473 K
– (white)	10^{18}	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-11 \cdot 10^{-9}$ m^{3}kg^{-1} (white) $-8{,}4 \cdot 10^{-9}$ m^{3}kg^{-1} (red)
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	11 GPa	–

45.1.5 P
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	0.63 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	12.4 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	315 $kJmol^{-1}$
Entropy S^0 at 298 K	41.09 $JK^{-1}mol^{-1}$ (white) 22.80 $JK^{-1}mol^{-1}$ (red)

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
13.7 (white)	23.84 (white) 21.21 (red)	26.1 (white)	20.8 (white)	21.2 (white)	22.1 (white)

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/5P+O_2 \rightarrow 2/5P_2O_5$	–540	–420	–335	–	–

45.1.6 P
Nuclear Properties and X-ray

Isotope range, natural and artificial	26–43

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{31}P	Stable	100	1/2+	1.132

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{31}P
Reference compound	H_3PO_4/D_2O
Frequency MHz (^1H = 100 MHz)	40.481
Receptivity D^P relative to ^1H = 1.00	0.0665
Receptivity D^C relative to ^{13}C = 1.00	380
Magnetogyric ratio, $radT^{-1}s^{-1}$	$10.839 \cdot 10^7$
Nuclear quadropole moment, barn	–

Characteristic X-radiation		
Z	**Element**	**Kα_2 keV**
14	Si	1.739
15	P	2.013
16	S	2.307

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	75.8
17.37 keV (MoKα_2)	8.07

Neutron absorption	**Thermal neutron capture cross section**	0.18 barns

45.2
A Sensation in Europe

Hennig Brand (ca. 1630–1710) discovered the element phosphorus. He was a glass blower and merchant in Hamburg, described as a bizarre and odd figure. Certainly, in the middle of the 17th century, it was people of that disposition who could still be devoted alchemists, at a time when alchemy had fallen into disrepute and chemistry was in a period of changing its character. It is said that he was an impoverished merchant who sought to restore his wealth by converting base metals into gold. He was firmly determined to find the *Philosophers' Stone* that would make it possible for him to make gold. His proficiency in glass blowing stood him in good stead for manufacturing chemical equipment. In 1669 he examined human urine. Its yellow color perhaps indicated secrets that were associated with gold. What he sought was a substance capable of transforming silver to gold. When he heated urine without admittance of air and let the vapors condense below water, a substance similar to wax was formed. Brand and others thought that a new element had been discovered. Its spontaneous combustion after moderate heating, and the fact that it was luminous in the dark, created a sensation in Europe. Brand's discovery was immortalized in the painting by Joseph Wright of Derby (see Figure 45.1).

The miraculous cold light was the reason behind naming the new element phosphorus, after the Greek word *fosforos*, meaning "light carrier". When knowledge about the new element and its cold light was spread, feelings were awakened similar to those which the discovery of radium was to produce more than two centuries later.

The details of the method of preparing phosphorus were kept secret, as was typical in alchemy. But the secret that it was made from urine leaked out, and a clever chemist, Johann Kunckel (ca. 1630–1703), found the preparation method by his own experiments. He was also well known for his book *Laboratorium Chymicum*, from which Carl Wilhelm Scheele acquired his knowledge of basic chemistry. Kunckel also attracted attention in Sweden, a great power at that time, with many possessions in Germany, and he was engaged by King Charles XI, who appointed him to be a member of the Royal Board of Mining and Metallurgy and raised him to the nobility as Baron von Löwenstern.

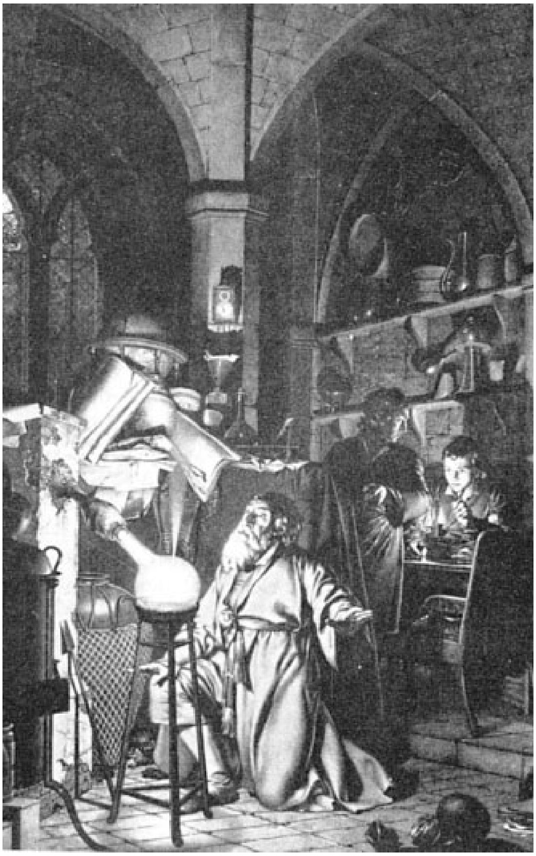

Figure 45.1 "The alchemist discovers phosphorus", a painting by Joseph Wright of Derby (1734–1779).

Robert Boyle also developed a method and described it at the Royal Society in 1680. He and his assistant Ambrose Godfrey Hanckwitz improved the method to a commercial process and exported *English phosphorus* to the continent.

45.3
Phosphorus – A New Medicine

Every new substance discovered aroused expectations that just that one was the key to human health. Thus also phosphorus should be tested medically in the spirit of iatrochemistry. Kunckel, the chemist, also was something of a businessman. He prepared small balls of phosphorus and left them in contact with solutions containing silver or gold. They became covered with a thin layer of the noble metal. Thus he had made “a very effective medicine”. The pills were for sale in drugstores in Leipzig, provided with the informative label:

> The pills cause no vomiting or other discomfort but act in a mysterious way against serious illness and pain. One to two pills daily strengthen the vital force and release a man, with God’s help, from fear of stroke or other sudden illness during the day. Infants, who cry night and day, may be offered a half pill together with an onion clove and breast milk.

Later on phosphorus preparations became available as means against epilepsy and cramps. When the manufacturing of matches started, in modest forms at the beginning, the toxicity of white phosphorus was discovered. The medical use of elemental phosphorus ceased and remedies against phosphorus poisoning had instead to be sought. In the light of these facts, we should perhaps show our gratitude to modern authorities for their very strong examination and control of chemical substances before they are accepted as medicines.

Nowadays, a new class of phosphorus medicines have been developed and accepted. These bis-phosphonates are used for bone diseases, among which osteoporosis is the most common.

45.4
Phosphorus in the History of Discovering the Elements

The method of producing phosphorus from urine was generally utilized for a hundred years. In Sweden, Scheele and Gahn were very interested in the remarkable element. They showed in 1769–1770 that phosphorus is present in the skeletons of mammals and human beings, and that the element can be prepared from bone ash by reduction with charcoal1). They analyzed the ash of burned deer horn (*Cornu cervi ustum*) and found that it consisted of lime and *acidum phosphori*, and thus was calcium phosphate.

In the coming century bone (and guano) became the raw material for the manufacture of phosphorus. The discovery resulted in increased availability and reduced price. Meanwhile new knowledge was acquired: phosphorus is a common element in the earth’s crust and is present there mainly as the mineral apatite, calcium phosphate. This mineral was discovered and identified about 1790 by Proust2) and Klaproth3). When electrical energy became available at the end of the 19th century, the technique of reducing apatite with coke in electric furnaces was developed. This technique is very energy-consuming. In spite of that, it led to the almost unlimited availability of the element. That was a big difference compared to the situation in 1669, when Brand had prepared just a few grams of it.

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1) Gahn’s and Scheele’s cooperation in the discovery of phosphorus in bone is described in ref. [45.1].

2) For more about J. L. Proust, see Chapter 2 The Knowledge of Matter.

3) For more about M. H. Klaproth, see Chapter 18 Titanium.

Antoine Laurent Lavoisier made important investigations about the burning of phosphorus. In 1772 he classified phosphorus as an element and showed that it is the oxide of that element which forms phosphoric acid with water. In the 1840s, Jakob Berzelius made the first observation that phosphorus has the two modifications, red and white.

N.-L. Vauquelin in Paris synthesized the first organic phosphorus compound in 1811. He found *lecithin*, a lipid. The cell membranes in the body are composed to a great extent of lecithin.

45.5
Dangerous Matches and the Safety Match

Already by the Neolithic Age fire was generated by frictional heating and the use of touchwood or other inflammable substances. Later on, easily inflammable lucifer matches, wood or yarn, with the ends dipped in molten sulfur, were used. A 19th century variant of the lucifer match, a drawing match, had a head of sodium chlorate and antimony sulfide. It was inflammable by drawing out from a doubled piece of sandpaper.

Immediately after the discovery of phosphorus, the possibility of utilizing the new element in a technique for generating fire was recognized. Kunckel was working along these lines. He coated a paper with phosphorus and ignited it by striking. During the 18th century many imaginative – and dangerous! – variants were presented.

The manufacture of the phosphorus match, the first pyrotechnic match, began industrially in Germany in 1832. It had a mixture of white phosphorus and sodium chlorate as match-head and was inflammable on striking against anything, the boots for instance. This obviously created a risk of fire. The white phosphorus was in addition a poisoning risk. This type of match was banned at the beginning of the 20th century.

The *safety match*, with red instead of white phosphorus, was invented by G. E. Berggren-Pasch in Stockholm and was improved to a commercial product by J. E. Lundström in Jönköping Sweden. The match-head is composed of a combustible substance, sulfur or antimony sulfide, and an oxidation agent, sodium chlorate. In the striking surface (on the box), red phosphorus, antimony sulfide and glass powders are included. The safety is constituted by the fact that the match is inflammable only if it is struck against the special surface of the box. The aspen wood in the match is porous, with good absorption ability. It is impregnated with ammonium hydrogenphosphate, which partly prevents the wood from after-glowing, and partly makes the burned head remain on the match. In addition, the wood nearest the match-head also contains paraffin, which supports the transfer of the flame from the head to the matchstick.

45.6
Phosphorus – Occurrence and Modern Manufacture

Phosphorus is the eleventh most abundant element in the earth's crust and occurs as the mineral apatite. Apatite is in fact a group of hexagonal minerals, pale and variously colored. They consist of calcium phosphate together with fluorine, chlorine or hydroxy groups. Hydroxyapatite is the major component of enamel in teeth and a large component of bone material. It can take up fluorine ions, forming, to a certain extent, fluorapatite $Ca_5[F(PO_4)_3]$, which is slightly stronger than hydroxyapatite. In this way fluoridated water strengthens the teeth.

The apatite minerals are the chief constituents of phosphate rock but occur in almost all igneous rocks. They are responsible for the high phosphorus content in some iron ores.

World production of apatite in 1999 was 141 Mtonne, the main producers being the USA, Russia, Morocco and China.

Elementary phosphorus is manufactured by reduction of apatite with coke in electric furnaces at a temperature of 1400–1500°C. Quartz is also present in the charge. It reacts with the calcium in apatite and forms a slag of liquid calcium silicate. If the apatite contains fluorine, SiF_4 gas is formed that is passed into water containing soda. The compound formed, sodium hexafluorosilicate Na_2SiF_6, is used for fluoridating drinking water. In the process described, white phosphorus is the product. In the world about 1 million tonnes per year are produced. White phosphorus is used to some extent for smoke bombs and incendiary bombs, but most of it is used for the manufacture of phosphoric acid and other chemicals and for preparing red phosphorus for the match industry.

A phosphorus product whose use has grown to a great volume in modern society is sodium tripolyphosphate $Na_5P_3O_{10}$, used in dishwater powders and in detergents. It softens water and keeps dirt, removed from the clothes, for example, in suspension.

45.7
Phosphorus for Plants

Plants that are short of phosphorus become stunted and their leaves attain a dark green or a bluish-violet color. Such crops need phosphorus-containing fertilizers. Without knowledge about the chemistry, the Inca Indians of Peru were aware of this and manured their fields with guano. As mentioned earlier, guano became a large export product for phosphorus (and nitrogen) manuring in the USA and Europe from the middle of the 19th century. When the occurrence of phosphorus in bones became known, an industry grew up that treated bone with sulfuric acid and prepared a "raw bone super-phosphate" that was sold as an alternative to guano [45.2] (see Figure 45.2).

Modern manufacture of phosphate fertilizers is based on treating rock phosphate, apatite, with sulfuric acid. A mixture of $Ca(H_2PO_4)_2 \cdot 2H_2O$ and $CaSO_4$ is obtained.

Figure 45.2 Advertisement from Philadelphia around 1867.

Super phosphate is the most important fertilizer, which contains 18–20% of P_2O_5, possible for the soil to assimilate. A special fertilizer is obtained by decomposing apatite by phosphoric acid treatment:

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2 \cdot 2H_2O$$

This product is called *triple phosphate* and contains 48% of assimilable P_2O_5.

Farmyard manure from cattle, pigs and horses also contains phosphorus, about 1–2 g per kilogram of manure.

45.8
We Cannot Live Without Phosphorus

Phosphorus is essential for all living matter, plants and animals. A human being contains about 770 g phosphorus, 90% of which is in the skeleton, 8% in the muscles, and the residue in the nerves. All living things, plants and animals, require a continual supply of energy in order to function. The energy is used for all the processes that keep the organism alive. Animals obtain their energy by oxidation of foods; plants do so by trapping sunlight using chlorophyll. However, before the energy can be used, it is first transformed into a form that the organism can handle easily. This special carrier of energy is the molecule *adenosine triphosphate* (ATP).

ATP works by losing the endmost phosphate group when instructed to do so by an enzyme [45.3]. This reaction releases a lot of energy, which the organism can then use to build proteins, contract muscles, etc. When the organism is resting and energy is not immediately needed, the phosphate group is reattached to the molecule, using energy obtained from food or sunlight. Thus the ATP molecule acts as a chemical "battery", storing energy when it is not needed, but able to release it instantly when the organism requires it.

The 1997 Nobel Prize for chemistry was awarded to three biochemists for the study of the ATP molecule: John Walker at the University of Cambridge in the UK, Paul Boyer of the University of California at Los Angeles, and Jens Skou of Aarhus University in Denmark.

References

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46
Arsenic, Antimony and Bismuth

46.1 As
Facts about Arsenic

46.1.1 As
The Element

Symbol:	As
Atomic number:	33
Atomic weight:	74.92
Ground state electron configuration:	[Ar]$3d^{10}4s^24p^3$
Crystal structure:	Solid arsenic occurs like phosphorus in different modifications. *Gray* or *metallic arsenic* is stable. Its structure is rhombohedral with $a = 4.13$ Å, $\alpha = 54.2°$. If vaporized and condensed at the temperature of liquid air, *yellow arsenic* is formed. At room temperature, yellow arsenic is transformed to metallic arsenic. Condensed on surfaces at 100–200°C, *black arsenic* ("arsenic mirror") is formed.

46.1.2 As
Discovery and Occurrence

Discovery: Realgar and orpiment were known to ancient peoples. The element was probably isolated by Albertus Magnus (1193–1280).

Most important mineral:	Arsenopyrite FeAsS
	Realgar (red) AsS (Figure M71)
	Orpiment (yellow) As_2S_3 (Figure M71)

Ranking in order of abundance in earth crust:	54
Mean content in earth crust:	1.8 ppm (g/tonne)
Mean content in oceans:	0.0037 ppm (g/tonne)
Residence time in oceans:	$100 \cdot 10^3$ years
Mean content in an adult human body:	0.05 ppm
Content in a man's body (weight 70 kg):	3.5 mg

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46.1.3 As

Chemical Characterization

Arsenic is a metalloid on the borderline between metals and nonmetals. Certain arsenic compounds, such as gallium arsenide (GaAs), are used as semiconductors. The white oxide As_2O_3 is the assassin's poison *arsenic*. Two- or three-tenths of a gram is a lethal dose. On the other hand, some persons have built up a tolerance for it, so that they can ingest each day an amount that would normally be fatal.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
As^{-III} as in AsH_3	$As(g) \rightarrow As^+(g) + e^-$	947	$As(g) + e^- \rightarrow As^-(g)$
As^{III} as in As_2O_3, AsF_3	$As^+(g) \rightarrow As^{2+}(g) + e^-$	1798	−78
and As_2S_3.	$As^{2+}(g) \rightarrow As^{3+}(g) + e^-$	2735	
As^V as in $H_3AsO_4 \cdot ½H_2O$,	$As^{3+}(g) \rightarrow As^{4+}(g) + e^-$	4837	
$AsCl_5$ and As_2S_5	$As^{4+}(g) \rightarrow As^{5+}(g) + e^-$	6043	
As^V in III–V compounds as GaAs	$As^{5+}(g) \rightarrow As^{6+}(g) + e^-$	12 310	

Standard reduction potential:
$H_3AsO_4(aq) + 2H^+(aq) + 2e^- \rightarrow HAsO_2(aq) + 2H_2O(l)$
$E^0 = +0.560\ V$
$HAsO_2(aq) + 3H^+(aq) + 3e^- \rightarrow As(s) + 2H_2O(l)$
$E^0 = +0.240\ V$

Electronegativity (Pauling): 2.18

Radii of atoms and ions: (WebElements™)		
	Atomic:	115 pm
	Covalent:	119 pm
	Van der Waals	185 pm
	As^{3+} (6-coordinate, octahedral):	72 pm
	As^{5+} (4-coordinate, tetrahedral):	47.5 pm
	As^{5+} (6-coordinate, octahedral):	60 pm

46.1.4 As
Physical Properties

Density	Molar volume	Melting point
5727 kgm^{-3} (gray, metallic) 5.73 g/cm^3 4700 kgm^{-3} (yellow, hexagonal) 4.70 g/cm^3	13.08 cm^3 (gray, metallic) 15.94 cm^3 (yellow)	1090 K (gray; triple point 3.70 MPa) 817 °C

Boiling point	Specific heat c_p at 298 K
876 K (gray; sublimation point) 603 °C	329 J K^{-1} kg^{-1}

Thermal conductivity Wm^{-1}K^{-1}

173 K	273 K	373 K	573 K	973 K
–	54	43	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$5 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	273 K	298 K	573 K	973 K	1473 K
55	260	333	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-0.92 \cdot 10^{-9}$ m^{3}kg^{-1} (gray, metallic)
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
8 GPa	–	22 GPa	–

46.1.5 As
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	27.7 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	32.4 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	302 $kJmol^{-1}$
Entropy S^0 at 298 K	35.15 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
16.7	24.64	27.4	–	–	–

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3As+O_2 \rightarrow 2/3As_2O_3$	–385	–351	–	–	–
$4/5As+O_2 \rightarrow 2/5As_2O_5$	–313	–270	–	–	–

46.1.6 As
Nuclear Properties and X-ray

Isotope range, natural and artificial 65–87

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{75}As	Stable	100	3/2–	1.439

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{75}As
Reference compound	$NaAsF_6$/MeCN
Frequency MHz (^1H = 100 MHz)	17.123
Receptivity D^P relative to ^1H = 1.00	0.0254
Receptivity D^C relative to ^{13}C = 1.00	145
Magnetogyric ratio, $radT^{-1}s^{-1}$	$4.596 \cdot 10^7$
Nuclear quadropole moment, barn	0.314

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV
32	Ge	9.856
33	As	10.509
34	Se	11.181

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	75.0
17.37 keV ($MoK\alpha_2$)	66.8

Neutron absorption	Thermal neutron capture cross section	4.3 barns

46.1 Sb
Facts about Antimony

46.1.1 Sb
The Element

Symbol:	Sb
Atomic number:	51
Atomic weight:	121.75
Ground state electron configuration:	$[Kr]4d^{10}5s^25p^3$
Crystal structure:	Metallic antimony has a rhombohedral crystal structure

46.1.2 Sb
Discovery and Occurrence

Discovery: Known in antiquity

Most important mineral:	Stibnite, antimonite Sb_2S_3 (Figure M72) Ullmannite NiSbS

Ranking in order of abundance in earth crust:	65
Mean content in earth crust:	0.2 ppm (g/tonne)
Mean content in oceans:	$2.4 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	$10 \cdot 10^3$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

46.1.3 Sb
Chemical Characterization

Antimony is a bluish white, brittle metal, and is a poor conductor of heat and electricity. It is resistant in air at room temperature, but when heated it burns brilliantly with the formation of white fumes. The element is used to harden other metals, and the most important utilization of antimony metal is as an alloying element in lead for storage batteries.

Sb^{-III} as in SbH_3	$Sb(g) \rightarrow Sb^+(g) + e^-$	834	$Sb(g) + e^- \rightarrow Sb^-(g)$
Sb^{III} as in Sb_2O_3, $SbBr_3$ and Sb_2S_3	$Sb^+(g) \rightarrow Sb^{2+}(g) + e^-$	1595	−103
Sb^V as in Sb_2O_5 and $SbCl_5$	$Sb^{2+}(g) \rightarrow Sb^{3+}(g) + e^-$	2440	
Sb^V in III–V compounds as GaSb	$Sb^{3+}(g) \rightarrow Sb^{4+}(g) + e^-$	4260	
	$Sb^{4+}(g) \rightarrow Sb^{5+}(g) + e^-$	5400	
	$Sb^{5+}(g) \rightarrow Sb^{6+}(g) + e^-$	10 400	

Standard reduction potential: $Sb_2O_5(s) + 6H^+(aq) + 4e^- \rightarrow 2SbO^+(aq) + 3H_2O(l)$
$E^0 = +0.605$ V
$SbO^+(aq) + 2H^+(aq) + 3e^- \rightarrow Sb(s) + H_2O(l)$
$E^0 = +0.204$ V

Electronegativity (Pauling): 2.05

Radii of atoms and ions: (WebElements™)		
	Atomic:	145 pm
	Covalent:	138 pm
	Sb^{3+} (6-coordinate, octahedral):	90 pm
	Sb^{5+} (6-coordinate, octahedral):	74 pm

46.1.4 Sb
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
6691 kg m^{-3} 6.69 g cm^{-3}	18.20 cm^3	903.8 K 630.6 °C	1860 K 1587 °C	207 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
33	25.5	22	19	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$9.1 \cdot 10^{-6}$	$11 \cdot 10^{-6}$	$11.7 \cdot 10^{-6}$	$11.7 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1273 K
80	390	590	–	1140	1235

Mass magnetic susceptibility χ_{mass} at 293 K	$-10 \cdot 10^{-9}$ m^3kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
55 GPa	20 GPa	73 GPa	0.37

46.1.5 Sb
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	19.8 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	68.0 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	262 $kJmol^{-1}$
Entropy S^0 at 298 K	45.69 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
20.6	25.23	27.4	31.4	18.7	18.7

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/5Sb+O_2 \rightarrow 2/5Sb_2O_5$	–332	–	–	–	–

46.1.6 Sb
Nuclear Properties and X-ray

Isotope range, natural and artificial	104–136

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{121}Sb	Stable	57.36	5/2+	3.359
^{123}Sb	Stable	42.64	7/2+	2.550

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{121}Sb	^{123}Sb
Reference compound	$KSbCl_6/MeCN$	
Frequency MHz (^1H = 100 MHz)	23.931	12.959
Receptivity D^P relative to ^1H = 1.00	0.0935	0.0199
Receptivity D^C relative to ^{13}C = 1.00	534	114
Magnetogyric ratio, $radT^{-1}s^{-1}$	$6.444 \cdot 10^7$	$3.489 \cdot 10^7$
Nuclear quadropole moment, barn	–0.36	–0.49

Characteristic X-radiation		
Z	**Element**	**$K\alpha_2$ keV**
50	Sn	25.044
51	Sb	26.110
52	Te	27.201

X-ray radiation absorbed by the element	
Incoming radiation energy	**Absorption coefficient μ (cm^2/g)**
8.028 keV ($CuK\alpha_2$)	261
17.37 keV ($MoK\alpha_2$)	33.1

Neutron absorption	**Thermal neutron capture cross section**	5.2 barns

46.1 Bi
Facts about Bismuth

46.1.1 Bi
The Element

Symbol:	Bi
Atomic number:	83
Atomic weight:	208.98
Ground state electron configuration:	$[Xe]4f^{14}5d^{10}6s^26p^3$
Crystal structure:	Metallic bismuth has a rhombohedral crystal structure

46.1.2 Bi
Discovery and Occurrence

Discovery: Up to the 1500s miners and chemists were of the opinion that there were three types of lead, i.e. common lead, tin and bismuth. In addition, antimony was a special form of bismuth. Agricola had another approach. Bismuth was neither *plumbum candidum* (tin) nor *plumbum nigrum* (lead). It was *bisemutum*, a metal in its own right, different from all others.

Most important mineral: Bismuthinite, bismuth glance Bi_2S_3.
Bismuth is usually obtained as a byproduct of lead and copper manufacture.

Ranking in order of abundance in earth crust: 71

Mean content in earth crust:	0.0085 ppm (g/tonne)
Mean content in oceans:	$2 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

46.1.3 Bi
Chemical Characterization

Bismuth is a metal, white with a pinkish tinge. It is a poor conductor of heat and electricity. Its electrical resistance is increased in a magnetic field to a larger extent than any other metal. Bismuth is also the most diamagnetic of all metals.

Bi^{III} as in Bi_2O_3, BiI_3 and Bi_2S_3	$Bi(g) \rightarrow Bi^+(g) + e^-$	703	$Bi(g) + e^- \rightarrow Bi^-(g)$
Bi^V as in $NaBiO_3$ and BiF_5	$Bi^+(g) \rightarrow Bi^{2+}(g) + e^-$	1610	−91.2
	$Bi^{2+}(g) \rightarrow Bi^{3+}(g) + e^-$	2466	
	$Bi^{3+}(g) \rightarrow Bi^{4+}(g) + e^-$	4370	
	$Bi^{4+}(g) \rightarrow Bi^{5+}(g) + e^-$	5400	
	$Bi^{5+}(g) \rightarrow Bi^{6+}(g) + e^-$	8520	

Standard reduction potential: $Bi^{3+}(aq) + 3e^- \rightarrow Bi(s) \quad E^0 = +0.317$ V

Electronegativity (Pauling): 2.02

Radii of atoms and ions: (WebElements™)		
	Atomic:	160 pm
	Covalent:	146 pm
	Bi^{3+} (6-coordinate, octahedral):	117 pm
	Bi^{3+} (8-coordinate):	131 pm
	Bi^{5+} (6-coordinate, octahedral):	90 pm

46.1.4 Bi
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
9747 kg m^{-3} 9.75 g cm^{-3}	21.44 cm^3	544.6 K 271.4 °C	1830 K 1557 °C	122 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
11	8.2	7.2	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$12.3 \cdot 10^{-6}$	$13.4 \cdot 10^{-6}$	$12.7 \cdot 10^{-6}$	–

Resistivity nΩm

78 K	273 K	298 K	573 K	973 K	1273 K
350	1070	1300	1290	1550	1720

Mass magnetic susceptibility χ_{mass} at 293 K	$-16.84 \cdot 10^{-9}$ m^3kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
32 GPa	12 GPa	32 GPa	0.33

46.1.5 Bi
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	10.9 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	179 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	207 kJmol^{-1}
Entropy S^0 at 298 K	56.73 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

100 K	298 K	600 K	1000 K	2000 K	2500 K
23.0	25.52	31.4	31.4	21.0	21.4

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$4/3Bi + O_2 \rightarrow 2/3Bi_2O_3$	–329	–293	–200	–	–

46.1.6 Bi
Nuclear Properties and X-ray

Isotope range, natural and artificial	185–217

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{209}Bi	Stable	100	9/2-	4.111

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{209}Bi
Reference compound	$Bi(NO_3)_3/D_2O/HNO_3$
Frequency MHz (^{1}H = 100 MHz)	16.069
Receptivity D^P relative to ^{1}H = 1.00	0.144
Receptivity D^C relative to ^{13}C = 1.00	825
Magnetogyric ratio, radT^{-1}s^{-1}	$4.375 \cdot 10^7$
Nuclear quadropole moment, barn	–0.50

Characteristic X-radiation Z	 Element	 $K\alpha_2$ keV
82	Pb	72.804
83	Bi	74.815
84	Po	76.863

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	236
17.37 keV (Mo$K\alpha_2$)	128

Neutron absorption	Thermal neutron capture cross section	0.034 barns

46.2
A Workshop for Alchemists

The sulfides of arsenic and antimony have been known as minerals since antiquity, and they attracted great interest from the alchemists[1]. The alchemistic symbolism expressed something typical for both elements, as is shown in Figure 46.1. Bismuth was also examined in an alchemistic way, but soon became a metal for practical, technical use.

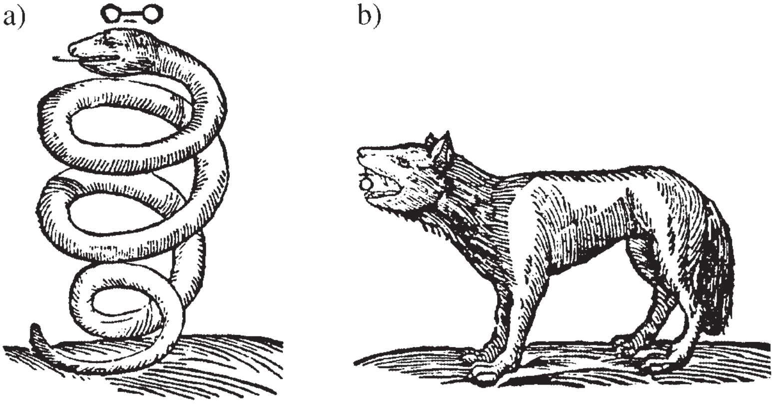

Figure 46.1 Alchemistic symbols for arsenic and antimony: (a) arsenic, symbolized as a venomous snake, and a deadly poison to handle; (b) antimony, symbolized as a wolf, ready to devour other metals, forming alloys.

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[1] For more about alchemy, see Chapter 2 The Knowledge of Matter.

46.2.1

Arsenic – Poison and Medicine

Arsenic sulfides were known in antiquity. Pliny described how orpiment (As_2S_3) was won in mines. Mortality was high among the slave workers who handled the substance. The situation was especially dangerous for those who had to treat minerals containing orpiment and prepare arsenic oxide.

Basilius Valentinus, a Benedictine monk in the 15th century, is given credit for various chemical writings. In one[2] he let the arsenic present itself (cited from Mary Weeks):

> Mein Nahme heisst Hütten-Rauch
> und ich bin ein giftiger böser Schmauch
> Da aber Ich verlier den Gifft
> Durch Kunst und rechte Handgriff
> So kann Ich Menschen und Vieh curiren
> Auss böser Kranckheit offtmals führen
> Doch bereit mit recht und hab gut Acht
> Dass du halst mit mir gute Wacht
> Sonst bin ich Gifft und bleibe Gifft
> Das manchems Hertz im Leib absticht.
>
> [My name is furnace smoke and I have a toxic and evil taste. But, when I lose the poison, by art and good craftsmanship, I can cure men and animals of severe illness. But, prepare me in the right way, be careful and keep a sharp eye on me. Otherwise I am and remain a poison that pierces the hearts of many people.]
>
> The miners in Bohemia followed this health advice when handling arsenious cobalt ores. On roasting, arsenic oxide sublimated off and the remaining ore could be treated reasonably safely. The arsenic oxide was delivered to the pharmacies.

46.2.2

Antimony – Needed for Making Gold

A central figure in many tales from the magical *Arabian Nights* was *Haru'n ar Rashid*, caliph of Baghdad AD 786–809. Contemporary with him was the famous alchemist *Ja'bir ibn Hayya'n*, working at the court in Baghdad. It was said that Ja'bir visited copper mines and observed how water, oozing out from the mine, had dissolved copper, which afterwards deposited as thin metallic shells in the arid sand. In these shells he could sometimes find pure gold. He concluded that copper could be naturally transmuted to gold. It made him search energetically for the substance that accomplished the transformation.

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[2] *Basilius Valentinus chymische Schriften*. Vol. 2, S. 156.
Gottfried Liebezeit, Hamburg, 1694.

Some had already found it. In *Arabian Nights* a tale is told about a Persian fire worshipper, who directs his blast towards copper in a crucible until it melts. From his turban he took out a folded paper and sprinkled a powder, colored as saffron, into the warm crucible. The blasting continues until the substance in the crucible had been changed to gold. It is believed that the mysterious powder could have been the bright red mineral *kermesite*, antimony oxysulfide.

Ja'bir ibn Hayya'n is considered to be the author of many alchemistic writings, which were not published until around 1300, at which time the author's name Ja'bir was changed to *Geber*. But perhaps they were written in Spain in the 14th century by another author who borrowed the name Ja'bir/Geber from the famous Arabian alchemist in order to improve the reputation of his own writings.

Alloys resembling gold were prepared in different ways and "mystery" was an essential ingredient. In Syrian writings from the time of the Crusades it is told how it is possible to make gold by melting red copper and adding antimony roasted in olive oil. But all that glitters is not gold! Already *Albertus Magnus* (1193–1280) had taught that the gold of the alchemists couldn't get through a *testing in fire*. This is also quite plain from Table 46.1. Putting the "new gold" into fire led to melting but also to oxidation and darkening. Genuine gold kept its color in the fire test.

Table 46.1 Melting points of gold and copper–antimony alloys

Metal/alloy	**Melting point, melting interval °C**
30% Sb, 70% Cu	645
6% Sb, 94% Cu	700–1050
Pure gold	1064

Basilius Valentinus is also said to have written *Triumphal Chariot of Antimony*. However, it has been questioned if this really is a work by a monk in the 1400s. It seems too modern for the 15th century and was in fact published by Johann Thölde in Germany in 1604. In the monograph it is emphasized that antimony minerals are the most suitable raw materials for the transmutation of metals into gold.

46.2.3
Alchemy, Iatrochemistry and Remedies

The discovery of phosphorus was a typical example of the two roles of alchemy: meaningless gold-making and purposeful experimental work, which sometimes gave unexpected, positive results. But is it correct to describe the alchemists' work as a meaningless gold-making? No! *Paracelsus* (1493–1541), the most distinguished alchemist, evidently prepared the way for the coming scientific revolution and its emphasis on experiment. As described in Chapter 2 The Knowledge of Matter, he was very critical of academic learning that was entirely theorizing, and he thus appeared as an opponent to scholasticism and ultimately also to Aristotle. Common sense and experience, theory and practice, had to walk hand in hand. During a short period as professor at the university of Basel he promised his students that he would teach them nothing but such things he himself had experience of and had acquired knowledge of in the open book of nature, *written with God's finger*. He also recommended his students to pick up real knowledge by study tours:

> Writings are interpreted through their letters, nature through journeys. The different countries and provinces are leaves in the book of nature.

Paracelsus was the founder of *iatrochemistry*, the chemistry of vital processes. Its leading idea was that the vital processes are of chemical nature. They cannot be understood without general knowledge of chemistry, and this knowledge is created in the laboratory. Health presupposed balance between the different chemical principles. Balance and health were obtained by the intake of medicines, often containing lead, mercury, antimony and even arsenic. Phosphorus was added to the medical list after its discovery. Perhaps iatrochemistry did not contribute so very much to public health but it did create chemical knowledge about many substances. Robert Boyle's criticism of the so-called chemical *principles* – sulfur, mercury, salt – in *The Sceptical Chymist* in 1661 took the sting out of iatrochemistry. The old ideas were superseded by new ones in the chemistry of the 18th century.

Paracelsus was a chemist of his time. He was however an alchemist for whom goldmaking was not in the forefront. With the knowledge he had acquired and with the ideas he represented, he would realize his basic attitude:

> It is the physical and mental health that is important, not the gold.

46.3
Arsenic

46.3.1
The Discovery of Arsenic

As early as 2000 BC arsenic compounds were known, and they were added to copper ores in metallurgical processes in order to make copper metal harder. This may be the background to the naming, later on, of the element. The Greek word *arsenikos* means "brave, male", related to "hard, strong".

Nobody knows for certain who first isolated the element. The learned alchemist and Dominican monk *Albertus Magnus* (1193–1280) may be the discoverer. In his book *De Mineralibus* he described how he prepared the metal by heating orpiment As_2S_3 with soap. He is also known for having translated Aristotle into Latin.

46.3.2
Arsenic Minerals

Arsenopyrite FeAsS constitutes the principal ore of arsenic. It is a white to steel gray orthorhombic mineral and occurs chiefly in lead and silver veins.

Realgar AsS is a red mineral, *orpiment* As_2S_3 a yellow mineral, often associated with each other, and found as deposits near hot springs and as a sublimates from volcanoes (see Figure M71).

Arsenic in ground water is largely the result of minerals dissolving from weathered rocks and soils. Several types of cancer have been linked to arsenic in water. In 2001 the US Environmental Protection Agency (EPA) lowered the maximum level of arsenic permitted in drinking water from 50 to 10 µg/l (micrograms per liter).

46.3.3
The Toxicity of Arsenic

The toxicity of arsenic is very different in various compounds. The sulfides have, like metallic arsenic, low toxicity. Scheele described the very toxic compounds arsenic oxide As_2O_3 and arsenic(III) hydride AsH_3 before 1775, thus at about the time he discovered hydrofluoric acid and phosphates in bones. These achievements made Scheele's name known in the whole chemical world.

The white oxide As_2O_3 is the assassin's poison *arsenic*. Two- or three-tenths of a gram is a lethal dose. There is however a remarkable accustoming effect, as the body can learn to accept a ten times greater dose. Perhaps this was the reason why Paracelsus and other iatrochemists could use arsenic as a medicine. Arsenic-containing remedies have been used even up to the 20th century, sometimes successfully, sometimes with disastrous results. Fowler's solution, containing potassium arsenite KH_2AsO_3, was used as a restorative, and many Victorian women died after taking toxic portions to achieve a chalky-looking complexion. Some arsenic-containing remedies were more successful. Arsenic iodide was used against leprosy. *Salvarsan*, an organic arsenic compound, was synthesized in 1909 and was used together with mercury and bismuth for the treatment of syphilis up to the 1940s. In 1945 penicillin became widely available and accepted for use against syphilis. Arsenic could almost entirely be rejected from the pharmacopoeia.

46.3.4
Was Napoleon Arsenic-Poisoned?

Hair contains proteins, rich in hydrogen sulfide groups SH^-, and arsenic is easily bound to these. If arsenic is added to the body, it is enriched in the hair, and for that reason analysis of hair is often used to diagnose arsenic poisoning.

Napoleon Bonaparte died in captivity on the island St Helena in 1821. The doctors did not agree about the cause of death. Was it poisoning? There is no doubt that the cause was in fact arsenic poisoning, but that does not necessarily imply murder. After Napoleon's death, his hair was tested. The arsenic content was determined to be

10–20 ppm, compared to a mean value of 1 ppm for people in general nowadays and 3–4 ppm in the 19th century. In what way had Napoleon been poisoned? There are two “natural” causes. One is that he had been prescribed medicines with arsenic, perhaps with increasing doses due to the accustoming effect. A second possibility is that the arsenic in Napoleon’s body had come from green curtains or wallpaper in his rooms. Copper hydrogen arsenite, *Scheele’s green*, was widely used as a pigment for textile printing in the 19th century. But, of course, a man like Napoleon, who had fought against the whole world, had many enemies, and intentional arsenic poisoning cannot be excluded.

46.3.5
Manufacture of Arsenic Products

Arsenopyrite FeAsS is the most important arsenic mineral. As a rule the arsenic-containing ores are mined mainly for their contents of the more attractive metals, gold, silver, copper, lead and zinc. On treatment of the complex ores, arsenic oxide As_2O_3 is obtained. Reduction with charcoal gives metallic arsenic. The most important commodity is however the oxide. The world production of As_2O_3 was 35 000 tonnes in 2001, with China as the largest producer country (16 000 tonnes), followed by Chile (8000 tonnes), Mexico and Peru (2500 tonnes each), Kazakhstan and Russia (1500 tonnes each), Belgium and France (1000 tonnes each).

46.3.6
Is There Any Use for Arsenic?

The main use of arsenic trioxide As_2O_3 is for the production of wood preservatives. These agents are effective as fungicides and herbicides. In 2002, however, the EPA announced that wood preservatives should be eliminated in dwelling houses from the end of 2003. Organic copper compounds will be the alternatives. Applications in which arsenic is enclosed in a medium or is so strongly bound that its injurious effect is negligible are still allowed. Arsenic-containing glass is used for screens, and highly pure arsenic selenide is used as a coating on drums for copying machines. High-purity arsenic metal (99.9999% or higher) is used for the manufacture of the semiconductor gallium arsenide GaAs.

46.3.7
The Assassin’s Poison and a Vital Element

Modern experiments with animals have shown that arsenic has a positive biological role, probably for protein synthesis. It is thus an essential element for some animals, perhaps also for humans. A low necessary intake, 0.1 mg per day, is obtained from drinking water.

46.4
Antimony

46.4.1
Ointment, Cosmetic and Medicine

The mineral antimony glance (stibnite, antimony sulfide) was known in antiquity. In Egypt an ointment containing the mineral was prepared. Supernatural virtues were attributed to it, and it was used for decoration. The black mineral was ground with a liquid in a mortar, and women in the Near East applied it with a paintbrush on eyebrows and eyelashes. The Greeks and Romans called the liquid used "collyrin", a word changed to *cohol*, which with an Arabic definite article became *al cohol*. Alcohol was for a long time just stibnite ground in a liquid. It was Paracelsus who began to use the word for concentrated spirits. Up to the end of the 18th century, the designation "alcohol" was used in parallel for both meanings.

Antimony compounds earlier played a great role in medicine and were used for antiseptic treatments and as an emetic. Nowadays the element is regarded as toxic, with an environmentally acceptable limit value for the metal and its oxides in the air of 0.5 mg Sb/m^3. The inexplicable early death of *Wolfgang Amadeus Mozart* was perhaps due to antimony poisoning. His doctor prescribed antimony tartrate for him as a medicine. He died in 1791 at the age of 35 with symptoms similar to those found in acute antimony poisoning.

46.4.2
The Name "Antimony"

The origin of the name "antimony" is a matter of dispute. The Egyptian ointment *stem* became the Greek word *stimmi* [46.1] and later the Latin element name *stibium*, which is the background to the mineral name stibnite and the chemical symbol Sb. Schelenz [46.2] stated that the word *stibium* was adopted in the Arabic language as *ithmid*, later *al ithmid*, which was Latinized to *antimonium* around 1100. It became a common name in the Middle Ages, at first as a mineral designation. When the metal was isolated later on, it was called a *regulus of antimonium*. Ball [46.3] says that the name has the meaning *anti monos* (not alone, not one). When we look at antimony from the viewpoint of today's technologies, the name "not alone" is appropriate. Pure antimony is not used, but the element is an important part in alloys and semiconductor materials.

46.4.3
Antimony Metal and Its Alloys in Ancient Times

The mysterious properties of antimony disappeared when alchemy languished. This metal – the sacral lead of the wise – became one of the everyday elements in chemistry.

Berthelot wrote that metallic antimony was known already by the old Chaldeans. He had analyzed a vase, brought to the Louvre from the ruins of Girso (Tello in present Iraq), where there was a Sumerian culture in 2700–2000 BC. The vase consisted of pure metallic antimony with only traces of iron. In Egypt, copper vessels coated with antimony have been found. They are dated 2500 BC. The use of pure antimony articles was the exception – the main application was for alloys. The metal is a component in Roman bronzes from the 1st century of our chronology. Agricola showed in the middle of the 16th century that if *stibium* is melted and reduced in a crucible, a regulus is formed, a metal earlier often regarded as lead. The pragmatic Agricola showed that the metal could be alloyed with tin, giving an alloy excellent for preparing printers' type. It was further developed to the classic type metal, consisting of 81% Pb, 15.5% Sb and 3.5% Sn. The alloy was ideal for its purpose, as its melt has the unusual property of expanding on cooling and solidifying (as when water freezes) and fills the mould well. The edges became sharp and the printing quality high. Modern offset printing has however made this old technique superfluous.

Geoffroy the Elder (Chapter 11 Sodium and Potassium) told in the 18th century about cups made of antimony. If the wine is kept overnight in such containers, its taste is said to be excellent. He also mentioned that it had been found that antimony gives a silver tone to bells made of tin, and that goldsmiths add antimony to the melt when refining gold. It removes all impurities from the gold melt and takes them up into the slag.

Nicolaus Lémery (1645–1715) was a French chemist and member of the Academy of Sciences. He had decided to make a careful analysis of the mineral called both antimony and stibnite. In 1707 he published his findings in a famous monograph *Treatise on antimony*. He described the mineral antimony as a black, heavy, shining mineral, crystallizing in long needles (see Figure M72). It occurs, he said, in many European mines. The alchemists called it *sacred lead* or *philosophers' lead* partly because the element had magic properties, partly because it is similar to lead in its tendency to "swallow" other metals (and form alloys; see Figure 46.1). Lémery had a small laboratory in Paris, which attracted students from Europe. In this he isolated the metal by heating the mineral to red heat in a crucible containing some organic reducing agent.

In the textbook *Cours de Chymie*, published in 1751, the author *Nicolas LeFevre* expresses criticism against Lémery and refers to Suchten and Basil Valentine, "Germans whose works are held in high esteems by connoisseurs". In his book LeFevre has a fascinating illustration of antimony calcination, with the use of a burning glass (Figure 46.2).

Antimony is not of great importance for chemistry students today, but once it was almost the most important [46.4]. When *Antoine François de Fourcroy*[3] (1755–1809) took an active part in the complete modernizing of his science, he also elucidated ancient chemistry. He wrote that no substance has been so carefully studied as antimony. It is possible to set up a whole library with writings about antimony. And in all

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[3] Fourcroy was one of the authors of *Méthode de nomenclature chemique*, which in 1787 expressed the leading ideas in Lavoisier's new antiphlogistic chemistry. His own modern textbook *Principes de chemie*, translated into eleven languages, contributed to the rapid breakthrough of the new chemistry.

Figure 46.2 Heating with a burning glass was utilized in early chemistry. This picture, from LeFevre, *Cours de Chymie*, shows calcination of an antimony mineral.

times antimony was looked upon as the most suitable material in the striving of the alchemists to reach their goal, metal transmutation to gold.

Antimonium had for centuries been used as a designation both for minerals and for the metal. One of Lavoisier's co-workers, *Jean-Baptiste Buquet,* proposed in 1771 that the word "antimony" should be reserved entirely for the metal. It was accepted, and Guyton de Morveau took the element antimony into the chemical nomenclature list in 1787.

46.4.4
Antimony – Occurrence and Modern Uses

Antimony is a rare element. Its content in the earth's crust is 0.2 g/tonne and it is the 65rd most abundant element. The principle mineral in ores is *stibnite, antimony glance,* a lead-gray sulfide Sb_2S_3 (Figure M72). It has a brilliant metallic luster and sometimes contains gold and silver. A second mineral is *ullmannite* NiSbS, steel gray to black.

In complex copper and lead ores antimony is also present as a minor element, and from these antimony is obtained as a byproduct in the winning of the main metals. One large antimony deposit, Gravelotte in the northeast of Transvaal in South Africa, can however be looked at as a primary antimony deposit. Antimony sulfide is found there together with gold, 1.8% antimony and 2 g gold/tonne. In the mine, antimony is the main element, gold a byproduct.

The world production of antimony in mines (counted as Sb) was 150 000 tonnes in 2001, of which China produced 135 000 tonnes or 90%, Russia and South Africa

2.5–3% each. In addition, some antimony is obtained as a secondary product from scrapped lead battery plates.

The most important use of antimony metal is as an alloying element in lead for storage batteries. An antimony content of 8% doubles the strength without changing the electrochemical behavior of lead. The result is a considerable weight saving compared to pure lead. New developments have however decreased the antimony content to 1.5%, or changed the alloy to lead–calcium. This has to a great extent infringed upon the main use of antimony in modern times.

The metal also finds applications in other alloys. Cable sheaths are made of lead that contains antimony, and lead shot for ammunition is not made of pure lead but of lead alloyed with 1–8% antimony. The American Isaac Babbitt (1798–1862) invented the bearing alloy named *babbitt metal*. It is an alloy of copper, antimony and tin, characterized by good antifriction properties, and used as the bearing material for axles and crankshafts. *Britannia metal* is another tin alloy with about 2% copper and 5–10% antimony. It is a silvery white alloy of tin, similar in appearance to pewter but harder. It is used for the manufacture of tableware.

Antimony trioxide is the most important of the antimony compounds and is primarily used, dissolved in organic solvents, for flame-retardancy of textiles, rubber and plastics in aircraft and automobile seat covers, and of children's clothing and toys. In the USA about 60% of all antimony use in 2001 was for flame-retardants.

Antimony pentasulfide Sb_2S_5 is used as an additive in rubber manufacturing. It causes a brick-red coloring of the rubber after vulcanization.

A modern use of antimony is for semiconductors. Most important are gallium, indium and aluminum antimonides, GaSb, InSb and AlSb.

46.5
Bismuth

46.5.1
Bismuth Metal and Its Alloys in Ancient Times

Up to the 1500s miners and chemists were of the opinion that there existed three types of lead: common lead, tin and bismuth. In addition, antimony was a special form of bismuth. In nature's own transmutation process, the metal silver was the ultimate aim for the lead metals. Bismuth had got on fairly well. When the miners found a vein of bismuth, it was however a disappointment: "We have arrived too early. Still bismuth!" But it was a hint. When the development had gone further and deeper, there perhaps silver could be found. They also called bismuth "the roof of silver", as they in fact often found silver below the bismuth deposit.

Agricola had another approach. Bismuth was neither *plumbum candidum* (tin) nor *plumbum nigrum* (lead). It was *bisemutum*, a metal of its own accord, different from all the others. In his book *De re Metallica* he described methods for the winning of bismuth from the mines in Erzgebirge: direct melting of native bismuth or roasting of bismuth sulfides, followed by charcoal reduction, melting and casting. He developed further the discovery that the alchemists had made in the middle of the 15th century, namely that an alloy containing bismuth ("the second sort of antimony") had such good casting properties that it could be used as a metal for type in Gutenberg's printing presses. Agricola laid the grounds for the knowledge of the chemistry of bismuth. But the further development got sidetracked. The name bismuth was sometimes used for zinc. It was also said that bismuth is nothing but tin, which the English miners in Cornwall had distorted. As late as 1713 the French Academy received a report, according to which bismuth was compacted from sulfur, mercury, arsenic and earth. *Caspar Neuman* (1683–1737) restored the order when in forceful words he stated that bismuth is a specific metal:

> It can be mined near Schneeberg in Saxony, but also in Bohemia and in England.

46.5.2
The Naming of Bismuth

At the beginning of more recent times there was still some confusion between the metals antimony and bismuth. Paracelsus wrote that there are two types of antimony. One is the common black one, with which gold is refined. It has a strong affinity to Saturn (lead). The other is the white one, also called magnesia and bismuth. It has large affinity to Jupiter (tin). The word "bismuth" is of disputed origin. Ball [46.3] gives it the meaning "white matter, white metal". This has a certain support in Paracelcus' description above. One interpretation is the following: The German words *Muten* (mining-claim) and *Wiesen* (a place with bismuth deposits in Erzgebirge) were combined into *Wiesen-mutung* (a mining-claim in Wiesen) and Latinized to *bisemutum*, a word used by Agricola. The word also got into the English language as *bismuth* and in the elements symbol list as Bi.

46.5.3
Occurrence and Manufacture of Bismuth

Bismuth is even more rare in the earth's crust than antimony. Its content is 0.0085 g/tonne and it is the 71th most abundant element. It occurs in nature partly native as metal but mainly as the sulfidic minerals *bismuthinite* Bi_2S_3 and *tetradymite* (telluric bismuth) Bi_2Te_2S. An oxidic mineral is *bismite* (bismuth ocher) Bi_2O_3. Bismuth is mainly obtained as a byproduct in the production of lead, copper and tungsten. In the working of sulfidic ores, bismuth concentrates are roasted to oxides, which are reduced by charcoal. Distillation in vacuum gives highly pure bismuth.

The only deposit with bismuth as the principal product was in Tasna Mine in Bolivia. The mine was closed in 1985 but there are plans to reopen it. World mine production was 4000 tonnes (as Bi) in 2001. China accounted for 37.5% of this, with Mexico and Peru at 25% each.

46.5.4
A Metal With Special Properties

Bismuth has some special properties:

- striking diamagnetic properties (Table 46.2)[4];
- very low heat conductivity (Table 46.3).

Table 46.2 Magnetic susceptibility of different metals

Metal	Magnetic susceptibility χ	Type of metal
Bismuth	$-17 \cdot 10^{-9}$	Diamagnetic
Antimony	$-10 \cdot 10^{-9}$	Diamagnetic
Copper	$-1.1 \cdot 10^{-9}$	Diamagnetic
Tungsten	$+4.0 \cdot 10^{-9}$	Paramagnetic
Molybdenum	$+12 \cdot 10^{-9}$	Paramagnetic
Chromium	$+44.5 \cdot 10^{-9}$	Paramagnetic

Table 46.3 Heat conductivity of different metals

Metal	Heat conductivity $\mathrm{W\,m^{-1}K^{-1}}$
Bismuth	8
Iron	80
Copper	400

46.5.5
Uses of Bismuth

Since the early 1990s bismuth has been replacing lead as a non-toxic alternative in many applications. Some examples can be mentioned here:

- fixtures and pipes for drinking water and food processing equipment;
- bismuth shot for hunting waterfowl;
- extreme-pressure lubricants;
- free-machining brasses;
- fishing sinkers;
- yellow bismuth vanadate as a non-toxic pigment alternative to lead chromate.

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4) A diamagnetic substance is weakly repelled by a magnetic field and has a negative magnetic susceptibility.

The property of bismuth alloys to expand on solidification is used to prepare vacuum-tight connections. A fused alloy may also be applied around the circumference of an optical lens. When the alloy has solidified, the lens is fixed for a grinding operation. After grinding, the alloy can be removed by heating in water or oil.

Wood's metal consisted originally of 50% bismuth, 25% lead, 12.5% tin and 12.5% cadmium. It had a melting point of 70°C. *Rose's metal*, with a melting point of 95°C, was an alloy of 50% bismuth, 25% lead and 25% tin. It takes its name from the German chemist and pharmacist *Valentin Rose Sr* (1736–1771).

> Members of the German family Rose have played a great role within chemistry and mineralogy. Valentin Rose Sr was a chemist with his own laboratory in Berlin. Some months before his death, he engaged M. H. Klaproth as a collaborator. Klaproth continued Rose's work in the laboratory and took care of and educated the two fatherless sons. One of them, *Valentin Rose Jr* (1762–1807), became a famous chemist too and continued the cooperation with Klaproth. Valentin Jr had two sons, *Heinrich Rose* (1795–1864) and *Gustav Rose* (1798–1873). Heinrich studied with Berzelius in Stockholm in 1820–1821. He became professor of chemistry at the University of Berlin in 1823, a position that Berzelius had been offered in 1817 but refused. Heinrich Rose developed analytical chemistry considerably and in the period 1840–1845 made great achievements to clarify the chemistry of niobium and tantalum. His brother Gustav became a mineralogist and, like his brother, professor at Berlin University. In 1864 Gustav Rose established the first systematic description of meteorites.

Today, a whole alloy family, with bismuth as base, is manufactured for soldering and for fuses in fire doors and sprinkler heads, due to the low melting points of the alloys.

The oxychloride BiOCl is utilized in an odd application of bismuth. The compound can be crystallized as small plates with a diameter of less than 10 µm. The small crystals have a very high refractive index and, dispersed in nail varnish or ointment, a pearlescent effect. For that reason, bismuth oxychloride has been an important pigment for cosmetics. Annually more than 500 tonnes of bismuth is used for this purpose.

Bismuth has a good contrasting effect in X-ray investigations and may be built into plastics that are implanted by doctors and dental surgeons. As a result of its content of bismuth, the implant can easily be localized.

Bismuth has a special use in *Peltier elements*. The Peltier effect is the thermocouple effect working backwards, and is utilized for thermoelectric cooling elements. The thermoelectric effect for temperature measuring was treated in Chapter 32 Platinum Group Metals. A thermocouple consists of two wires of different materials, joined together at each end. If one junction is placed in ice–water, the other in boiling water, an electric current will flow in the wires. On the contrary, an external electric current in the wires will cause a change of temperature between the junctions. With suitable materials, a temperature difference as big as 100°C can be obtained. Bismuth telluride Bi_2Te_3 is a material used for this application. Combinations of suitable p- and n-semiconductors are also utilized. When connected to a DC current, one side of the thermocouple cools, while the other side generates heat. The use in food and beverage coolers has increased, although the main applications are for cooling of infrared detectors, laser diodes, integrated circuits and medical instrumentation.

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47
Oxygen

47.1 O
Facts about Oxygen

47.1.1 O
The Element

Symbol:	O
Atomic number:	8
Atomic weight:	16.00
Ground state electron configuration:	$[He]2s^2 2p^4$
Crystal structure:	Monoclinic below 23.8 K, rhombohedral between 23.8 and 43.8 K, and cubic between 43.8 and m.p. 54.8 K.

47.1.2 O
Discovery and Occurrence

Discovery: Scheele discovered oxygen, probably in 1772. He prepared oxygen by heating mercury oxide and silver carbonate. The result was published in 1777. In 1774 Priestley discovered oxygen independently. Lavoisier gave the name *oxygène* to the element.

Important raw materials: The atmosphere O_2
The water H_2O

Ranking in order of abundance in earth crust:	1
Mean content in earth crust:	$46.1 \cdot 10^4$ ppm (g/tonne) (46.1%)
Mean content in oceans:	$85.7 \cdot 10^4$ ppm (g/tonne) (85.7%)
Residence time in oceans:	–
Mean content in an adult human body:	$61 \cdot 10^4$ ppm (61%)
Content in a man's body (weight 70 kg):	42.7 kg

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47.1.3 O
Chemical Characterization

Oxygen is a colorless, odorless and tasteless gas O_2. As liquid and solid it is a pale blue substance. The most important industrial method for the manufacture of oxygen is fractional distillation of liquid air. Oxygen is utilized in the chemical industry and in steel-making. In biology, oxygen is necessary for respiration of all plants and animals. Ozone O_3 is formed in electrical discharges or when ultraviolet light acts on O_2.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
O^{-II} as in MgO	$O(g) \rightarrow O^+(g) + e^-$	1314	$O(g) + e^- \rightarrow O^-(g)$
O^{-I} as in H_2O_2 and Na_2O_2	$O^+(g) \rightarrow O^{2+}(g) + e^-$	3388	–141
O^{I} as in O_2F_2	$O^{2+}(g) \rightarrow O^{3+}(g) + e^-$	5301	
O^{II} as in OF_2	$O^{3+}(g) \rightarrow O^{4+}(g) + e^-$	7469	
	$O^{4+}(g) \rightarrow O^{5+}(g) + e^-$	10 990	
	$O^{5+}(g) \rightarrow O^{6+}(g) + e^-$	13 327	
	$O^{6+}(g) \rightarrow O^{7+}(g) + e^-$	71 330	

Standard reduction potential:	$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	$E^0 = +0.695$ V
	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(aq)$	$E^0 = 1.229$ V

Electronegativity (Pauling):	3.44	
Radii of atoms and ions:	Atomic:	60 pm
(WebElements™)	Covalent:	73 pm
	Van der Waals:	152 pm
	O^{2-} (4-coordinate, tetrahedral):	124 pm
	O^{2-} (8-coordinate):	128 pm

47.1.4 O
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
1.429 kg m^{-3} 1.43 g/l	1.10	54.8 K –218.4 °C	90.19 K –182.96 °C	918 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 73 K	173 K	273 K	373 K	1273 K
–	0.0159	0.0245	0.0323	0.086

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K) a	b	c
29.96	$4.18 \cdot 10^{-3}$	$-1.67 \cdot 10^{5}$

Ratio C_p/C_v (ideal gas = 5/3 = 1.667)

O_2 1.4 (278–287 K)
O_3 1.29

Solubility in water m^3 gas at STP per m^3 water 273 K	293 K	313 K	333 K	353 K	373 K
O_2/0.0489 O_3/0.45	O_2/0.0310 O_3/0.24	O_2/0.0231 O_3/0.11	O_2/0.0195	O_2/0.0176	O_2/0.0170

Mass magnetic susceptibility χ_{mass} at 293 K	$1355 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)
Critical point:	T_c 154.8 K P_c 5.08 MPa

47.1.5 O
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	0.444 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	6.82 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	249 kJmol^{-1}
Entropy S^0 at 298 K	205.14 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	29.11	29.38	32.09	34.88	37.78	38.93

47.1.6 O
Nuclear Properties and X-ray

Isotope range, natural and artificial	12–24

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{16}O	Stable	99.76	0+	–
^{17}O	Stable	0.04	5/2+	–1.894
^{18}O	Stable	0.20	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{17}O
Reference compound	D_2O
Frequency MHz (^1H = 100 MHz)	13.556
Receptivity D^P relative to ^1H = 1.00	$1.11 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.0632
Magnetogyric ratio, radT^{-1}s^{-1}	$-3.628 \cdot 10^7$
Nuclear quadropole moment, barn	–0.026

Characteristic X-radiation

Z	Element	Kα_2 keV
7	N	0.393
8	O	0.525
9	F	0.677

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	11.5
17.37 keV (MoKα_2)	1.24

Neutron absorption	**Thermal neutron capture cross section**	$2.9 \cdot 10^{-4}$ barns

47.2
Oxygen in History

47.2.1
Knowledge About Oxygen Before Its Discovery

The discovery that air is complex and not simple removed one of the keystones in the ancient idea of matter, namely that air is one of the fundamental elements. It is generally accepted that Carl Wilhelm Scheele and Joseph Priestley independently discovered oxygen in the period 1772–1774. Were they first? Well, their priority is not questioned. Both expressed the view that air consists of two elements, oxygen and nitrogen. However, as happens for many important discoveries, they arrived at their conclusion when the time was right. Many other scientists had been on the same track but had taken longer to arrive at the right conclusion.

The orientalist *Heinrich Julius Klaproth*, son of Martin Klaproth, had found a Chinese manuscript from the middle of the 8th century AD, in which a learned Chinese man, *Mao-Khóa*, wrote that the air is composed of two gases, *Yang* and *Yin*. The two components acted differently with metals, sulfur and carbon. When these substances burn, the air is deprived of its content of *Yin*. *Yin* is never found free but is a constituent of minerals. *Yin* can be driven out from saltpeter by heat. Obviously *Yin* is oxygen, while *Yang* is nitrogen. *Yang* and *Yin* are, moreover, the fundamental principles in the religious philosophy of Taoism, from which Niels Bohr derived courage and inspiration. In reality *Yang* and *Yin* are two indivisibly woven principles, yet separable, when they were applied as air in contact with hot metals.

The first European to maintain that air is not one element was *Leonardo da Vinci* (1452–1519). He had observed that air is consumed during breathing, but not entirely. He taught that “where a flame cannot burn, an animal cannot breath”. *Robert Hooke* (1635–1703) was one of the leading scientists and inventors in 17th century England. As a young man he was employed at the Royal Society, where his job was to carry out experiments and perform demonstrations. Later on he became its secretary. He came early into contact with the problem of air and its properties. He designed and built the air pump, which Boyle used for the investigation of the relation between the pressure and volume of gases (Boyle’s law). In his book *Micrographia* (1665), Hooke formulated a theory for burning and expressed the opinion that air is composed of two substances, one inert, one active, the latter also present solid in saltpeter. Another of England’s many pioneers within the field of gas chemistry and physics was *John Mayow* (ca. 1640–1679). He showed that in air there is a substance present, *spiritus nitroaeraeus*, essential for candles to burn and for animals to breath.

M. V. Lomonosov (1711–1765) in St Petersburg observed that metals increase their weights on burning. In 1756 he heated metals in sealed test tubes containing air. The metals reacted to oxides. He weighed the tubes before and after (when the heated tubes had cooled to room temperature). The weight was unchanged. Thus the enclosed air had decreased its weight just as much as the metal had increased. The air had placed its oxygen at the disposal of the metal for oxide formation. His conclusion was important. No doubt these experiments formed the background to his early rejection of the phlogiston theory. It places him in the front line of the chemical revolution in the 18th century.

47.2.2
Carl Wilhelm Scheele's Discovery of Oxygen

Scheele (Figure 47.1) prepared oxygen in different ways, such as for instance heating saltpeter together with mercury oxide and pyrolusite mixed with sulfuric acid. He showed that oxygen is essential for burning and absolutely necessary for breathing. Professor P. T. Cleve in Uppsala [47.1] described the simple equipment that Scheele utilized for his discovery of oxygen (Figure 47.2). In the 1930s the historian and genealogist professor Bengt Hildebrand [47.2] made an analysis of Scheele's research, especially regarding the time of the oxygen discovery and the priority dispute between Priestley and Scheele. His conclusion was that Scheele had already isolated oxygen in 1771–1772, whilst still active in Uppsala. Priestley's discovery was on August 1, 1774.

Figure 47.1 Carl Wilhelm Scheele. (Reprinted from ref. [47.1].)

Professor Arne Fredga [47.3] treated the priority problem again in 1942, and says in his conclusion that it is incontrovertible that Scheele delivered two important reports to Torbern Bergman, in the first part of the 1770s. The first was a description of the preparation of oxygen; the second was his famous paper on pyrolusite. This latter one was handed over in November 1773. Jan Trofast [47.4] writes that Scheele prepared oxygen before 1773 by calcination of silver carbonate, mercury carbonate, red mercury oxide, a mixture of saltpeter and magnesium nitrate, as well as by distillation of arsenious acid and pyrolusite.

Scheele seems to have been first with the discovery of oxygen, even if his publication of the results came later. His great work *Chemische Abhandlung von der Luft und dem Feuer* (*Air and Fire*) was published in German in Uppsala and Leipzig in 1777, in English in 1780 and in French in 1781. This is treated in Chapter 44 Nitrogen. Priest-

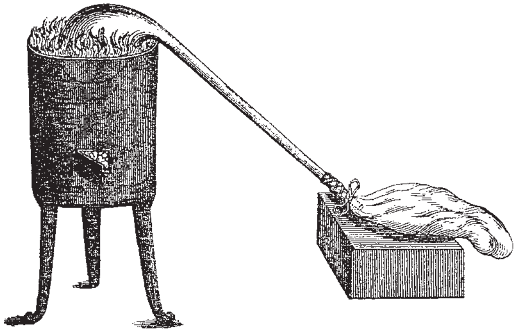

Figure 47.2 Scheele's equipment for production of oxygen. (Reprinted from ref. [47.1].)

ley made his discovery in 1774 without knowledge about Scheele's work. It is quite correct that both of them share the priority.

> In his analysis Fredga discussed the reasons for Scheele's impressive results. How could he make a success of everything, as a French chemist expressed it? There are of course many reasons. One important thing was that Scheele forced his own way into science. He learned everything by testing and believed only in the testimonies of his own senses. By that means he came to see and to discover much that a trained *systematicus* regarded as impossible, because it was contrary to some principles. The scientific community in the 18th century had a strong utilitarian character and its intent was "useful findings". In all essentials Scheele had a different attitude. As he himself expressed it, he liked to analyze what seemed to be obscure. His own way led him to large and unexpected discoveries. Many of them caused astonishment in his time and bore fruit for coming generations.
>
> Scheele's all-absorbing interest in chemistry and his great rate of working gave results. But it came at a price. After 15 intense years of apprenticeship and 15 years of intense scientific production, he was physically worn out. He died in 1786 at the age of only 44.

47.2.3
Joseph Priestley – Faith and Knowledge

Society in England during the late 18th century presented striking personalities with unconventional professional combinations. *William Gregor* in Cornwall was a vicar and at the same time a prominent mineralogist. He discovered (independently of Klaproth) the element titanium. *Henry Cavendish* was Duke of Devonshire. He discovered hydrogen and elucidated the composition of water. *Joseph Priestley*, pastor of a non-conformist congregation, discovered photosynthesis and was, in parallel with Scheele, the discoverer of the element oxygen.

Priestley and Cavendish were of very similar ages; the former was born in 1733 in Fieldhead, an isolated village near Leeds, in the northern English county of Yorkshire, and the latter was born in 1731 to an aristocratic London family. Their conditions were as unlike as could be imagined, and they also grew up into quite different personalities. But one thing they had in common. Both of them became important scientists within the field of the chemistry of gases.

Various protestant groups refused to conform to the established Anglican Church [47.5]. They were called non-conformists or dissenters. The movement had its roots in the 17th century but became especially strong during the 1700s. Joseph Priestley lived in that tradition. Early motherless, he was adopted by his childless Aunt Sarah when he was nine. In her house he came into contact with theological questions and liberal political attitudes. His aunt was a very valuable support to the restless, energetic boy, who was always on the move. Joseph had a decided aptitude for studies, with a habit from youth for hard work. He was sent to several schools, where he rapidly learned more than expected.

In local schools he learned Greek and Latin, and, during school holidays, Hebrew. He also studied modern languages, German, and French, with great gusto. At this time, Dissenting Academies became the center of liberal education since the doors of the great universities were closed to non-conformists. In 1752, aged 19, Joseph was admitted as a student to such an academy in Daventry. Waiting for the beginning of the courses he studied mathematics privately with pastor Haggerston who had been educated by the renowned professor Colin MacLaurin in Edinburgh. In the Academy his dominant inclination was still towards theology. Ordinary education, however, did not offer him sufficient occupation. His energy was large enough also for science. He started to read – thoroughly – Boerhaves textbook *Elementa Chemiae*, which came out in a new edition in 1753.

After three years in Daventry he accepted positions as pastor in small congregations. His responsibilities expanded to teaching in local schools. The increased income enabled him to buy an electric motor and an air pump, and he spent much time on experiments.

His school activity opened the door to a post as teacher at a new Dissenting Academy in Warrington, where he spent six happy years. With his usual energy he started to modernize the teaching. His textbook *Theory of Language and Universal Grammar* was printed as a workbook, with possibilities for students and teachers to fill in and complete. It attracted rather a lot of attention. He taught languages, rhetoric and civics. It was not these subjects that later on made him world-famous, but the post as teacher was important for Joseph's development. He became used to analyzing and solving problems in cooperation with a group. He learned to appear in public, freely and safely.

At this time his interest in science deepened. During a visit to London an event occurred that became decisive in his life. He met *Benjamin Franklin* (1706–1790) and was introduced to scientific society. Priestley was so inspired that he started to write The History and Present State of Electricity, which included original experiments and illustrations. This led to his election as a Fellow of the Royal Society in 1766. Priestley was 33 and his scientific career had begun.

This is not to imply that he finished his religious activity. Soon he got a post in a congregation in Leeds. There his house happened to be next door to a big brewery. He had carbon dioxide gas, *fixed air*, within easy reach. He started to carry out experiments with gases and found that some have greater solubility in water than others. If he were to measure the volume of a soluble gas, he could not collect it over water. Instead, as he had learnt from Henry Cavendish, he had to collect it over mercury. Carbon dioxide in contact with water was interesting for another reason. At high pressure (as mentioned, he owned an air pump) the gas dissolved considerably in water. The water got a refreshing taste and he recommended the drink to his friends.

William Petty, Earl of Shelburne, offered Priestley a position as librarian and tutor to his sons. The years 1773 to 1780, when he cooperated with Lord Shelburne, were the most fruitful of Priestley's career as a chemist. In this time he published Experiments and Observations *on Different Kinds of Air*, which contained his major chemical achievements.

About 1780 Priestley withdrew from his position with Lord Shelburne and settled at Fairhill, on the outskirts of Birmingham. There he joined the learned *Lunar Society*, an informal group of men who were interested in natural science and literature. Benjamin Franklin was a frequent guest. The society met once a month on the Monday nearest the full moon. This time was chosen so that the members could return to their homes by moonlight. In this society he met *James Watt* (1736–1819), who in 1774 opened a factory in Birmingham for manufacturing the steam engines he himself had invented. Also Erasmus Darwin (1731–1802) was a member. He was a doctor, but also philosopher and author with great interest in the secrets of creation and nature. Further, so was Josiah Wedgewood (1730–1795), distinguished ceramicist and industrialist. Erasmus Darwin was moreover paternal grandfather and Josiah Wedgewood maternal grandfather to Charles Darwin.

The existence could be carefree and idyllic in Birmingham in the 1780s, but there was a storm brewing in the world. The British colonies in North America had fought a bitter war against the mother country and made themselves free. Near by, on the other side of the Channel, the French Revolution raged. The sympathies of the Dissenters lay with those who were struggling against oppression. Priestley pronounced himself in favor of both the American liberation and the French Revolution. This was not quite without risk in royalist England. On July 14, 1791, the second anniversary of Bastille Day, about 80 people attended a dinner in a restaurant in Birmingham. This was taken as support for a revolution also in England. After the dinner, a crowd broke the windows in the restaurant. Priestley had declined to attend the dinner, but the riots continued and reached the New Meetinghouse, where Priestley preached. It was burned as a demonstration against Priestley's revolutionary and putative heretical writings. His home, laboratory and library, with not yet published manuscripts, were also destroyed. With the assistance of friends, the Priestley family were able to escape to London. In 1794, two weeks after Priestley's 61st birthday, he moved with his family to America. Whilst Priestley was on his journey, Lavoisier met his death at the guillotine in the Place de la Revolution.

At the end of his life, Priestley expressed the following to his new scientific colleagues at the American Philosophical Society [47.6]:

> Having been obliged to leave a country, which has been long distinguished by discoveries in science, I think myself happy by my reception in another, which is following its example, and which already affords a prospect of its arriving at equal eminence.

It was a prophetic statement.

> Priestley died in 1804. On the centennial of his oxygen discovery, thus in 1874, American chemists assembled in order to honor his memory. The occasion was significant, as then the initiative was taken to form the American Chemical Society, now the largest scientific association in the world. It was founded in 1876 after two years of preparation work.

47.2.4
The Discovery of Photosynthesis in 1771

Priestley is known for the discovery of oxygen in 1774, but other important achievements preceded it. In 1771, in the experiment illustrated in Figure 47.3, he observed that plants emit a gas that can purify air.

In the publication *Experiments and observations on different kinds of air* (Birmingham, 1790) Priestley wrote:

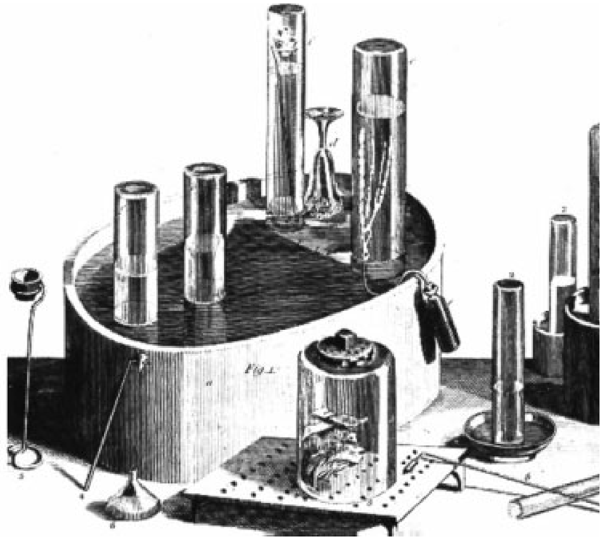

Figure 47.3 Priestley's equipment for pneumatic experiments. In the jar in the foreground, turned upside-down, is a mouse.

> I have been so happy, as by accident have hit upon a method of restoring air, which has been injured by the burning of candles, and to have discovered at least one of the restoratives, which nature employs for this purpose. It is vegetation. Finding that candles could burn very well in air, in which plants had grown a long time, and having had some reason to think that there was something attending vegetation, which restored air that had been injured by respiration. I thought it was possible that the same process might also restore the air that had been injured by the burning of candles. Accordingly, on the 17th of August 1771, I put a sprig of mint into a quantity of air in which a wax candle had burned out and found that, on the 27th of the same month, another candle burned perfectly well in it ...

Priestley also made air noxious by letting mice breath and die in an air volume (Figure 47.3). He divided this volume in two parts. In one part he put a sprig of mint, in the other not. After eight to nine days one mouse was placed in each of the jars. In the one with mint the mouse lived perfectly well, but in the other one it died immediately.

In 1773 Priestley was honored with the Royal Society's gold medal for his air investigations. In the citations it was expressed that:

> ... these experiments show us plainly that no plant grows in vain, but that every one of them, from the oak in the forest to the grass in the field, is useful to mankind. Even those, who seem to have no special use help to keep the atmosphere sufficiently pure for animal life.

At the beginning Priestley was not aware of which substance in the air the vegetation restored. Much later, in 1778, he identified this gas as dephlogisticated air, thus oxygen.

In the big cities today, much oxygen is consumed by the millions of people living and working there. Correspondingly, much carbon dioxide is produced. The large and/or numerous parks in the cities, for example Hyde Park in London, Central Park in New York, and Humlegården in Stockholm, take care of this carbon dioxide and recreate oxygen, just like the sprig of mint in Priestley's experiments in the 1770s. The rainforests on earth are worth fighting for.

47.2.5
Priestley's Discovery of Oxygen in 1774

On August 1, 1774, Joseph Priestley heated mercury oxide using a burning glass. A gas was liberated and he collected it over water. He found that combustible substances burned in that gas with a clearer flame than in air. When he tested the new gas on himself, breathing after drawing it through a glass siphon, he stated that:

> The feeling of it to my lungs was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that, in time, this pure air may become a fashionable article in luxury? Hitherto only two mice and myself have had the privilege of breathing it.

William Hewson (1739–1774) had in 1770 shown experimentally that there is a difference between the blood in veins and in arteries. The former is dark, the latter is light red. The color change occurs on passage of the blood through the lungs. Priestley found that the component of the atmosphere that restores the bright red color to the dark blood is dephlogisticated air (oxygen).

47.2.6
Oxygen Discoveries and the Chemical Revolution

In France, Lavoisier was informed about Scheele's and Priestley's oxygen discoveries. In the posthumous collections of the French chemist, a letter from Scheele, dated September 30, 1774, was found. In it Scheele gives information about how oxygen can be prepared by heating of silver carbonate. He recommends Lavoisier to utilize his big burning glass for heating of the substance. During this operation, Scheele wrote, equal parts of oxygen and carbon dioxide will be formed. On collecting the gas mixture over limewater, the latter will be absorbed, while pure oxygen remains. Scheele writes [47.7]:

> Je vous serai infinement obligé, si vous me faites savoir le resultat de cet experiment.
> [I should be very grateful if you might let me know the result of this experiment.]

There is no information available that Lavoisier actually carried out this experiment.

In October 1774 Priestley followed Lord Shelburne on a tour to France and met Lavoisier. When he informed Lavoisier about his recent isolation of the gas from mercury oxide, he was in fact unaware of the large importance of his discovery. At that time Lavoisier already had done several experiments showing that metals, burning in air, increase their weights. According to the phlogiston theory the weights should decrease. Now the pieces fitted together. The two phlogiston advocates, Scheele and Priestley, had given Lavoisier the ammunition he needed to sink the phlogiston theory. In the burning of metals, phlogiston is not removed, as the 17th and 18th chemists had thought. Nor did the metals combine with air, as Lavoisier himself had thought. No – on burning, metals combine with oxygen. The role of oxygen on burning was elucidated clear. It was the chemical revolution.

47.3
The Occurrence of Oxygen

Oxygen is the most common element on earth and the third most abundant in the universe. Its occurrence is described in Table 47.1.

Table 47.1 Oxygen occurrence in different "regions"

Region	Comments
Entire universe	In the whole universe, hydrogen and helium are the most common elements. Oxygen has the third position
Whole earth	29% of the total mass of the earth is estimated to consist of oxygen
Earth's crust	46% of the earth's crust consists of oxygen, which makes it the most common element in the crust. Oxygen is present in oxides, silicates, carbonates, phosphates and so on
The hydrosphere	Oxygen is of course a major component of the water of oceans, lakes and rivers, and is also present in the water as dissolved oxygen gas and in dissolved sulfates, carbonates, etc. The ice near the poles also is a considerable part of the hydrosphere. The total mass of the hydrosphere is ca. $1.5 \cdot 10^{18}$ tonne, of which oxygen represents 86%
The atmosphere	The oxygen content in the atmosphere is 21% by volume at the surface of the sea. The total amount of oxygen in the atmosphere is an impressive $1.2 \cdot 10^{15}$ tonnes. However, this is only one-millionth of the total amount of oxygen on the earth
The biosphere	In living organisms, oxygen is present bound in water, phosphates, carbohydrates and proteins. An adult is made up of 65% oxygen. The oxygen supply occurs by breathing in daily an air volume corresponding to 630 liters of oxygen. A further ca. 225 g is taken in from food

47.3.1
Oxygen in the Air and Photosynthesis

The development of microorganisms able to split the water molecule was an important, early step in evolution. In this process carbon dioxide and water are transformed to carbohydrates, such as for instance glucose and free oxygen. Sunlight is essential for the process (Figure 47.4). The photosynthesis reaction for the production of glucose $C_6H_{12}O_6$ can be written simply as

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

However, Table 47.2 is an attempt to show, more realistically, how the complicated photosynthesis reaction actually functions.

Almost all the oxygen in the atmosphere has been formed by photosynthesis. Until conditions for this reaction were favorable, about 3 billion years ago, the oxygen

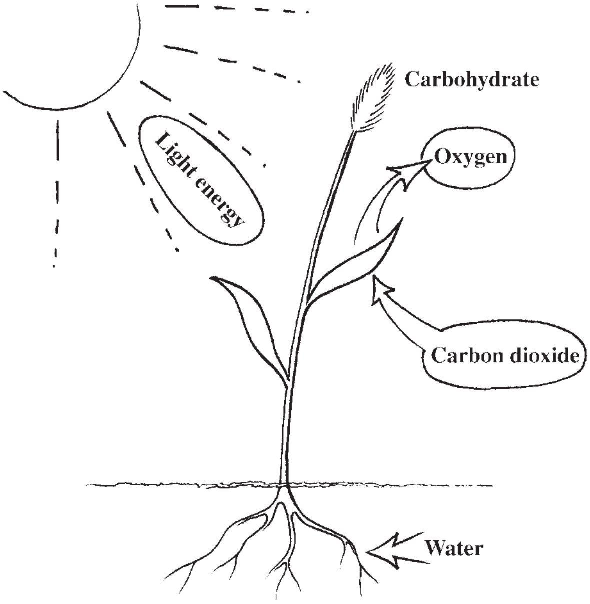

Figure 47.4 Schematic illustration of photosynthesis.

content of the earth's atmosphere was very low. With the right conditions, the process started and the oxygen content increased. The oxygen formed in photosynthesis gave problems. For what purpose should it be used? The chemist can see from the photosynthesis reaction equation that increasing the oxygen content in the atmosphere makes it more difficult for the reaction to proceed to the right.

Table 47.2 The complex photosynthesis reaction

$6CO_2$	+	$12H_2O$	+	light	→
Carbon dioxide. Its oxygen goes to make glucose and newly formed water		Available water. This provides the oxygen formed in photosynthesis			
→ $6O_2$	+	$C_6H_{12}O_6$	+	$6H_2O$	
Oxygen. Formed from water available at the beginning		Glucose. Made with oxygen from carbon dioxide		Formed water. Its oxygen comes from carbon dioxide	

Thus from the viewpoint of the carbohydrates, the oxygen formed was a poison. The content of oxygen, however, increased during geological epochs and became a threat to green vegetation. But, in contrast, the increasing oxygen content created the necessary conditions for a new type of living matter, animals. They utilized oxygen for their vital processes. A balance arose with an atmosphere, well suited for both animals and vegetation. Photosynthesis is the basis for the generation and maintenance of this balance. The behavior of mankind in our time may disturb the balance, as has been treated in Chapter 39 Carbon.

47.3.2
Ozone

47.3.2.1 Ozone in the Stratosphere – A Useful and Protective Molecule

At a very high altitude in the stratosphere[1], some oxygen molecules are split into oxygen atoms:

$$O_2 \rightarrow 2O$$

The latter react with oxygen molecules to form *ozone*, the triatomic oxygen molecule:

$$O_2 + O \rightarrow O_3$$

Both processes are influenced by the short-wave ultraviolet radiation in sunlight. The formation of ozone mainly occurs over the pole that is experiencing summer. With the wind systems in the stratosphere, the ozone gas is transported across the equator and up to the winter pole. The content of ozone is never high. In the lower region of the stratosphere, at a level of 15–30 km, it has its highest value, about 0.001% by volume. That is the *ozone layer*.

In the ozone layer pronounced absorption of ultraviolet radiation occurs. Without the ozone layer, ultraviolet would reach the earth's surface and injure animal life and vegetation. Malignant melanomas, a form of skin cancer, would increase considerably. However, it is possible to destroy the ozone layer.

If the hydrogen in a hydrocarbon, such as for instance CH_4 or C_2H_6, is totally substituted by fluorine and/or chlorine, a group of substances, the *chlorofluorocarbons*, also called freons or CFCs, are formed. Two examples are CCl_3F (designated CFC-11) and CCl_2F_2 (CFC-12). The former is a liquid with a boiling point of +23.8°C; the latter is a gas with the boiling point of –29.8°C. The liquid has been used as a refrigerant, the gas as a foam-blowing agent. Some freons have also been utilized as degreasing agents in industry. The great stability of CFCs made them much appreciated in the different functions.

The American chemists F. S. Rowland and M. J. Molina in 1974 called the world's attention to the fact that the stability of CFCs could be disastrous. The CFC gas that blows out the aromatic deodorant from its bottle or can is stable and not decomposed under normal atmospheric conditions in the troposphere. When it gradually reaches the stratosphere, its stability is decreased. Affected by the ultraviolet radiation in sun-

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[1] The *troposphere* starts at the earth's surface and extends 8–15 km high. The *stratosphere* starts just above the troposphere and extends to 50 km high.

light, CFCs are decomposed and chlorine atoms are released. They catalyze the decomposition of ozone, creating *ozone holes*. The term “ozone hole” refers to a large and rapid decrease in the abundance of ozone molecules, not to the complete absence of them. This phenomenon is especially observed over the Antarctic, where the weather is very special. Ice clouds freeze substances that otherwise would be able to neutralize the chlorine compounds. The ozone-demolishing substances then are free to act and may deplete the ozone layer in a very short time. British scientists first observed the ozone hole over Antarctica in 1985. As a result, an international agreement was reached (the Montreal Protocol), which implements controls on the consumption of ozone-depleting substances. The Protocol was signed on September 16, 1987, and originally negotiated between 24 countries. The Protocol has been amended from time to time, and, to date, over 175 countries have signed up to it.

Actual information is given in ref. [47.8].

47.3.2.2 **Ground-Level Ozone – A Harmful and Poisonous Molecule**

Ground-level ozone, thus ozone in the air up to a level of about 1000 m, is formed from nitrogen oxides, and leakage from industrial equipment for ozone manufacturing. It may also have its origin in the electrical discharges that occur during thunderstorms.

This ozone can be harmful to people, animals, vegetation and materials in different ways. It irritates the respiratory system, it can make asthma, emphysema and bronchitis worse, and it may even cause permanent lung damage. Ground-level ozone also hastens the aging of spruce needles and causes brittleness in polymer materials, such as plastics and rubber products.

Ozone absorbs not only ultraviolet but also infrared radiation. Thus ozone contributes to the greenhouse effect. Ozone is typically a summertime pollutant and a chief component of summertime smog.

Actual information is given in ref. [47.9].

47.4
Manufacture and Use

47.4.1
Oxygen Gas

Liquid and gaseous oxygen are produced in very large quantities, mainly by fractional distillation of liquid air. The annual production is about 100 million tonnes. New methods are being developed. If air is forced through a ceramic based on zirconium oxide, the oxygen preferentially passes through.

The steel industry is a big consumer of oxygen, as it utilizes oxygen to transform cast iron to steel. This is described in Chapter 8 Iron. Large amounts of oxygen are also used in the engineering industry for welding and cutting of metals. In organic chemistry, oxygen is used for synthesizing methanol and ethylene oxide (epoxyethane). The use of oxygen in hospitals as breathing support is not large, as far as tonnage is concerned, but it is of vital importance from a medical point of view. Passengers in aircraft are always informed about the oxygen supply for use in emergency situations. In that case oxygen is stored as sodium chlorate. When needed, the oxygen masks are activated by a small detonation. Chlorate and iron particles are mixed, reacting to produce oxygen [47.10].

47.4.2
Ozone

Ozone is manufactured industrially by letting oxygen pass through an electric arc. The energetic electrons, which constitute the arc, decompose some oxygen molecules to atoms and these react with O_2 to form O_3. A gas mixture with 15% ozone may be obtained. Ozone is utilized as an oxidation agent in the organic chemical industry and for the disinfection of water. Chlorine gas was earlier used for the bleaching of paper pulp, but more ecofriendly alternatives have been sought; the main substitute is hydrogen peroxide H_2O_2, but ozone has also been tested.

47.5
The Biological Role of Oxygen

Oxygen is critical for life on our planet and for the fate of mankind. It is the central atom for many of the functional groups, such as hydroxyl, carboxylate and carbonyl, among others, that are essential in nearly all the molecules involved in life. To provide the body with oxygen from the atmosphere, specific molecules – proteins containing iron – have been developed. Myoglobin stores oxygen in the muscle cells, and hemoglobin transports it in the blood. The reversed role of oxygen in photosynthesis has been described above.

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48
Sulfur

48.1 S
Facts about Sulfur

48.1.1 S
The Element

Symbol:	S
Atomic number:	16
Atomic weight:	32.07
Ground state electron configuration:	[Ne]$3s^2 3p^4$
Crystal structure:	α-S orthorhombic with a = 10.44 Å, b = 12.85 Å, c = 24.37 Å. β-S monoclinic with a = 11.02 Å, b = 10.96 Å, c = 10.90 Å; β = 96.7°. $\alpha \to \beta$ at 368.7 K

48.1.2 S
Discovery and Occurrence

Discovery: Sulfur, also called brimstone, has been known since prehistoric times. Due to its flammability, alchemists regarded sulfur as essential in combustion

Most important mineral: Native sulfur S is found near volcanoes and hot springs (Figure M73)
Pyrite FeS_2 (Figure M74)
Sulfur occurs also in many sulfide ores and in natural gas and crude oil.

Ranking in order of abundance in earth crust:	16
Mean content in earth crust:	350 ppm (g/tonne)
Mean content in oceans:	905 ppm (g/tonne)
Residence time in oceans:	$8 \cdot 10^6$ years
Mean content in an adult human body:	2000 ppm
Content in a man's body (weight 70 kg):	140 g

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48.1.3 S
Chemical Characterization

Sulfur is a yellow nonmetallic element. It is insoluble in water but soluble in carbon disulfide. Hydrogen sulfide H_2S is a colorless gas with the odor of rotten eggs. It is poisonous and must be handled extremely carefully. Sulfur dioxide SO_2 is one of the most troublesome air pollutants. It is the cause of acid rain, which is detrimental to life in forests and lakes as well as to buildings and monuments. The most important use of sulfur is in the manufacture of sulfuric acid, but it is also utilized in the production of matches, vulcanized rubber, dyes and gunpowder. Sulfur is a vital element and a component in many amino acids, the building blocks for proteins. The SH group of cysteine takes an active part in the building of proteins and forms sulfur bridges between peptides.

Oxidation states:

S^{-II} as in ZnS and $(S_n)^{2-}$ (polysulfides)
S^{I} as in S_2F_2
S^{II} as in SCl_2
S^{III} as in $Na_2S_2O_4$
S^{IV} as in SO_2 and $SOCl_2$
S^{V} as in S_2F_{10}
S^{VI} as in SO_3, SO_2Cl_2, and HSO_3Cl

Ionization energy (kJ mol^{-1}):

$S(g) \rightarrow S^{+}(g) + e^{-}$	1000
$S^{+}(g) \rightarrow S^{2+}(g) + e^{-}$	2252
$S^{2+}(g) \rightarrow S^{3+}(g) + e^{-}$	3357
$S^{3+}(g) \rightarrow S^{4+}(g) + e^{-}$	4556
$S^{4+}(g) \rightarrow S^{5+}(g) + e^{-}$	7004
$S^{5+}(g) \rightarrow S^{6+}(g) + e^{-}$	8496
$S^{6+}(g) \rightarrow S^{7+}(g) + e^{-}$	27 107

Electron affinity (kJ mol^{-1}):

$S(g) + e^{-} \rightarrow S^{-}(g)$
–200

Standard reduction potential:

$HSO_4^{-}(aq) + 3H^{+}(aq) + 2e^{-} \rightarrow H_2SO_3(aq) + H_2O(l)$	$E^0 = +0.16$ V
$H_2SO_3(aq) + 4H^{+}(aq) + 4e^{-} \rightarrow S(s) + 3H_2O(l)$	$E^0 = +0.50$ V
$S(s) + 2H^{+}(aq) + 2e^{-} \rightarrow H_2S(aq)$	$E^0 = +0.14$ V

Electronegativity (Pauling): 2.58

Radii of atoms and ions:
(WebElements™)

Atomic:	100 pm
Covalent:	102 pm
Van der Waals:	180 pm
S^{2-} (6-coordinate):	170 pm[1]
S^{4+} (6-coordinate, octahedral):	51 pm
S^{6+} (4-coordinate, tetrahedral):	26 pm
S^{6+} (6-coordinate, octahedral):	43 pm

[1] From ref. [1.12] p. 1388

48.1.4 S
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
2070 kg m^{-3} (α) 2.07 g cm^{-3} 1957 kg m^{-3} (β) 1.96 g cm^{-3}	15.49 cm^3 (α) 16.39 cm^3 (β)	392.8 K 119.6 °C	717.8 K 444.6 °C	710 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	298 K	373 K	573 K	973 K
–	0.269	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$60 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	298 K	373 K	573 K	973 K	1473 K
–	$2 \cdot 10^{24}$	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-6.09 \cdot 10^{-9}$ m^3kg^{-1} (α) $-5.83 \cdot 10^{-9}$ m^3kg^{-1} (β)
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
–	–	7.7 GPa	–

48.1.5 S
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	1.73 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	9.8 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	279 $kJmol^{-1}$
Entropy S^0 at 298 K	32.05 $JK^{-1}mol^{-1}$ (α-sulfur)

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	12.8	22.75	34.4	21.5	21.3	21.6

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$S+O_2 \rightarrow SO_2$	–300	–290	–300	–255	–220
$2/3S+O_2 \rightarrow 2/3SO_3$	–246	–197	–143	–	–

48.1.6 S
Nuclear Properties and X-ray

Isotope range, natural and artificial 27–45

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{32}S	Stable	95.02	0+	–
^{33}S	Stable	0.75	3/2+	0.6438
^{34}S	Stable	4.21	0+	–
^{36}S	Stable	0.02	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{33}S
Reference compound	$(NH_4)_2SO_4/D_2O$
Frequency MHz (^1H = 100 MHz)	7.670
Receptivity D^P relative to ^1H = 1.00	$1.70 \cdot 10^{-5}$
Receptivity D^C relative to ^{13}C = 1.00	0.0972
Magnetogyric ratio, $radT^{-1}s^{-1}$	$2.056 \cdot 10^7$
Nuclear quadropole moment, barn	–0.068

Characteristic X-radiation Z	Element	$K\alpha_2$ keV
15	P	2.013
16	S	2.307
17	Cl	2.620

X-ray radiation absorbed by the element Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	93.7
17.37 keV ($MoK\alpha_2$)	10.1

Neutron absorption	Thermal neutron capture cross section	0.53 barns

48.2
Sulfur in History

48.2.1
Native Sulfur

Sulfur has been known from time immemorial. In the very first book of the Bible, Genesis 19:23–24, the Lord destroys the cities of Sodom and Gomorrah in a rain of sulfur and fire. No useful application is described in the Scriptures, but at least one is mentioned in *The Odyssey*. Homer let Odysseus exclaim, after killing of the suitors: "Bring sulphur Eurycleia that cleans all pollution and bring me fire, that I may purify the house with sulphur!" Sulfur and sulfur dioxide were obviously used early for disinfection.

It was in volcanic regions that native sulfur was available. Pliny described in detail the Sicilian deposits and how sulfur could be used for medical purposes, for impregnation of candlewick, for manufacturing of sulfur matches as well as for bleaching of cloth.

> One of the most interesting sulfur mines lies within the crater of Popocatepetl in Mexico [48.1]. On Good Friday, April 21, 1519, Hernando Cortez and his six hundred "men of iron" landed at a place, later called Vera Cruz. Popocatepetl was in a state of unusual activity, corresponding to the meaning of its Indian name, "Smoky Mountain". Cortez conquered the ancient capital of Mexico in a struggle against Montezuma. In order to consolidate his new position, Cortez needed powder for guns and cannons. Charcoal and saltpeter were available, sulfur was not. Cortez thought of the Smoky Mountain. Could sulfur be found there? He sent two contingents. The stories about these expeditions and their fabulous achievements have been told so many times that they have attained the character of legends. But were the expeditions carried out at all? If we accept the tales, we can follow the most exciting mineral prospecting ever. The first expedition under the command of Diego de Ordaz was to examine the mountain. Ordaz did reach the crater of Popocatepetl and was able to observe its interior, blazing like molten glass. Sulfur was found, not near the rim of the crater, but inside, on the nearly vertical walls of the abyss. So Ordaz got no sulfur but the information necessary for a still more remarkable expedition. Cortez sent a small group of men with the soldier Fransisco Montano as leader. They were equipped with baskets

> and ropes to make descents possible and sacks for transporting the sulfur. An extremely arduous trek brought the Spaniards not far from the snow line. The continuous rumbling and the sulfurous exhalations were terrifying. At last they reached the crater and met the yawning abyss. Modern estimations indicate a width of 500 m and a depth of 300 m. The critical moment had arrived to carry out the bold plans. Lots were drawn and it fell to Montano himself to make the descent. He is said to have made seven trips in a basket, carried by ropes down the rocky walls to a depth of near 150 m. After filling his basket with chunks of yellow sulfur, he was raised back up to the rim by his companions, responsible for the ropes. The volcano was in a state of turmoil, erupting showers of ashes and cinders, emitting noxious, sulfurous vapors and smoke. Montano became prostrate and weak. Another member of the group, Juan de Larios, had to make another six descents. The expedition returned with about 150 kg sulfur. Fifty kegs of gunpowder was made with the sulfur. But from then on, Cortez decided to import sulfur from Spain. The Popocatepetl exploit was not repeated.

Georgius Agricola, also living in the middle of the 16th century, expressed a more negative attitude to gunpowder. He wrote1): "sulfur is made to enter into gunpowder – execrable invention – which hurls iron, brass, or stone, instruments of war of a new kind". In the Hoovers' translation2) of Agricola's *De Re Metallica* [48.2], the translators, in a note (page 119), inform us that the use of gunpowder for blasting in mines was first introduced at Schemnitz in 1627.

48.2.2
Sulfur From Pyrite

In countries without volcanic sulfur deposits, sulfur had to be prepared from pyrite, FeS_2. The handling may be exemplified by the manufacturing at Dylta, north of Örebro in central Sweden. A pyrite deposit had been discovered and a sulfur plant was built at the beginning of the 16th century. The mining of the ore was very labor-intensive and, as in many mines at this time, the breaking occurred using a method in which the rock was heated up by fire and burst by water. This is described for lead–silver ore at Sala in Chapter 6 Silver. Although the main product was sulfur for gunpowder, it was unimaginable to use powder for blasting in the mine. Warfare was too important. Up at ground level the ore was crushed and collected in sulfur pots, a type of conical retort. Each of these was connected to a smaller pot, a receiver. When the big pots were heated to red-heat, part of the sulfur was liberated and distilled over to the receivers. Some sulfur leached out and sublimated on the roof and walls. It was scraped off and sold to pharmacies. Sulfurous vapors cured aching all over, and sulfur was in fact an appreciated medicine for external use. In the plant, molten sulfur from many receivers was collected in a big iron pot. Impurities came up to the surface and were skimmed off. The pure sulfur was cast into bars in wooden molds and

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1) According to R. Jagnaux, *Histoire de la Chemie*, Baudry et Cie, Paris, 1891, Vol. 1, p. 458.

2) A translation into English in 1912 by Herbert C. Hoover, mining engineer, and his wife Lou, geologist. In 1929 Herbert Hoover became the 31st President of the United States.

sold to gunpowder makers. Because of its military and strategic importance, sulfur manufacturing was strongly supervised and regulated by the authorities. King Charles XII of Sweden himself signed in Bender, Turkey, an official letter regarding the small Dylta factory.

The residue after sulfur distillation contained all the iron from the pyrite and also much sulfur. It was heaved out onto "pot mountains" and weathered there for twenty years. In this process two layers were formed – one lower, hard and salty; one upper, loose as mold. The lower was iron(II) sulfate, from which iron vitriol was prepared for use in textile dyeing. The upper layer contained iron oxide hydrate FeOOH, iron ocher, and was the raw material for the manufacture of red ocher paint. During the weathering processes in the pot mountains, sulfur dioxide was evolved, evil-smelling but disinfecting. In periods of plague in the country, prominent persons, such as those from the King's court in Stockholm, arrived at Dylta for protection on or near the pot mountains.

48.3
Occurrence of Sulfur

Sulfur occurs in the following forms:

- elemental sulfur (Figure M73);
- as a component in minerals such as pyrite FeS_2 (Figure M74);
- as sulfate in gypsum and other salts;
- as H_2S in natural gas;
- organosulfur compounds in oil and coal.

48.3.1
Volcanic Sulfur Deposits

Large deposits of the yellow "burning stone" have been found in volcanic regions, such as those of Sicily, and in Texas and Louisiana, USA. Some sulfur deposits are located offshore. The sulfur that the conquistadors cut from the insides of the volcanic crater had been formed when hydrogen sulfide gas from the interior of the earth had reacted with oxidizing gases, sulfur dioxide or air. Historically, volcanic sulfur was the main source of supply. That is not the case today.

48.3.2
Sulfur-Containing Rocks

Sulfate reducing bacteria can deprive gypsum of its oxygen content. Elemental sulfur is thereby formed and can be found, associated with limestone and excess gypsum, in salt-dome caprocks. Large deposits of this type have been found in the Gulf of Mexico, in Louisiana and in Texas, USA.

48.3.3
Sulfur in Natural Gas and Mineral Oil

The breakdown and transformation of the plant and animal residues embedded in sedimentary rocks have formed natural gas and mineral oil. Hydrogen sulfide formed in these processes is included especially in natural gas but also in mineral oil. This has been an important source for large-scale sulfur manufacture. In Canada, the world's leading sulfur producer in 2001, natural gas has been obtained with more than 30% hydrogen sulfide. The majority of the sulfur production in Canada that year came from natural gas plants in Alberta.

48.3.4
Pyrite

As a raw material for sulfur, the mineral pyrite FeS_2 is important, but more so in earlier times than nowadays. It is a brass-yellow mineral with such a brilliant metallic luster that it has been mistaken for gold. It commonly crystallizes in cubes. Pyrite is the most abundant of the sulfide minerals and occurs in all kinds of rocks and coal seams. Pyrite is an important ore of sulfur, less so of iron, and is sometimes mined for the associated gold and copper. In modern sulfur production, China is the only country (among the top producers of the world) whose primary sulfur source is pyrite.

48.4
Manufacture of Sulfur and Its Compounds

48.4.1
Elemental Sulfur

Elemental sulfur is won from sulfur-containing rocks via the Frasch process. Superheated water, at 160°C and 16 atm, is forced down into an underground bed of sulfur-containing rock. The sulfur melts. The liquid sulfur is forced up to the surface by the use of compressed air.

H_2S in oil and natural gas must be removed for environmental reasons, and the corresponding processes have been important for sulfur production. H_2S is removed from natural gas by ethanolamine, in which hydrogen sulfide is soluble. The gas is then recovered and oxidized to elemental sulfur in a two-step process. A stream of H_2S is divided into two parts. The smaller part, one-third of the volume, is burned to convert H_2S to SO_2. The streams are rejoined in a converter, where the following reaction occurs:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

48.4.2
Sulfuric Acid

The principal raw material source for sulfuric acid production is SO_2 obtained on burning sulfur. In addition, the main minerals of many metals, for example, zinc, lead, copper and silver, are sulfides. A significant quantity of SO_2 is also obtained as a byproduct from the metallurgical treatment of these ores. Partly this is a result of laws restricting SO_2 emissions, but partly it is also due to the desire to improve process economics. Sulfur dioxide is oxidized to the trioxide SO_3 in the *contact process* at 450°C. A catalyst is used, which has V_2O_5 as the main component. SO_3 is absorbed in 98% H_2SO_4 giving *oleum* or *fuming sulfuric acid*, formally with more than 100% H_2SO_4. Its concentration is however kept constant at 98.5% by continuous addition of water.

48.4.3
Global Sulfur Production

In 2001, sulfur production in all forms, counted as sulfur, was 57.3 million tonnes. Of this quantity, Canada and the USA accounted for 16% each, Russia 11%, China 9%, Japan 6%, Saudi Arabia 4%, Kazakhstan 3%, Mexico, Poland and the United Arab Emirates 2.5% each, and South Korea, Germany, Chile and France 2% each [48.3].

48.5
Uses of Sulfur and Sulfur Compounds

48.5.1
Sulfuric Acid

Sulfuric acid is one of the most important industrial raw materials in many sectors of the industrial world, first of all fertilizer production. In the chemical industry, it is also used in the manufacture of explosives, rayon, paper pulp, detergents, dyestuffs and a lot of other products.

48.5.2
Sulfur Dioxide

Sulfur dioxide is easily recognized by its characteristic smell, which irritates the respiratory passages. As already mentioned, it is mainly used for the production of sulfuric acid, but it also has some applications of its own, as it kills bacteria and is an antioxidant. SO_2 or sodium sulfite preserves the natural color of fruits and vegetables – for instance, peeled potatoes remain white. Sulfite is also added to wine before bottling to prevent further fermentation. Sulfur dioxide in wines may however cause health problems.

48.5.3
Elemental Sulfur

About 90% of all sulfur produced is burned to SO_2 and converted to sulfuric acid. A very interesting, alternative use of sulfur is for the vulcanization of rubber. From the beginning, natural rubber was of limited value, because such rubber components adhered to everything, melted in hot weather, and froze and cracked in cold. *Charles Goodyear* (1800–1860), in Connecticut, USA, performed many experiments in order to improve rubber quality. One day he accidentally dropped some rubber mixed with sulfur onto a hot stove. A great surprise! The rubber was strengthened and completely changed its character. From then it could be applied to a variety of industrial components, eventually automobile tires. The process became known as *vulcanization*. The process was patented in 1844 and revolutionized the rubber industry. However the inventor was unable to profit financially from his discovery. He died a poor man.

Chemically, vulcanization is a process in which the polymer molecules of rubber are linked to each other by atomic bridges. The crosslinking is still achieved with sulfur, but peroxide is an alternative.

48.5.4
Sulfur in Various Compounds

Sulfur is an important component of different compounds, so many that only a few examples may be given here.

48.5.4.1 Sulfa Drugs, Penicillin and Vitamins

In 1935 the German chemist *Gerhard Domagk* (1895–1964) discovered *sulfa drugs*, in which the active substance is sulfanilamide. Sulfa drugs are effective against a number of infectious diseases. Since the discovery of *penicillin*, which is as effective as the sulfa drugs, although far less toxic, the use of sulfa drugs has declined considerably. Alexander Fleming (1881–1955) discovered the sulfur-containing penicillin compound in 1929.

Thiamin has a sulfur atom incorporated in the ring structure of its molecule. The compound constitutes *vitamin B1*, important for many bodily functions. In children it is required for growth. Vitamin B1 deficiency may result in beriberi.

48.5.4.2 Awful Smell and Sweet Taste

Sulfur-containing compounds may smell awful, like rotten eggs. A mixture of sulfur-containing butane thiols and butenyl methyl disulfide is the *skunk's* defense spray.

In contrast, the first artificial sweetener, saccharin, is a substance that also contains sulfur (Figure 48.1). The American chemist Ira Remsen (1846–1927), together with his German student Constantin Fahlberg, investigated the substance benzosulfamide in 1880. They observed its remarkable sweetness and called it saccharin. For a compound to taste sweet, it must be able to cause a nerve impulse to carry the mes-

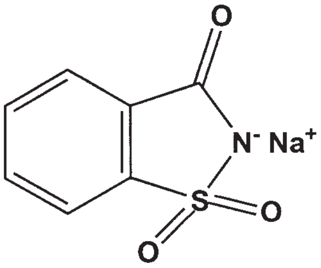

Figure 48.1 Sodium saccharin.

sage of sweetness from the tongue to the brain. Saccharin does so. In fact, saccharin is 300 times sweeter than sucrose.

48.5.5
Sulfur in Steel

As described in Chapter 8 Iron, sulfur is detrimental to steel. It causes hot-shortness, an embrittlement in the red-hot state as a consequence of the formation of molten iron sulfides at the grain boundaries. This is especially dangerous in steels intended for welding. A high content of manganese reduces the risk. In spite of this, special steels utilize sulfur contents as high as 0.2–0.3% in order to improve machinability. On turning, the chips become more fragile and balls of long chips are avoided. The machining speed can thus be increased.

48.6
Sulfur in Life

Proteins are macromolecules built up of amino acids. Sulfur is a component in many amino acids, which are present in all plant and animal cells, and a vital element. The structure of two amino acids is shown in Figure 48.2.

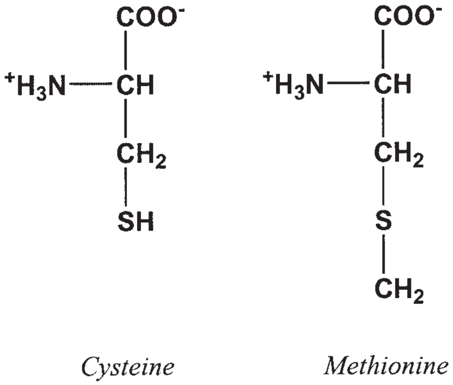

Figure 48.2 Two amino acids containing sulfur.

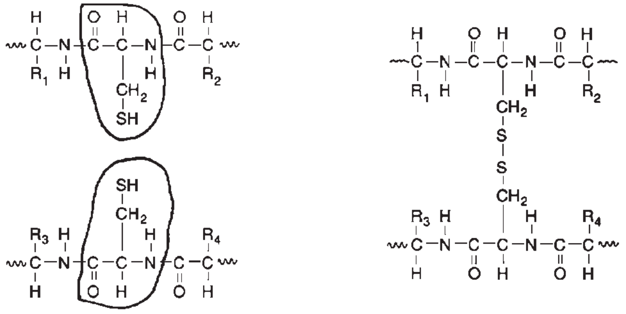

Figure 48.3 Two peptide chains joined by sulfur links [48.4].

The SH group of cysteine takes an active part in the building of proteins and forms sulfur links or *bridges* between peptides (Figure 48.3). Sulfur bridges of the type to the right in Figure 48.3 are important in many proteins. An example is keratin in nails and hair.

The heavy metals lead, cadmium and mercury are toxic because they combine with sulfur in proteins. They can occupy sites where no metal is normally present, a serious disturbance, or they can push vital metals such as iron out of their positions. The liver prepares a remarkable protein, *metallothionein*, especially rich in cysteine groups, which can act as a scavenging substance, taking care of toxic elements up to a certain level. Even essential elements, copper for instance, may be removed if present in too high, toxic concentrations.

Plants absorb sulfur as sulfates. They are very soon reduced and sulfur is bound in organic molecules. For human beings and animals, such a process is not possible. Organic sulfur must be taken in with the food, vegetable or animal. Milk, eggs, meat, bread and beans are important sources.

> The photosynthesis is driven by sun energy, water and carbon dioxide, and without light no new formation of organic material can occur.

This was the opinion at the beginning of the 20th century. The Russian microbiologist *Sergej Winogradskij* (1856–1953) showed, a hundred years ago, that there are bacteria that can form organic material from carbon dioxide without the supply of solar energy. Instead, energy is created by the oxidation of sulfur, hydrogen sulfide or hydrogen. One species, *Thiobacillus ferrooxidans*, grows by oxidizing ferrous iron such as iron pyrites, FeS_2. Another example is *Thiotrix*, a sulfur-oxidizing bacterium, which gets its energy from sulfide sulfur, toxic to humans but vital for the actual microbe.

These types of microorganism have the name *lithotrophs* (from the Greek words *lithos*, stone, and *trophe*, nutriment). Lithotrophs are thus “stone eaters”. They are quite independent of the sun and are adapted to a life of sulfides, well away from the earth’s surface, on the ocean floor and in the water in rocks. Investigations have been made to a depth of 1700 m. Even at this depth the water in rocks has 100 million bacteria per liter. And unquestionably they do not have any access to sunlight for their survival. Several scientists believe that lithotrophs represented the first forms of life on earth. This might have occurred in a warm environment, 70–100°C. If so, sulfide minerals may have been involved in the origin of life itself.

48.7
The Disturbed Sulfur Cycle

Sulfur takes part in a complex cycle. From volcanoes and hot springs, large quantities of sulfur are, at least periodically, brought to the atmosphere, mainly as sulfur dioxide. The decay of dead plants and animals causes the release of hydrogen sulfide, a gas that is also formed from sulfates with the assistance of bacteria. This occurs preferentially in marshy regions, where the bad smell of hydrogen sulfide is often perceptible. The different gaseous sulfur substances are oxidized to sulfur trioxide in the atmosphere, where it forms sulfuric acid with water. Sulfur is brought back to the earth with rain, and the cycle is closed. The quantity of sulfate ions that are transported to the sea after weathering of gypsum and other sulfate minerals is comparatively constant and takes part in chemical and biological processes only to a limited extent.

As well as the sulfur cycle, there are other cycles in nature: water, nitrogen, phosphorus and carbon. Man has influenced them all, but the sulfur cycle is the most disturbed among all these cyclic processes. Fossil fuels are burned in order to warm up houses and to provide cars, power stations and industries with energy. Then the sulfur that was built into coal, oil and natural gas, millions of years ago, is set free. It is transported as sulfur dioxide to the atmosphere, the SO_2 content of which has increased considerably compared to the equilibrium content of the natural cycle. The acid gas is transported by the winds over the continents, and, long distances from a specific source, people experience a "rain of sulfuric acid". This acid rain not only attacks the needles and leaves of trees but also damages the roots of plants. In acidified lakes the ability of fish to reproduce is disturbed. If acidification is not neutralized by liming, metal ions may be leached from rocks and damage animal life.

Large quantities of sulfur dioxide are liberated in the roasting of sulfide ores, as mentioned above. Modern technology has made it possible to take care of this gas and transform it to sulfuric acid. A corresponding technique is utilized in large power stations. They do not, however, produce sulfuric acid, but gypsum, as the exhaust gases pass over limestone before being allowed to discharge to the atmosphere. For the central heating in apartments and private houses, it is prescribed by law that oil with low sulfur content must be used. These measures, as well as the liming of lakes, have led to considerable improvements in the environment.

A special sulfur cycle is expressed as part of the Gaia hypothesis [48.5]. According to this the compound dimethyl sulfide (DMS) is produced by marine plankton in the oceans. It vaporizes to the atmosphere and is oxidized to an aerosol of sulfuric acid. On the nuclei of this aerosol, water droplets are formed, supporting cloud formation. The sulfur is brought back to the ocean with rain and the plankton production of

DMS can start again. The increased cloud cover reflects sunlight and cools the earth's surface. The DMS emissions may in this way regulate the global climate.

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49
Selenium and Tellurium

49.1 Se
Facts about Selenium

49.1.1 Se
The Element

Symbol: Se
Atomic number: 34
Atomic weight: 78.96
Ground state electron configuration: $[Ar]3d^{10}4s^24p^4$
Crystal structure: Gray, “metallic” is trigonal.
Red Se is monoclinic with $a = 9.05$ Å, $b = 9.08$ Å, $c = 11.60$ Å; $\beta = 90.81°$

49.1.2 Se
Discovery and Occurrence

Discovery: Berzelius found the element in 1817 in the lead chamber mud in a sulfuric acid plant. He named it selenium (*Selene*, the moon) due to its similarity with tellurium (the earth)

Most important mineral: Selenium is present as a trace element in some sulfide ores. It is won as byproduct in copper manufacturing. A few selenium minerals are known. One is berzelianite, a silver-white mineral Cu_2Se.

Ranking in order of abundance in earth crust: 69
Mean content in earth crust: 0.05 ppm (g/tonne)
Mean content in oceans: $2 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans: $10 \cdot 10^3$ years
Mean content in an adult human body: 0.05 ppm
Content in a man’s body (weight 70 kg): 3.5 mg

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49.1.3 Se
Chemical Characterization

Elemental selenium is relatively non-toxic, but hydrogen selenide H_2Se and other selenium compounds are extremely toxic, resembling arsenic in their physiological reactions. Selenium is a better conductor of electricity in light than in darkness, the conductivity varying directly with the intensity of the light. It is therefore used in many photoelectric devices. Selenium is an essential element for life but toxic if present in higher concentrations. In some parts of the world selenium is deficient in the soil, and food does not supply the necessary quantity of selenium. It causes diseases, the best known of which is heart failure among children in the *Keshan* region of China (Kashin-Beck syndrome). The soil is now treated with selenate, with very positive results.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Se^{-II} as in H_2Se	$Se(g) \rightarrow Se^+(g) + e^-$	941	$Se(g) + e^- \rightarrow Se^-(g)$
Se^{I} as in Se_2Br_2	$Se^+(g) \rightarrow Se^{2+}(g) + e^-$	2045	–195
Se^{IV} as in SeO_2 and H_2SeO_3	$Se^{2+}(g) \rightarrow Se^{3+}(g) + e^-$	2974	
Se^{VI} as in SeO_3 and H_2SeO_4	$Se^{3+}(g) \rightarrow Se^{4+}(g) + e^-$	4144	
	$Se^{4+}(g) \rightarrow Se^{5+}(g) + e^-$	6590	
	$Se^{5+}(g) \rightarrow Se^{6+}(g) + e^-$	7880	
	$Se^{6+}(g) \rightarrow Se^{7+}(g) + e^-$	14 990	

Standard reduction potential:	$SeO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow H_2SeO_3(aq) + H_2O(l)$	$E^0 = +1.15V$
	$H_2SeO_3(aq) + 4H^+(aq) + 4e^- \rightarrow Se(s) + 3H_2O(l)$	$E^0 = +0.74$ V
	$Se(s) + 2H^+(aq) + 2e^- \rightarrow H_2Se(aq)$	$E^0 = -0.399$ V
Electronegativity (Pauling):	2.55	
Radii of atoms and ions:	Atomic:	115 pm
(WebElements™)	Covalent:	116 pm
	Van der Waals:	190 pm
	Se^{2-} (6-coordinate):	184 pm1)
	Se^{4+} (6-coordinate, octahedral):	64 pm
	Se^{6+} (4-coordinate, tetrahedral):	42 pm
	Se^{6+} (6-coordinate, octahedral):	56 pm

1) From ref. [1.12] p. 1388

49.1.4 Se
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
4810 kg m^{-3} 4.81 g cm^{-3}	16.42 cm^3	490 K 217 °C	958 K 685 °C	322 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	298 K	373 K	573 K	973 K
–	2.04	–	–	–

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$40 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	298 K	373 K	573 K	973 K	1473 K
–	120	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-4.0 \cdot 10^{-9}$ m^3kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
10 GPa	3.7 GPa	11 GPa	0.35

49.1.5 Se
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	5.4 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	26.3 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	227 kJmol^{-1}
Entropy S^0 at 298 K	42.44 JK^{-1}mol^{-1}

Molar heat capacity Cp at temperature K. JK^{-1}mol^{-1}

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	18.2	25.36	35.1	18.8	19.6	20.0

49.1.6 Se
Nuclear Properties and X-ray

Isotope range, natural and artificial	67–91

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{74}Se	Stable	0.89	0+	–	–	–	–
^{76}Se	Stable	9.36	0+	–	–	–	–
^{77}Se	Stable	7.63	1/2-	0.5355	–	–	–
^{78}Se	Stable	23.78	0+	–	–	–	–
^{80}Se	Stable	49.61	0+	–	–	–	–
^{82}Se	Active	8.73	0+	–	$1.1 \cdot 10^{20}$ y	$\beta^-\beta^-$	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{77}Se
Reference compound	$Se(CH_3)_2$
Frequency MHz (^{1}H = 100 MHz)	19.072
Receptivity D^P relative to ^{1}H = 1.00	$5.37 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	3.07
Magnetogyric ratio, radT^{-1}s^{-1}	$5.125 \cdot 10^7$
Nuclear quadropole moment, barn	0.760

Characteristic X-radiation **Z**	 **Element**	 **Kα_2 keV**
33	As	10.509
34	Se	11.181
35	Br	11.878

X-ray radiation absorbed by the element **Incoming radiation energy**	 **Absorption coefficient μ (cm^2/g)**
8.028 keV (CuKα_2)	80.4
17.37 keV (MoKα_2)	70.3

Neutron absorption	**Thermal neutron capture cross section**	12 barns

49.1 Te
Facts about Tellurium

49.1.1 Te
The Element

Symbol:	Te
Atomic number:	52
Atomic weight:	127.60
Ground state electron configuration:	[Kr]4d^{10}5s^{2}5p^4
Crystal structure:	Trigonal

49.1.2 Te
Discovery and Occurrence

Discovery: In 1783 F. J. Müller von Reichenstein in what is now Romania found the element. The name tellurium (after *Tellus*, the earth) was given by Klaproth in 1798

Most important mineral: Calaverite AuTe$_2$ is a pale bronze-yellow monoclinic mineral. It is an important source of gold.
Tellurite TeO$_2$ is a rare, white or yellowish orthorhombic mineral. The principal commercial source of selenium is the slime from lead and copper refineries.

Ranking in order of abundance in earth crust:	77–80
Mean content in earth crust:	0.001 ppm (g/tonne)
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

49.1.3 Te

Chemical Characterization

Crystalline tellurium has a silvery white appearance and exhibits a metallic luster when pure. Tellurium is used in the manufacture of rectifiers and thermoelectric devices and in semiconductor research. All tellurium compounds are highly toxic.

Te^{-II} as in H_2Te	$Te(g) \rightarrow Te^+(g) + e^-$	869	$Te(g) + e^- \rightarrow Te^-(g)$
Te^{IV} as in TeO_2 and Te_4Br_{16}	$Te^+(g) \rightarrow Te^{2+}(g) + e^-$	1790	–190
Te^{V} as in Te_2O_5	$Te^{2+}(g) \rightarrow Te^{3+}(g) + e^-$	2698	
Te^{VI} as in TeO_3, $Te(OH)_6$ and TeF_6	$Te^{3+}(g) \rightarrow Te^{4+}(g) + e^-$	3610	
	$Te^{4+}(g) \rightarrow Te^{5+}(g) + e^-$	5668	
	$Te^{5+}(g) \rightarrow Te^{6+}(g) + e^-$	6820	
	$Te^{6+}(g) \rightarrow Te^{7+}(g) + e^-$	13 200	

Standard reduction potential:	$H_2TeO_4(aq) + 6H^+(aq) + 2e^- \rightarrow Te^{4+}(aq) + 4H_2O(l)$	$E^0 = +0.93$ V
	$Te^{4+}(aq) + 4e^- \rightarrow Te(s)$	$E^0 = +0.57$ V
Electronegativity (Pauling):	2.1	

Radii of atoms and ions:	Atomic:	140 pm
(WebElements™)	Covalent:	135 pm
	Van der Waals:	206 pm
	Te^{2-} (6-coordinate):	207 pm[1]
	Te^{4+} (4-coordinate, tetrahedral):	80 pm
	Te^{4+} (6-coordinate, octahedral):	111 pm
	Te^{6+} (4-coordinate, tetrahedral):	57 pm
	Te^{6+} (6-coordinate, octahedral):	70 pm

[1] From ref. [1.12] p. 1388

49.1.4 Te

Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
6240 kg m^{-3} 6.24 g cm^{-3}	20.45 cm^3	722.7 K 449.5 °C	1261 K 988 °C	201 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	**298 K**	**373 K**	**573 K**	**973 K**
–	2.35	–	–	–

Coefficient of linear expansion K^{-1}

100 K	**298 K**	**373 K**	**500 K**	**800 K**
–	$18 \cdot 10^{-6}$	–	–	–

Resistivity nΩm

78 K	**273 K**	**373 K**	**573 K**	**973 K**	**1473 K**
–	$5 \cdot 10^{6}$	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K $-3.7 \cdot 10^{-9}$ m^3kg^{-1}

Magnetic characterization Diamagnetic (as susceptibility is negative)

Elastic properties

Young's modulus E	**Shear modulus G**	**Bulk modulus K**	**Poissons ratio ν**
43 GPa	16 GPa	46 GPa	0.34

49.1.5 Te

Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	17.5 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	50.6 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	197 $kJmol^{-1}$
Entropy S^0 at 298 K	49.71 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	21.6	25.73	32.3	37.7	18.7	18.7

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$Te+O_2 \rightarrow TeO_2$	–270	–233	–138	–	–

49.1.6 Te

Nuclear Properties and X-ray

Isotope range, natural and artificial	106–138

Naturally occurring isotopes

Nuclide	**Type**	**Abundance %**	**Nuclear spin**	**Magnetic moment μ**	**Half-life**	**Decay mode**	**Decay energy Q**
^{120}Te	Stable	0.10	0+	–	–	–	–
^{122}Te	Stable	2.60	0+	–	–	–	–
^{124}Te	Stable	4.82	0+	–	–	–	–
^{125}Te	Stable	7.14	1/2+	–0.8871	–	–	–
^{126}Te	Stable	18.94	0+	–	–	–	–
^{123}Te	Active	0.91	1/2+	–0.7359	$1 \cdot 10^{13}$ y	EC	0.053 MeV
^{128}Te	Active	31.69	0+	–	$2.2 \cdot 10^{24}$ y	β^-	–
^{130}Te	Active	33.80	0+	–	$7.9 \cdot 10^{20}$ y	β^-	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{123}Te	^{125}Te
Reference compound	$Te(CH_3)_2$	
Frequency MHz (^1H = 100 MHz)	26.170	31.550
Receptivity D^P relative to ^1H = 1.00	$1.67 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	0.953	13.1
Magnetogyric ratio, $radT^{-1}s^{-1}$	$-7.059 \cdot 10^7$	$-8.511 \cdot 10^7$
Nuclear quadropole moment, barn	–	–

Characteristic X-radiation Z	 Element	 Kα_2 keV
51	Sb	26.110
52	Te	27.201
53	I	28.317

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	268
17.37 keV (MoKα_2)	34.2

Neutron absorption	Thermal neutron capture cross section	4.7 barns

49.2
Discovery

49.2.1
Tellurium (1783)

In 1740 *Baron Franz Joseph Müller von Reichenstein* was born in the town of Sibiu (known as Hermannstadt in German) in Transylvania, a province in present Romania. He studied philosophy and law in Vienna. Later he became very much interested in the mining industry and began a thorough study of chemistry, metallurgy and mining technology. He was appointed as manager of all the mines in his home province, with the assignment to restore the mines, which were in a bad condition. Since the middle of the 18th century, different gold deposits had attracted great interest and been subjected to many speculations. Minerals with metallic luster had been found, some in fact containing gold. But it was not pure gold. For the miners and the mineralogists, it was impossible to find out the composition. So this became a task for the newly appointed mining director. In a badly equipped laboratory in Sibiu, Müller von Reichenstein analyzed different mineral samples and stated, in 1783, that a particular mineral contained gold and another, for him unknown, element. He isolated and examined it. A small sample quantity was sent to “the greatest chemist in our century” (as he expressed it), Professor Torbern Bergman in Uppsala, with whom he maintained contacts. Bergman answered in April, 1784, confirming that it was in fact a new element that the Baron had discovered, and making a comparison with the discovery of tungsten by the brothers d’Elhuyar in 1783. Bergman asked for more specimens, which would make it possible for him to do more careful investigations. But time had run out for Bergman, who died in July, 1784. Twelve years later, Müller von Reichenstein sent a sample to Martin Heinrich Klaproth in Berlin. There, in January, 1798, at the Academy of Sciences, Klaproth reported on his investigation and confirmed that the actual element was new, and that he had named it *tellurium* after *Tellus*, the earth. He carefully specified Müller von Reichenstein as the discoverer. The mineral in which tellurium had been found was *calaverite*, gold telluride, $AuTe_2$.

49.2.2
Selenium (1817)

Near to Gripsholm in central Sweden there was a plant for manufacturing sulfuric acid. In 1816, Berzelius became part owner of the plant, together with his colleagues Gahn and Eggertz from Falun. It gave him much trouble, and insignificant profit, but it led to the discovery of a new element. In the summer of 1817 the three owners spent several weeks at the factory, working on technical projects and problems in production. The previous plant management had observed that roasting of pyrite from the copper mine in Falun (to make sulfur dioxide) gave a reddish lead chamber mud. They thought that this coloration was due to arsenic and so had stopped using pyrite from Falun. The new owners with their "Falun majority" returned to the earlier raw material and commissioned Berzelius to examine the mud. Did it contain arsenic? Or something else that made it reddish? Berzelius promptly stated that it was not arsenic. Probably it was tellurium. But that was also a mistake, which may be concluded from Berzelius' letter to a French colleague at the beginning of 1818 [49.1].

> What I wrote in my earlier letter about the finding of tellurium in sulfur from the copper mine in Falun (used at the production of sulfuric acid in Gripsholm) is not correct. Now I have, here in Stockholm, investigated the substance more carefully and have found that what assessor Gahn and I supposed to be tellurium, instead is a new element with most interesting properties. This element has a metallic character, but resembles sulfur to such a high degree that it could be called a new type of sulfur ... If heated it burns with an azure blue flame and emits a penetrating smell of black radish ... Its similarity to tellurium has been a cause for giving the new element the name selenium.

Tellurium had got its name after *Tellus*, the earth. The earth's neighbor, the moon, *Selene*, became the logical source of the name of the new element, selenium.

49.3
Occurrence

Selenium and tellurium never occur in concentrations high enough to justify mining solely for those elements. Instead, selenium and tellurium are recovered as byproducts in the electrolytic refining of copper.

Worn-out and damaged photocopier drums, other industrial scrap and residues from chemical processes are of increasing importance as raw material. About 15% of selenium production come from these secondary sources.

49.4
Manufacture

The anode slime from the electrolytic refining of copper contains precious metals as well as selenium and tellurium, among other elements. The Se and Te contents in the slime vary, depending on the original copper ore. Selenium contents of 10% in slime are not unusual, while the tellurium content is lower, with a maximum of 5%. In the electrolytic refining of copper, selenium and tellurium have to be separated from silver, gold and platinum metals in the anode slime. Otherwise they would interfere with the refining of the precious metals. Selenium and tellurium are isolated and separated using various chemical and metallurgical methods.

The world refinery production in 2001 was 1580 tonnes of selenium and 140 tonnes of tellurium (USA excluded). Japan produced 47% of this selenium, whilst Canada produced 57% of the tellurium [49.2].

49.5
Uses

Selenium and tellurium have properties similar to sulfur, but they are more metallic. Both are semiconductors. Selenium also has the property of *photoconductivity*. In light, selenium is a good conductor of electricity, whereas it is a poor conductor in darkness.

49.5.1
Selenium

Some 35% of the selenium used in 2001 was for glass applications. Addition of selenium decreases the solar heat transmission through plate glass for buildings. Selenium decolorizes a glass melt that is tinted green by iron. The pink color caused by selenium combines with the green to give a gray color that is not observable to the human eye. More selenium in the glass creates a red color, which is utilized in traffic lights.

Selenium was once a greatly used element in electronics. Its photoconductivity opened up applications as photocells and exposure meters. In the period 1970–1980 high-purity selenium compounds were dominant as photoreceptors on the drums of paper copiers. Organic photoreceptor compounds (OPC) have replaced them nowadays to a great extent. Selenium's role as a rectifier material has largely been taken over by silicon.

The addition of selenium to alloys, including steels, improves their machinability, as the chips produced on turning become more fragile. Balls of long chips are avoided and the machining speed can be increased. Owing to their good free machining and acceptable environmental properties, selenium and bismuth may replace lead for plumbing in installations for human water consumption. Different metallurgical applications account for about one-fourth of the total selenium consumption.

Selenium is used in cadmium sulfide pigments. The yellow color becomes redder as a result of selenium addition. However, such use must be restricted to very special applications because of the toxicity of cadmium-based pigments.

Due to the biological role of selenium (see below), the element is used in pharmaceutical applications, as a supplementary additive for grazing ground and as an additive in anti-dandruff shampoos.

49.5.2
Tellurium

The addition of tellurium to steel improves machinability, as already described for selenium. In fact, this accounted, in quantity, for half the market of tellurium in 2001. Tellurium compounds are also used as accelerators in the vulcanization process for rubber.

Mercury cadmium telluride is used for recording thermal images in infrared cameras. The use of high-purity tellurium in cadmium telluride solar cells is very promising, and some of the highest efficiencies for electric power generation have been obtained by using this material.

Thermoelectric cooling devices, treated in Chapter 46 Arsenic, Antimony and Bismuth, with bismuth telluride as semiconductor material, are utilized for cooling purposes.

49.6
Roles of Selenium and Tellurium in Biology

In Chapter 2 The Knowledge of Matter, it was shown in the last section, “Inorganic chemistry of life”, that selenium is an essential element for life. But selenium is also toxic if present in higher concentrations. Thus, as so often, too much or too little spoils everything. A normal diet provides 100–200 micrograms (µg) per day to a person. Selenium sources are mostly wheat and cereals but also important are fish, shellfish, liver and kidney. In some parts of the world, selenium is deficient in the soil, and food does not supply the necessary quantity of selenium. This selenium deficiency causes diseases, the best known of which is heart failure among children in the *Keshan* region of China (Kashin-Beck syndrome) [49.3]. The soil there is now treated with selenate, with very positive results. Selenium is a component in the molecule *glutathione peroxidase*, which functions as an antioxidant enzyme. It removes peroxides before they form free radicals in the body. There is also some evidence that selenium can give protection against cancer. A remarkable effect of selenium, toxic in itself, is that it counters the effect of other poisons such as mercury and cadmium. Thus, selenium tablets may be wholesome, but the habit of eating too many of them must be questioned, as it can cause selenium poisoning, selenosis. Prolonged industrial exposure of selenium compounds can also cause different symptoms, from brittle nails and hair to liver and kidney malfunctions.

Grazing animals in regions where the soil is selenium-deficient develop "white muscle disease" and have to be provided with supplements, such as selenium additions in fertilizers or in sprays for the crops. In contrast, in some districts, certain plants, growing on selenium-rich ground, may accumulate an excess of the element. Such a leguminous plant, *Astragalus* ("locoweed"), is found in Wyoming, USA. Cattle grazing there develop a disease that attacks balance and sense of locality, while horses lose their hooves.

Tellurium has no known biological function, but its volatile compounds are toxic.

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50
Halogens

The elements fluorine, chlorine, bromine, iodine and astatine constitute the *halogen group* of the periodic table. Astatine is a radioactive, very rare element, which is treated, not in this chapter, but in Chapter 52 Radioactive elements. The Elements are designated halogens (= salt formers) due to their tendency to form salts with metals.

50.1 F
Facts about Fluorine

50.1.1 F
The Element

Symbol:	F
Atomic number:	9
Atomic weight:	19.00
Ground state electron configuration:	[He]$2s^2 2p^5$
Crystal structure:	α-fluorine, monoclinic, a = 5.50 Å, b = 3.28 Å, c = 7.28 Å, angle β = 102.17° β-fluorine, cubic, a = 6.67 Å Transition α → β at 45.6 K

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50.1.2 F
Discovery and Occurrence

Discovery: Carl Wilhelm Scheele discovered hydrofluoric acid in 1771. The element fluorine was isolated by H. Moissan in Paris in 1886.

Important raw materials: Fluorite, fluorspar CaF_2 (Figure M75)
Apatite $Ca_5(PO_4)_3F$
Cryolite Na_3AlF_6

Ranking in order of abundance in earth crust: 13

Mean content in earth crust:	585 ppm (g/tonne)
Mean content in oceans:	1.3 ppm (g/tonne)
Residence time in oceans:	$0.5 \cdot 10^6$ years
Mean content in an adult human body:	37 ppm (in bone 0.2–1.2%)
Content in a man's body (weight 70 kg):	2.6 g

50.1.3 F
Chemical Characterization

Fluorine is a pale yellow gas, poisonous and corrosive. It the most electronegative and reactive of all elements. Nearly all compounds are decomposed by fluorine to form fluorides that are very stable. Atom bomb projects and nuclear energy applications made it necessary to produce large quantities of fluorine since isotopes of uranium can be separated as fluorides.

Oxidation states:	**Ionization energy ($kJ\ mol^{-1}$):**		**Electron affinity ($kJ\ mol^{-1}$):**
F^- as in hydrofluoric acid HF and calcium fluoride CaF_2	$F(g) \rightarrow F^+(g) + e^-$	1681	$F(g) + e^- \rightarrow F^-(g)$
	$F^+(g) \rightarrow F^{2+}(g) + e^-$	3374	–328
	$F^{2+}(g) \rightarrow F^{3+}(g) + e^-$	6050	

Standard reduction potential: $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ $E^0 = +2.866$ V

Electronegativity (Pauling): 3.98

Radii of atoms and ions:
(WebElements™)

Atomic	50 pm
Covalent:	71 pm
Van der Waals:	147 pm
F^- (4-coordinate, tetrahedral):	117 pm
F^- (6-coordinate, octahedral):	119 pm

50.1.4 F
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
1.696 kg m^{-3} 1.70 g/l	1.3	53.53 K –219.62 °C	85.01 K –188.14 °C	824 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 73 K	173 K	273 K	373 K	1273 K
–	0.0156	0.0254	0.0347	–

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K) a	b	c
34.56	$2.51 \cdot 10^{-3}$	$-3.51 \cdot 10^{5}$

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) –

Solubility in water m^3 gas at STP per m^3 water 273 K	293 K	313 K	333 K	353 K	373 K
–	–	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K –

Magnetic characterization –

Critical point: T_c 144.3 K
P_c 5.22 MPa

50.1.5 F
Thermodynamic Properties (per mol F_2)

Enthalpy of fusion ΔH_{fus} at m.p. 0.52 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p. 6.54 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K 79.0 $kJmol^{-1}$
Entropy S^0 at 298 K 202.78 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$	100 K	298 K	600 K	1000 K	2000 K	2500 K
	29.11	31.30	35.17	37.065	38.935	38.91

50.1.6 F
Nuclear Properties and X-ray

Isotope range, natural and artificial	15–25

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{19}F	Stable	100	1/2+	2.629

Nuclear magnetic resonance NMR

Isotope	^{19}F
Reference compound	$CFCl_3$
Frequency MHz (^1H = 100 MHz)	94.094
Receptivity D^P relative to ^1H = 1.00	0.834
Receptivity D^C relative to ^{13}C = 1.00	4900
Magnetogyric ratio, radT^{-1}s^{-1}	$25.181 \cdot 10^7$
Nuclear quadropole moment, barn	−0.094

Characteristic X-radiation

Z	Element	Kα$_2$ keV
8	O	0.525
9	F	0.677
10	Ne	0.848

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα$_2$)	15.8
17.37 keV (MoKα$_2$)	1.65

Neutron absorption	**Thermal neutron capture cross section**	0.0095 barns

50.1 Cl
Facts about Chlorine

50.1.1 Cl
The Element

Symbol:	Cl
Atomic number:	17
Atomic weight:	35.45
Ground state electron configuration:	[Ne]$3s^2 3p^5$
Crystal structure:	Tetragonal with $a = b = 8.56$ Å, $c = 6.12$ Å Orthorhombic with $a = 6.22$ Å, $b = 4.46$ Å, $c = 8.18$ Å Transition tetragonal → orthorhombic at 100 K

50.1.2 Cl
Discovery and Occurrence

Discovery: Chlorine was discovered by Carl Wilhelm Scheele in 1774. He obtained it in the reaction between the mineral pyrolusite and hydrochloric acid (HCl, then known as muriatic acid). Scheele thought the resulting gas contained oxygen. Sir Humphry Davy proved that chlorine was an element and gave it its present name.

Important raw materials: Halite, rock salt NaCl
Sylvite, sylvine KCl
Sylvinite NaCl · KCl
Carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$

Ranking in order of abundance in earth crust:	19
Mean content in earth crust:	145 ppm (g/tonne)
Mean content in oceans:	$1.94 \cdot 10^4$ ppm (g/tonne)
Residence time in oceans:	$79 \cdot 10^6$ years
Mean content in an adult human body:	1200 ppm
Content in a man's body (weight 70 kg):	84 g

50.1.3 Cl
Chemical Characterization

The greenish yellow gas chlorine is one of our most essential elements, in life and in industry. In spite of that, it has become the target of serious criticism and looked upon as one of the most harmful among the elements. Both opinions are true. Perhaps it was in seawater with its chloride milieu that life began. The element is essential for life and is present as *chloride* in all cells and body fluids. In contrast, *elemental chlorine* is dangerous – so toxic that it was used in gas warfare in World War I. Also in times of peace chlorine has found dangerous applications as chlorinated hydrocarbons, such as for instance DDT and PCB. Chlorinated hydrocarbons have also been used as industrial solvents for degreasing. These types of agent irritate mucous membranes and injure the brain. In many countries chlorinated hydrocarbons are banned for metal cleaning. Freons, containing fluorine and chlorine, were once an attractive alternative, which promptly had to be abandoned due to their influence on the ozone layer. Chlorine is used as an effective disinfectant of water and has provided great contributions in the fight against epidemics of typhoid and cholera.

Oxidation states:

Cl^{-I} as in NaCl
Cl^{I} as in Cl_2O and ClO^-
Cl^{III} as in $[ClO_2]^-$
Cl^{IV} as in ClO_2 and Cl_2O_4
Cl^{V} as in $[ClO_3]^-$
Cl^{VI} as in Cl_2O_6
Cl^{VII} as in Cl_2O_7 and $HClO_4$

Ionization energy (kJ mol^{-1}):

$Cl(g) \rightarrow Cl^+(g) + e^-$	1251
$Cl^+(g) \rightarrow Cl^{2+}(g) + e^-$	2298
$Cl^{2+}(g) \rightarrow Cl^{3+}(g) + e^-$	3822
$Cl^{3+}(g) \rightarrow Cl^{4+}(g) + e^-$	5159

Electron affinity (kJ mol^{-1}):

$Cl(g) + e^- \rightarrow Cl^-(g)$
–349

Standard reduction potential: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^0 = +1.358$ V
$OCl^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$
[alkaline solution]
$E^0 = +0.890$ V

Electronegativity (Pauling): 3.16

Radii of atoms and ions:

Atomic	100 pm
Covalent:	99 pm
Van der Waals:	175 pm
Cl^- (6-coordinate, octahedral):	167 pm
Cl^{7+} (6-coordinate, octahedral):	41 pm
Cl^{7+} (4-coordinate, tetrahedral):	22 pm

50.1.4 Cl
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
3.214 kg m^{-3} 3.21 g/l	2.47	172.17 K –100.98 °C	239.1 K –34.1 °C	479 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 73 K	173 K	273 K	373 K	1273 K
–	–	0.0079	0.0115	–

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K) a	b	c
37.03	$0.67 \cdot 10^{-3}$	$-2.85 \cdot 10^{5}$

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) –

Solubility in water m^3 gas at STP per m^3 water 273 K	293 K	313 K	333 K	353 K	373 K
4.610	2.260	1.414	1.006	0.672	0.380

Mass magnetic susceptibility χ_{mass} at 293 K	$-7.2 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)
Critical point:	T_c 417.1 K P_c 7.71 MPa

50.1.5 Cl
Thermodynamic Properties (per mol Cl_2)

Enthalpy of fusion ΔH_{fus} at m.p.	6.41 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	20.41 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	121.3 $kJmol^{-1}$
Entropy S^0 at 298 K	223.07 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$	100 K	298 K	600 K	1000 K	2000 K	2500 K
	42.3	33.95	36.55	37.44	38.47	39.38

50.1.6 Cl

Nuclear Properties and X-ray

Isotope range, natural and artificial 31–46

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{35}Cl	Stable	75.77	3/2+	0.8219
^{37}Cl	Stable	24.23	3/2+	0.6841

Nuclear magnetic resonance NMR

Isotope	^{35}Cl	^{37}Cl
Reference compound	KCl/D_2O	
Frequency MHz (^{1}H = 100 MHz)	9.798	8.156
Receptivity D^P relative to ^{1}H = 1.00	$3.58 \cdot 10^{-3}$	$0.66 \cdot 10^{-3}$
Receptivity D^C relative to ^{13}C = 1.00	21.0	3.87
Magnetogyric ratio, radT^{-1}s^{-1}	$2.624 \cdot 10^7$	$2.184 \cdot 10^7$
Nuclear quadropole moment, barn	−0.082	−0.064

Characteristic X-radiation

Z	Element	Kα_2 keV
16	S	2.307
17	Cl	2.620
18	Ar	2.956

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	106
17.37 keV (MoKα_2)	11.7

Neutron absorption **Thermal neutron capture cross section** 34 barns

50.1 Br
Facts about Bromine

50.1.1 Br
The Element

Symbol:	Br
Atomic number:	35
Atomic weight:	79.90
Ground state electron configuration:	$[Ar]3d^{10}4s^24p^5$
Crystal structure:	Orthorhombic with $a = 6.73$ Å, $b = 4.65$ Å, $c = 8.70$ Å

50.1.2 Br
Discovery and Occurrence

Discovery: A. J. Balard in Montpellier, France, and C. Löwig in Heidelberg, Germany, discovered bromine independently in 1824–1825

Important raw materials: In evaporated salt lakes. In the water of the Dead Sea.

Ranking in order of abundance in earth crust:	50
Mean content in earth crust:	2.4 ppm (g/tonne)
Mean content in oceans:	67.3 ppm (g/tonne)
Residence time in oceans:	$100 \cdot 10^6$ years
Mean content in an adult human body:	2.9 ppm
Content in a man's body (weight 70 kg):	0.2 g

50.1.3 Br

Chemical Characterization

Bromine is a poisonous element, the only nonmetallic element that is liquid at room temperature. The liquid is reddish brown and has a strong unpleasant odor. Bromine compounds have found two modern applications, both connected with fire. Organobromine compounds, *halons*, are used as fire extinguishers. Damage to the ozone layer caused by halon gases have however been confirmed. For this reason, the Montreal Protocol forbids their use. The other application for bromine is in polybrominated organic compounds as flame-retardants, to avoid starting of a fire in buildings, furniture and textiles. In 1999 flame-retardants were the primary use of bromine and accounted for 40% of total consumption of the element. Bromides are also used in photographic compounds and in natural gas and oil production.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Br^{-I} as in AgBr	$Br(g) \rightarrow Br^+(g) + e^-$	1140	$Br(g) + e^- \rightarrow Br^-(g)$
Br^{I} as in Br_2O and BrO^-	$Br^+(g) \rightarrow Br^{2+}(g) + e^-$	2103	–325
Br^{IV} as in BrO_2	$Br^{2+}(g) \rightarrow Br^{3+}(g) + e^-$	3470	
Br^{V} as in $HBrO_3$	$Br^{3+}(g) \rightarrow Br^{4+}(g) + e^-$	4560	

Standard reduction potential: $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ $E^0 = +1.087$ V
$OBr^-(aq) + H_2O(l) + 2e^- \rightarrow Br^-(aq) + 2OH^-(aq)$
[alkaline solution]
$E^0 = +0.766$ V

Electronegativity (Pauling): 2.96

Radii of atoms and ions: (WebElements™)		
	Atomic	115 pm
	Covalent:	114 pm
	Van der Waals:	185 pm
	Br^- (6-coordinate, octahedral):	182 pm

50.1.4 Br
Physical Properties

Density (at 293 K)	**Relative density (air = 1)**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
3120 kg m^{-3} 3.12 g/m^{-3}	–	266.0 K –7.2 °C	332.0 K 58.8 °C	474 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 73 K	173 K	298 K	373 K	1273 K
–	–	0.122	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-4.44 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)
Critical point:	T_c 584 K P_c 10.34 MPa

50.1.5 Br
Thermodynamic Properties (per mol Br_2)

Enthalpy of fusion ΔH_{fus} at m.p.	10.57 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	30.0 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	112 $kJmol^{-1}$
Entropy S^0 at 298 K	152.23 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$	**100 K**	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	43.6 (solid)	75.7 (liquid)	37.3	37.8	39.1	40.4

50.1.6 Br

Nuclear Properties and X-ray

Isotope range, natural and artificial 70–94

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{79}Br	Stable	50.69	3/2–	2.106
^{81}Br	Stable	49.31	3/2–	2.271

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{79}Br	^{81}Br
Reference compound	NaBr/D_2O	
Frequency MHz (^{1}H = 100 MHz)	25.054	27.007
Receptivity D^P relative to ^{1}H = 1.00	0.0403	0.0491
Receptivity D^C relative to ^{13}C = 1.00	230	280
Magnetogyric ratio, radT^{-1}s^{-1}	$6.726 \cdot 10^7$	$7.250 \cdot 10^7$
Nuclear quadropole moment, barn	0.313	0.262

Characteristic X-radiation

Z	Element	Kα_2 keV
34	Se	11.181
35	Br	11.878
36	Kr	12.598

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	89.4
17.37 keV (MoKα_2)	76.4

Neutron absorption **Thermal neutron capture cross section** 6.8 barns

50.1 I
Facts about Iodine

50.1.1 I
The Element

Symbol:	I
Atomic number:	53
Atomic weight:	126.90
Ground state electron configuration:	[Kr]$4d^{10}5s^25p^5$
Crystal structure:	Orthorhombic with $a = 7.18$ Å, $b = 4.71$ Å, $c = 9.81$ Å

50.1.2 I
Discovery and Occurrence

Discovery: B. Courtois in France discovered iodine in 1811.

Important raw materials: Iodine is obtained from brines and from Chilean nitrate ores in which it occurs as an impurity. To a lesser extent, iodine is also derived from sea organisms, such as brown seaweed.

Ranking in order of abundance in earth crust:	63
Mean content in earth crust:	0.45 ppm (g/tonne)
Mean content in oceans:	0.06 ppm (g/tonne)
Residence time in oceans:	$1 \cdot 10^6$ years
Mean content in an adult human body:	0.2 ppm
Content in a man's body (weight 70 kg):	14 mg

50.1.3 I
Chemical Characterization

Iodine is a bluish black, lustrous solid and chemically reactive element. It volatilizes into a blue-violet gas with an irritating odor. Iodine is medicinally very important because it is an essential element for formation of the hormone thyroxine in the thyroid gland. Deficiency of iodine will cause goitre and stunted growth. This has to be treated with addition of potassium iodide or iodine casein. In developed countries, iodine deficiencies are however rare because iodine is added to table salt. Radioactive iodine isotopes are spread as a result of nuclear power plant disasters. Especially ^{131}I with a half-life of eight days is important. When this iodine isotope is taken up by the thyroid gland, it causes cancer. People living and working near a nuclear power station are therefore recommended to have iodine tablets available and to use them in an emergency situation. The "normal" iodine in the tablets is taken up by the thyroid gland and saturates it. This blocks the uptake of radioactive iodine.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
I^{-I} as in KI	$I(g) \rightarrow I^+(g) + e^-$	1008	$I(g) + e^- \rightarrow I^-(g)$
I^{I} as in $[IO]^-$	$I^+(g) \rightarrow I^{2+}(g) + e^-$	1846	–295
I^{V} as in I_2O_5 and HIO_3	$I^{2+}(g) \rightarrow I^{3+}(g) + e^-$	3180	
I^{VII} as in $[IO_6]^{5-}$			

Standard reduction potential: $I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $E^0 = +0.535$ V
$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$
[alkaline solution]
$E^0 = +0.485$ V

Electronegativity (Pauling): 2.66

Radii of atoms and ions:	Atomic	140 pm
(WebElements™)	Covalent:	133 pm
	Van der Waals:	198 pm
	I^{1-} (6-coordinate, octahedral):	206 pm
	I^{5+} (6-coordinate, octahedral):	109 pm
	I^{7+} (6-coordinate, octahedral):	67 pm
	I^{7+} (4-coordinate, tetrahedral):	56 pm

50.1.4 I
Physical Properties

Density	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
4930 kg m^{-3} 4.93 g/m^{-3}	–	386.7 K 113.5 °C	457.5 K 184.3 °C	215 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 73 K	173 K	298 K	373 K	1273 K
–	–	0.449	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-4.40 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)
Critical point:	–

50.1.5 I
Thermodynamic Properties (per mol I_2)

Enthalpy of fusion ΔH_{fus} at m.p.	15.52 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	41.80 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	107 $kJmol^{-1}$
Entropy S^0 at 298 K	116.14 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	45.7	54.44	37.61	38.07	40.47	41.60

50.1.6 I

Nuclear Properties and X-ray

Isotope range, natural and artificial 108–141

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{127}I	Stable	100	5/2+	2.809

Nuclear magnetic resonance NMR

Isotope	^{127}I
Reference compound	KI/D_2O
Frequency MHz (^1H = 100 MHz)	20.009
Receptivity D^P relative to ^1H = 1.00	0.0954
Receptivity D^C relative to ^{13}C = 1.00	545
Magnetogyric ratio, $radT^{-1}s^{-1}$	$5.390 \cdot 10^7$
Nuclear quadropole moment, barn	−0.71

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
52	Te	27.201
53	I	28.317
54	Xe	29.459

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	289
17.37 keV ($MoK\alpha_2$)	37.1

Neutron absorption **Thermal neutron capture cross section** 6.2 barns

50.2
The History of Halogen Discoveries

50.2.1
The Discovery of Chlorine in 1774

Carl Wilhelm Scheele discovered the element chlorine in 1774 when he investigated pyrolusite. On treating this substance with hydrochloric acid, or *spiritus salis*, as he called it, a gas with suffocating smell was developed, very trying on the lungs. The smell reminded Scheele of what he felt when he prepared and warmed *aqua regia*. He thought that the metal in pyrolusite had absorbed phlogiston from the hydrochloric acid. Because of that he named the gas "dephlogisticated hydrochloric acid".

For chemists in our time, everything is so simple. Hydrochloric acid is HCl. If hydrogen H is removed, chlorine Cl remains. In the times of Scheele, our formula system had not yet been invented. Berzelius introduced it in 1813. Much of what we consider natural about the nature of substances was shrouded in mystery. If we accept Cavendish's way of looking at matter (in 1735), i.e. that phlogiston is hydrogen, what then is chlorine if not dephlogisticated hydrochloric acid? We ought not to speak condescendingly about the phlogiston theory. Instead, we have every reason to hold those chemists in high esteem, because, with the conceptual ideas then available, they were able to solve essential and difficult chemical problems. The results have since been adapted to new theories and a new symbolic language. Scheele had discovered the element chlorine, but he never used that designation. Nor did any other of his contemporaries. Now he would collect all the facts about his evil-smelling greenish gas. In his pharmacy he found that it had some solubility in water and made the water acid. It bleached flowers and green leaves and attacked all metals.

According to Lavoisier, a chemical element was a substance that had not yet been decomposed. If so, was Scheele's dephlogisticated hydrochloric acid an element? The answer had to be no, as it was an acid ... and all acids contain oxygen. This was the second principal idea of Lavoisier. Thus, the substance that later on was to get the name "chlorine" *had* to contain oxygen. And it seemed to be logical that, when hydrochloric acid and pyrolusite, rich in oxygen, reacted, the evolved gas should have taken up oxygen and really contain this substance. It also got the name *oxy-muriatic acid*, indicating that it was *muriatic acid* (hydrochloric acid) to which oxygen had been added. The famous French scientists J.-L. Gay-Lussac and L.-J. Thénard tried in vain to detect oxygen in it. In 1810 *Sir Humphry Davy* [50.1] carefully investigated oxy-muriatic acid. Davy reasoned that, if the substance really were composed of oxygen and muriatic acid, charcoal would react with it and set muriatic acid free. He heated charcoal electrically to drive off all volatile matter and then led a stream of oxy-muriatic gas through it at white heat. There was no reaction. Davy made additional experiments. He let the gas pass over phosphorus and got nothing but phosphoric chlorides. With metallic potassium, the gas formed potassium chloride, a substance that Davy was a real specialist to identify. As a result of these investigations, Davy concluded that the behavior of oxy-muriatic acid was more easily explained by assuming it to be one of the elements. He also suggested that the name of the gas should be changed to *chlorine*, meaning green. He also declared a revolutionary new idea: oxygen is not unique in its chemical properties, as had been assumed. Chlorine may be regarded as an analogous substance. It supports combustion and may – like oxygen – be an essential constituent of acids. A formulation of his became a chemical truth a century ahead of its time:

> May it [chlorine] not in fact be a peculiar acidifying and dissolving principle, forming compounds with combustible bodies, analogous to acids containing oxygen ... On this idea muriatic acid may be considered as having hydrogen for its basis and oxy-muriatic acid for its acidifying principle.

Scheele discovered chlorine, but Davy named it and has the credit for establishing its elemental nature.

50.2.2
Chlorine Bleaching – A Simple but Historical Process

In connection with the element's discovery in 1774, Scheele had observed that the gas bleaches flowers. In 1785 C.-L. Berthollet in France made the same observation. He contacted several scientists about this, even James Watt in Birmingham. This latter practical man and inventor saw the possibilities of utilizing chlorine gas for the effective cleaning of dirty linen. He tested chlorine treatment of clothes in a plant near Glasgow. Thereafter many laundries grew up in Great Britain and in many countries in Europe. The use of chlorine gas was however very trying for personnel in the laundries. So already at the turn of the century 1800 a new bleaching agent – chlorine combined with lime to calcium hypochlorite $Ca(OCl)_2$ – was developed. It also worked well as a cleaning agent but was a little more environmentally friendly.

50.2.3
The Discovery of Iodine in 1811

Bernard Courtois (1777–1838) was born in Dijon, France, the son of a maker of potash and saltpeter. From his youth he helped his father in manufacturing the chemicals. His father, Jean-Baptiste, used to assist *Louis-Bernard Guyton de Morveau*[1] in his chemical work in the famous *Académie de Dijon*, founded in 1740. Now it was the time of the French Revolution, and in 1791 citizen Morveau was called to the capital to be a member of the legislative assembly. Jean-Baptiste Courtois then finished his work as an assistant at the academy and returned to full-time saltpeter manufacture. Bernard got a job as apprentice in a pharmacy. When Guyton de Morveau became director of the École Polytechnique in Paris, he offered Bernard a position as laboratory worker and student. Young Bernard pursued his work and studies with great enthusiasm.

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[1] Louis-Bernard Guyton de Morveau (1737–1816) was professor of chemistry at the École Polytechnique from 1794. He worked in the circle around Lavoisier on the development of the new chemical nomenclature.

At the beginning of the 19th century, Napoleon's armies were in urgent need of gunpowder. Potash was needed for its manufacture, as described in Chapter 11 Sodium and Potassium. Potash was a commodity in short supply, and attempts to win it from seaweed started. Bernard Courtois was by now a well-educated chemist and familiar with potash and saltpeter. It was natural that he got the assignment to investigate marine plants on the Normandy coast. In 1811 he collected algae at ebb tide, burned them and leached the ashes in water. The leach was evaporated and different substances crystallized in order after their solubilities – sodium chloride first, then potassium chloride and potassium sulfate. In the calcination process, some sulfates had been reduced and the mother liquor after crystallizations contained sulfites and polysulfides. In order to transform these to sulfates, he added sulfuric acid and evaporated until this acid had been concentrated and fumed. Something miraculous happened! Clouds of a violet vapor rose up from the beaker. It was beautiful, but its smell was irritating, reminiscent of chlorine. On condensation on a cold surface, no droplets were formed, but dark crystals with the luster of metal appeared.

Courtois examined the substance he had found. It was not decomposed by heat, not even red heat. It formed compounds with hydrogen and phosphorous, but not with carbon and oxygen. He began to think that he had discovered a new element. However, he was not self-confident enough to go forward with such a sensational claim. Nor did he dare to spend his time completing the investigations. Instead, he asked two friends from Dijon to continue the experiments and gave them permission to publish the results. And so they did2). It is fitting that the discoverer himself was mentioned in the title. Gay-Lussac confirmed that a new element had been discovered, and he named it *iodine* after the Greek word for "violet". Shortly after the element's discovery, iodine became very much appreciated as a remedy against goitre.

Jacque Daguerre (1787–1851) invented photography (*daguerreotypy*) in the 1830s. The photographic plates were made of copper, coated with silver. On this, iodine (and bromine) had been vaporized, resulting in a coating of a light-sensitive layer of silver iodide/bromide. On exposure to light, the silver iodide/bromide was converted to silver metal and free iodine/bromine, which was removed by mercury vapor. The fixing was achieved by a solution of sodium thiosulfate, which removed all the silver iodide/bromide not acted upon by light. The French Academy of Sciences made the invention public in 1839. The French Government took the noteworthy step to buy the invention from Jacque Daguerre and *donate it to mankind*.

50.2.4
The Discovery of Bromine in 1825–1826

More than 3000 years ago, long before the discovery of the element, a bromine compound was known. *Royal purple* or *Tyrian purple* (Figure 50.1) was a reddish violet dye that was extracted from the sea mollusk *Murex brandaris*. Textile dying was performed especially in the Phoenician cities of Tyros and Sidon. The availability of the purple

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2) N. Clement and C.-B. Desormes, Découverte d'une substance nouvelle dans le Vareck par M. B. Courtois. *Ann. Chim. Phys.* **88** (1813) 304–10.

dye was limited and it became extremely expensive. In Roman times, dye use was restricted. The emperors themselves were given **the** exclusive right to wear purple garments, and the manufacture of higher-quality purple became a state monopoly. It was literarily a dye imperialism. Nowadays purple dye is made synthetically.

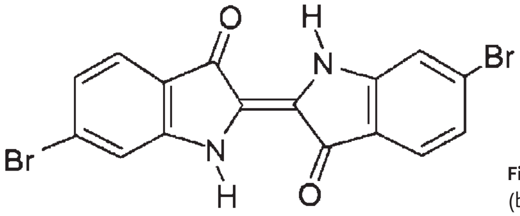

Figure 50.1 Tyrian purple or royal purple (bromine indigo).

Two young men discovered the element bromine quite independently and almost simultaneously. *Carl Löwig* (1803–1890) made the discovery in 1825 at the age of 22. He had examined water from a mineral water spring in his home village of Kreuznach in Germany. He observed that the water was colored red on addition of chlorine and that the colored substance could be extracted into an ether phase. He distilled off the ether and got a red, smelly liquid. The year after he went as a new student to the University of Heidelberg, and showed the liquid to Leopold Gmelin, whom he had as his professor. The teacher became interested and asked Carl to prepare a bigger sample for examination. Winter exams and holidays delayed Löwig and things took a new turn. In France, another student, Antoine-Jéròme Balard, aged 23, also discovered the new element. As he published the discovery and described the element's properties, he was credited with the discovery. Young Carl seemed to have accepted this with composure. After his education in Heidelberg, however, Löwig continued his bromine research. In 1829 he edited a publication about bromine and its chemistry. In 1833 he was offered the chair of chemistry in Zurich, and in 1853 he succeeded Bunsen as professor in Bratislava.

Antoine-Jéròme Balard (1802–1876) grew up in Montpellier near the French Mediterranean coast. At the age of 17 he began to study at the École de Pharmacie and was examined in 1826. During his studies, he examined the flora in some salt marshes near Montpellier. Salt was won there from numerous lagoons on an annual cycle – dammed in the spring, allowed to evaporate in the summer and collected in the fall [50.2]. The young student observed that crystallized sodium sulfate was thrown away. Could it not be used in some way? At least for Antoine-Jéròme himself the substance became useful. In spite of his youth, he discovered a new element, which took him into the history of science. It occurred when he made different experiments with crystals and mother liquor.

Pierre Louis Dulong, professor at the École Polytechnique, wrote on July 1st, 1826, in a letter to Berzelius in Stockholm (cited from Mary Weeks):

> ... But there is another piece of recent news ... It is a new simple body which will find its place between chlorine and iodine. The author of this discovery is M. Ballard of Montpellier. This new body, which he calls muride, is found in seawater. He has extracted it from the mother liquor of Montpellier brines

> by saturating them with chlorine and distilling. He obtains a dark red liquid substance, boiling at 47°. The vapor resembles that of nitrous acid. Its specific gravity is 3. One preserves it under concentrated sulfuric acid. It combines with metals and gives compounds sensibly neutral, of which several are volatile, notably the muride of potassium ...

Antoine-Jéròme Balard published information about his discovery and described the new element in 1826 in *Annales de Chimie et de Physique*. He was credited with the discovery, but it is fair to say that part of the priority ought to be given to Carl Löwig. The nomenclature committee of the French Academy of Sciences, of which Vauquelin, Thénard and Gay-Lussac were members, did not accept the name muride. Instead, the name bromine was selected, named after the Greek word *bromos* meaning "stench". Anyone who has worked with bromine will affirm that this is a suitable name.

In 1842 Balard succeeded Thénard as teacher and in 1851 was appointed professor at the Collège de France.

50.2.5

The Discovery of Hydrofluoric Acid in 1771

> In *Bermannus*, a writing by Agricola in 1529, the experienced Bermannus and the young, inquisitive Anton are described with fictitious dialogs. Bermannus answers all Anton's questions, and explains many chemical and mineralogical problems. For example:
>
> *Bermannus*: These stones are of various and bright colors. They resemble gems but are not so hard. Miners and metallurgists call them fluores. To my mind a suitable designation. By the heat of fire they liquefy and flow away like ice in the sun.
>
> *Anton*: What then is the use of fluores?
>
> *Bermannus*: Fluores are added when metals shall be prepared in furnace processes. They make the slag much more fluid.

It is fluorspar that Bermannus describes and Agricola called it *fluores mineralis*. By that means he had named the halogen it contains, some 350 years before it was discovered. In 1670 *Heinrich Schwanhard* in Nuremberg found that if fluorspar was treated with sulfuric acid a gas was evolved, a gas with peculiar properties: it etched glass. It created quite a new method – an alternative to engraving with a diamond needle – to prepare writing and decoration on glass articles. It is also reported that hydrofluoric acid was prepared in the early 18th century by an unknown English glassworker who used it to etch glass.

A. S. Marggraf, whom we have met many times in the history of the discovery of the elements, in 1768 carried out a chemical investigation of fluorspar. He treated pulverized fluorspar with sulfuric acid in order to distill off the remarkable gas and examine it. The experiment failed, as his glass retort was attacked so strongly that it was perforated. In 1771 Carl Wilhelm Scheele did the same experiment but was able to collect sufficient gas for examination. He established that it was a gaseous acid that left the retort, and that the residue was calcium sulfate. In fact Scheele had solved the fluorspar problem: it was a mineral, composed of lime and an unknown acid. As usual Scheele took a second step. He added limewater to the acid he had distilled off and found that he had synthesized fluorspar. Its properties were quite the same as the natural mineral's, including *phosphorescence*[3] in both. The discovery of the new acid was described by Scheele[4] in a publication that attracted much attention from the 18th century scientific community.

The acid, which we now call hydrofluoric acid, was for a long time called *the Swedish acid*. It was to take a long time – more than one hundred years – until its main atom, fluorine, was isolated. When in 1789 Lavoisier established his famous table of the simple substances in chemistry – an element table – he left space also for the main element of the Swedish acid, not yet discovered. In 1811 Ampère suggested that the name of this unknown element should be fluorine, analogous to chlorine.

50.2.6
The Discovery of Fluorine in 1886

Fluorine is the most active of all elements. On contact with the gas, a person's mucous membranes and respiratory organs are seriously injured. It is one of the interesting paradoxes in chemistry that this dangerous substance is, as the fluoride ion, also useful and vital. In our schools we see that children may get fluorine tablets for their dental health.

After Davy's pioneering work on the electrolysis of alkali halogenide melts, it was most likely that fluorine would be prepared by electrolysis. Humphry Davy himself tried but failed. In the attempts to isolate fluorine, one problem, among others, was that the equipment was so seriously attacked. Still worse, the discovery history of fluorine is filled with personal tragedy. Two brothers, George and Thomas Knox, members if the Irish Academy of Science, intended in the 1830s to isolate fluorine from mercury fluoride by purely chemical means, utilizing chlorine. They made equipment of fluorspar, which they thought should withstand attack from fluorine. The experiments had to be interrupted as they were badly injured. The young Belgian chemist Paulin Louyet took over the equipment from the Knox brothers in 1840 and made many investigations regarding fluorine. His lungs were destroyed and he died in 1850, at the age of only 32. The French chemist Jérome Nicklès of Nancy also tried to isolate fluorine but died in 1869 of hydrofluoric acid poisoning. He was then 49 years of age.

Edmond Fremy (1814–1894), a professor at the École Polytechnique in Paris, had watched some of Louyet's experiments in Brussels but was not frightened of his fate. In 1855 he tried to electrolyze a molten fluorspar. He got calcium at the cathode and a gas at the anode. It must have been fluorine, but at the high temperature of the melt it reacted so rapidly with the anode material that he was not able to capture it. An Eng-

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[3] Phosphorescence is a type of luminescence in which the substance continues to emit light after the external light is shut off. It differs from fluorescence, in which the emission of light ceases when the external stimulus ceases.

[4] C. W. Scheele, Undersökning om Fluss-spat och dess Syra (in Swedish) [Investigation of fluorspar and its acid]. *Transactions of the Royal Swedish Academy of Sciences*, 1771, April, May, June, pp. 120–138.

lish chemist, *George Gore*, made thorough investigations in 1869. He used anodes of gold, palladium and platinum. The noble metals were rapidly destroyed without giving any gas. The preparation of fluorine seemed to be hopeless. Even carbon anodes were attacked, but a small amount of gas could be obtained and examined. Gore found that it combined explosively with hydrogen.

Professor Fremy had a student, *Henri Moissan* (1852–1907). He solved the problem with the isolation of fluorine. As did so many eminent chemists in the history of discovery of the elements, he began his career with medical chemistry. At 18 he became an apprentice in a Paris pharmacy. He continued to study chemistry with Edmond Fremy at the École Polytechnique, and he attended lectures by E. H. Sainte-Claire Deville. Most likely it was Professor Fremy who interested him in fluorine chemistry and aroused his curiosity.

> Moissan gained his doctoral degree in 1880 and became assistant lecturer and senior demonstrator at the School of Pharmacy. In 1886 he was elected Professor of Toxicology, and in 1899 he took the Chair of Inorganic Chemistry of that School. In 1900 he became Professor of Inorganic Chemistry at the University of Paris. In 1906 he was awarded the Nobel Prize for chemistry. He died suddenly in Paris on February 20, 1907, shortly after his return from the prize-giving ceremony in Stockholm. Certainly his health had been injured by his fluorine work.

It was in 1884 that Moissan turned his attention to fluorine chemistry. He electrolyzed arsenic fluoride but had to interrupt his work several times due to toxic symptoms. Finally he succeeded in preparing arsenic powder on the cathode and some gas bubbles on the anode. Before the bubbles reached the surface they were absorbed by the molten arsenic(III) fluoride, forming the pentafluoride. Moissan sat down to think and analyze the problem, in the light of all the failures, his own and those of others. He concluded that electrolysis had to be done at a lower temperature, compared to what had been used in previous experiments. That would of course decrease the rate at which any evolved fluorine gas would attack the anode material. Moissan now built some equipment, consisting of a platinum U-tube with platinum–iridium electrodes. Sealing was achieved with powdered fluorspar. The electrolyte was anhydrous hydrofluoric acid, containing potassium hydrogen fluoride KHF_2. The whole equipment was cooled with methyl chloride and the electrolysis was performed at a temperature of –23°C (Figure 50.2).

On June 26, 1886, a considerable quantity of fluorine was prepared. When Moissan brought the gas into contact with silicon, a spontaneous reaction occurred and the product – obviously silicon fluoride – was red hot. Two days later the result was made public to the Academy of Science. Professor Emery, who was present, said that a professor is always happy when he sees one of his students proceed farther and higher than himself.

In 1986, many scientists attended a conference in Paris arranged in order to celebrate the one-hundredth anniversary of Henri Moissan's first preparation of fluorine [50.4].

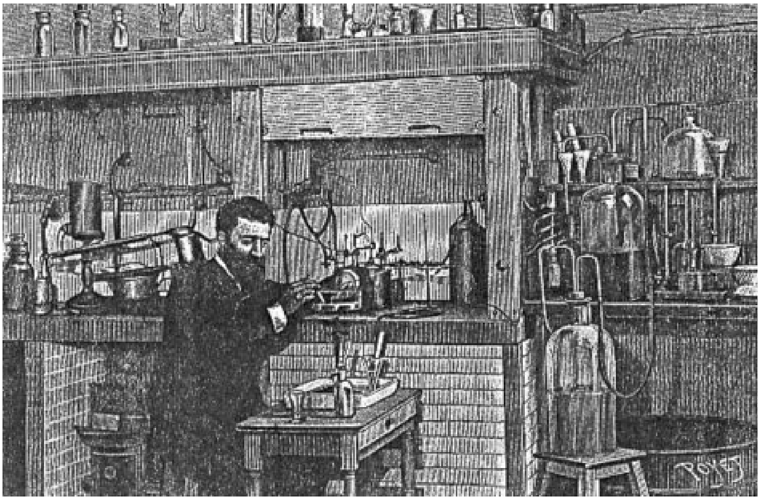

Figure 50.2 Henri Moissan prepares fluorine in his laboratory [50.3].

50.3
Occurrence and Manufacture

50.3.1
Fluorine

The most important minerals containing fluorine are fluorite (fluorspar), fluorapatite and cryolite. Some information about them is given in Table 50.1.

Table 50.1 Fluorine minerals

Mineral	Formula	Comments
Fluorite, fluorspar	CaF_2 (Figure M75)	Crystalline cubes with octahedral cleavage. Found in different colors (often blue or purple). It is the principal ore mineral of fluorine. It is used in the manufacture of hydrofluoric acid, and as a flux in the metallurgical and glass industries
Fluorapatite	$Ca_5(PO_4)_3F$	Occurs as the chief constituent of phosphate rock and of bones and teeth. This mineral provides around 10% of the fluorine used
Cryolite, “ice stone”	Na_3AlF_6	A white monoclinic mineral of waxy luster. It has been found chiefly in a pegmatite at Ivigtut, Greenland. Natural and synthetic cryolite is used in the manufacture of aluminum, as the molten mineral has the property to dissolve aluminum oxide Al_2O_3

In the manufacture of hydrofluoric acid, a powdered concentrate of fluorspar is kneaded with concentrated sulfuric acid (100% H_2SO_4 content). The paste passes through a rotating tube furnace at 300°C. The HF gas formed goes backwards, leaves the entrance port, and is condensed to anhydrous hydrofluoric acid (boiling point 20°C). Calcium sulfate is transported through the furnace. Elemental fluorine is prepared by the electrolysis of fused potassium hydrogen fluoride at 60°C using graphite electrodes.

In 2001 the world fluorspar production was about 4.5 million tonnes (contained fluorine). China accounted for half of this. Large deposits of fluorspar are also found in Mexico, South Africa, Mongolia and Russia.

50.3.2
Chlorine

Important minerals containing chlorine are collected in Table 50.2.

Table 50.2 Chlorine minerals

Mineral	**Formula**	**Comments**
Halite, rock salt	NaCl (Figure M12)	It occurs in cubic-crystalline forms as native salt
Sylvite, sylvine	KCl	Occurs as a saline residue together with halite and other evaporites. Sylvite is the principal ore mineral of potassium compounds
Sylvinite	$NaCl \cdot KCl$	A mixture of halite and sylvite mined as a potash ore
Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$	A milk-white to reddish orthorhombic mineral. It occurs as a saline residue and is used as a raw material in the manufacture of fertilizers

Seawater is rich in chlorine – in fact 2% of its weight is chloride ions. This represents tremendous quantities. By evaporation in ancient seas, the rock salt layers mentioned in Table 50.2 were formed. Their content of chloride is also tremendous, certainly billions of tonnes.

The *chlor-alkali process* produces annually about 40 million tonnes of chlorine gas by electrolysis of sodium chloride:

$$2Cl^- + 2H_2O \rightarrow 2OH^- + H_2 + Cl_2$$

A voltage of about 3.5 V is used. The current may – according to the intended production – be very high, typically 100 000 A.

The technique utilizes cells divided into two compartments, one anodic, one cathodic. Chlorine is formed in the former, sodium hydroxide in the latter. The cell compartments are separated by diaphragms working both as cathodes and as obstacles to chlorine passage from anode to cathode compartments. The diaphragms are made of a steel wire mesh, combined with a polymer, giving pores with suitable sizes. The anodes are made of titanium (graphite in older equipment). The level of the sodium chloride solution in the anode compartment is kept higher than that in the cathode compartment. This creates a flow of NaCl from anode to cathode and reduces the backflow of NaOH. The chlorine gas produced in the anode compartment is pumped off, while the cathode solution, 10–15% each of NaOH and NaCl, is concentrated and purified to NaOH. As an alternative to the conventional diaphragm technique, a cation-exchange membrane cell has also been introduced. The membrane is made of a fluorocarbon polymer. It permits sodium ions Na^+ to pass between the anode and cathode compartments but restricts the backflow of chloride and hydroxide ions, Cl^- and OH^-. In the cathode compartment, sodium hydroxide with 20–40% NaOH is obtained.

In the older chlor-alkali process, separated anode and cathode compartments were not used. A sodium chloride solution was electrolyzed in one cell with an anode of titanium (coated with ruthenium) and a cathode of mercury. Chlorine gas was formed at the anode, sodium amalgam at the cathode:

$$2Na^+ + 2Cl^- \rightarrow 2Na(\text{in Hg}) + Cl_2$$

When the amalgam was removed from the cell and treated with water, sodium hydroxide was obtained:

$$2Na(\text{in Hg}) + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2$$

The mercury was recycled back to the process. Because of the toxic effects of mercury leaching to the environment, the mercury cell process has been replaced more and more by the diaphragm or membrane processes.

50.3.3
Bromine

The oceans contain 67 ppm bromine, which means 67 g/m^3. A limited amount of bromine winning occurs at several coastal sites. Water intended for bromine winning is enclosed in basins, to which chlorine gas is added. Bromine is set free and extracted in rather complicated chemical processes. Great producers are China, the United Kingdom and Japan. However, the two dominant bromine-producing countries are Israel and the USA. The total bromine production in the world in 2002 was 540 000 tonnes. Israel accounted for 206 000 tonnes (38%) and the USA produced 222 000 tonnes (41%).

In the Dead Sea the salt content is 275 g/l, which is eight times higher than the mean content in the oceans. The bromine content is relatively higher still, 80 times as large as the common content of the seas. This implies that the Dead Sea contains 5.4 g bromine per liter. This is the basis for the very great bromine winning there.

The American bromine is obtained from natural brines in Michigan and Arkansas. In Arkansas, very deeply situated brines are found. They were formed as evaporates in the late Jurassic, thus about 150 million years ago. In these brines the bromine concentration is as high as 5000 ppm, while iodine is almost non-detectable. As in the Dead Sea, the bromine concentration is much higher than would be expected from the chloride concentration. The brines are transported up to the surface through 25 cm wide boreholes. Oil, hydrogen sulfide, methane and carbon dioxide are removed, and bromide is transformed to elementary bromine by chlorine.

50.3.4
Iodine

The content of iodine in seawater is low, 0.06 ppm, but the element is enriched in seaweed, algae and corals. On burning brown seaweed, ash is obtained with as much as 5 kg of iodine per tonne. This product was used for the first winning of the element. Iodine is also enriched in natural brines and oil-well brines. However, the main iodine source is Chilean nitrate deposits. Water solutions, rich in sodium iodide, are extracted from Chile saltpeter or brines. Chlorine gas is bubbled through these aqueous solutions, and converts the iodide to iodine.

In 2001 the world production of iodine was 20 700 tonnes, almost entirely produced in Chile (55%) and Japan (32%).

50.4
Uses of the Halogens

50.4.1
Fluorine

Ever since its discovery in ancient times, fluorspar has been used in metallurgy to make slag liquid. Also old is the utilization of hydrofluoric acid for etching of glass. For fluorine itself, however, several modern applications have been found.

50.4.1.1 Local Stability but Global Instability

In Chapter 47 Oxygen, it was seen that fluorine is an essential part of chlorofluorocarbons, a group of substances called freons or CFCs. Two examples are CCl_3F (designated CFC-11) and CCl_2F_2 (CFC-12). The former is a liquid with the boiling point of +23.8°C, the latter a gas with a boiling point of –29.8°C. The liquid has been used as a refrigerant, the gas as a foam-blowing agent. Some freons have also been utilized as degreasing agents in industry. The great stability of the CFCs made them much appreciated in their different functions.

As they cause the decomposition of the ozone layer, creating *ozone holes*, their use however is now banned.

50.4.1.2 Teflon – Discovered Quite Accidentally

In 1938 *Roy J. Plunkett* (1911–1994), working at Du Pont in New Jersey, discovered a new substance with striking properties. He investigated *tetrafluoroethylene*, a monomer $CF_2{=}CF_2$. In the reaction cylinder he found a white powder that appeared to be a solid formed in the spontaneous polymerization of the monomer. Du Pont began to produce *polytetrafluoroethylene*, or *Teflon* (PTFE), as they named it. Teflon is very resistant to almost all reagents, and it has many applications in the chemical industry. It also became used as a low-friction material for many mechanical purposes as well as domestically. We are all used to Teflon non-stick coatings on cookware. However, as the substance has outstanding insulating properties, more than 50 percent of the Teflon produced has been used in the electrical industry.

50.4.1.3 **Uranium and Fluorine**

In the development of the atomic bomb, the so-called Manhattan Project, it was necessary to find a method for the very difficult separation of the ^{235}U and ^{238}U isotopes (see Chapter 52 Radioactive Elements). The research and planning work culminated in a process in which the hexafluorides of the two isotopes were separated. Uranium oxide was first treated with hydrogen fluoride to make uranium tetrafluoride. This in turn was treated with elemental fluorine to prepare the hexafluoride.

The equipment for the enrichment process was built up of barriers with millions of tiny holes, through which the gas mixture passed. The fluorides of ^{238}U and ^{235}U move with different speeds, which makes differentiation possible. After thousands of repetitions in passing the gas mixture through such barriers, a quite pure fraction of uranium-235 fluoride was obtained, from which the metal for the first atomic bombs could be prepared.

Uranium hexafluoride is a very reactive and corrosive compound, almost as reactive as fluorine itself. For building the separation equipment, Teflon and other fluorine compounds were utilized.

The nuclear industry, both for production of weapons and for nuclear reactors, is still a major consumer of fluorine compounds. In the USA annually about 5000 tonnes of fluorine are produced. Of this quantity, about 80% is used to produce uranium hexafluoride for the uranium enrichment process [50.4].

50.4.2
Chlorine

50.4.2.1 **Disinfection of Water**

Chlorine has provided great contributions in the fight against epidemics of typhoid and cholera. It is also used as an effective disinfectant of water in everyday situations for cleaning of drinking water and swimming baths. Chlorine also provides residual protection, and is easier and cheaper to use than other disinfection technologies.

Chlorine may be applied as chlorine gas Cl_2, sodium hypochlorite NaOCl, or calcium hypochlorite $Ca(OCl)_2$. All three agents produce the hypochlorite ion OCl^- in water:

$$Cl_2 + H_2O \rightarrow OCl^- + Cl^- + 2H^+$$
$$NaOCl \rightarrow OCl^- + Na^+$$
$$Ca(OCl)_2 \rightarrow 2OCl^- + Ca^{2+}$$

Together the three compounds contribute to what is known as the *free residual chlorine concentration*. When chlorine is added, it reacts with organic matter and ammonia to form organochlorine compounds and chloramines [50.5]. So much chlorine has to be added that a "break-point chlorination" is obtained. Above the break-point the bactericidal effect is considered good and the viricidal effect moderate.

50.4.2.2 Chlorine in the Chemical Industry

Chlorine is very much utilized in the synthesis of organic chemicals. If one or more hydrogen atoms are substituted with chlorine in molecules like ethene, propene, benzene and toluene, it will be possible to accomplish syntheses that are not possible with the original molecules with their low reactivity. The final products, such as for instance silicones, polyurethanes and polycarbonates, contain no chlorine, as the substituted element reacts to chlorides of hydrogen or sodium and leaves the reaction. However, important syntheses are also performed, in which chlorine stays in the product. Polyvinyl chloride (PVC) is an example.

Chlorinated hydrocarbons have been very much utilized as industrial solvents for degreasing, paint stripping and dry-cleaning. Mostly trichlorethylene[5] C_2HCl_3, alternatively methylene chloride (dichloromethane) CH_2Cl_2 or tetrachlorethylene (perchlorethylene) $CCl_2 \cdot CCl_2$, have been used.

The health hazards with using these types of agents are confirmed. They irritate the skin and mucous membranes, injure the brain, and are perhaps also carcinogenic. In many countries, chlorinated hydrocarbons are banned for metal cleaning and ecofriendly water-based alternatives are being developed.

Freons were once an attractive alternative, which however promptly had to be abandoned due to their influence on the ozone layer.

50.4.3
Bromine

Environmental thinking and claims have very much influenced the use of bromine. Methyl bromide was for a long time used as a biocide and insecticide. In the 1990 Clean Air Act the compound was however characterized as a Class 1 ozone-depleting substance and will be phased out before 2005.

Dibromomethane was used as an additive to leaded gasoline. The bromine compound acted as a scavenger and reacted with lead to form lead bromide, which passed out with the exhaust gases. Thus lead deposits in the engine were avoided. For environmental reasons, lead was banned in gasoline. This very large bromine use was almost entirely eliminated when unleaded gasoline was introduced.

Instead, bromine compounds have found two other applications, both connected with fire. One is as a fire extinguisher. Organobromine compounds, *halons*, such as halon-1211 $CBrClF_2$ and halon-1301 $CBrF_3$, are used. Damage to the ozone layer caused by from halon gases has however been confirmed. For this reason, the Montreal Protocol forbids their use.

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5) The IUPAC name for ethylene is *ethene* but the older designation is used here.

The other use for bromine is as a flame retardant, to avoid the starting of a fire. In many situations the course of a fire is violent, resulting in disastrous injury to people and damage to property. Polybrominated compounds are used as flame retardants for plastics in computers and other electronic components, for transformers, as well as for buildings, furniture and textiles. There are different types:

- polybrominated biphenyls (PBB);
- polybrominated diphenyl ether (PBDE);
- tetrabromobisphenol-A (TBBP-A);
- hexabromocyclodecane (HBCD).

In 1999 flame retardants were the primary use of bromine and accounted for 40% of the total consumption of the element. But, even this very useful bromine application is questioned from an environmental point of view. When protected components, not destroyed by fire, are scrapped, brominated organic compounds follow the sludge from the sewage treatment works and reach ground. This implies health hazards. Especially PBB and PBDE are considered to be dangerous. At present TBBP-A is the most widely used brominated flame retardant. As it is primarily bound into epoxy resins, the risk of its escaping into the environment is limited. The use of brominated flame retardants will certainly continue for a number of years. Substances that make ignition more difficult and delay the time to flashover are indeed very valuable and at present no suitable substitutes are available. Possible effects on the environment may be regarded as less significant than the increased fire risk that would be the result of refraining from using them.

There are in fact some bromine applications that are not questioned from an environmental point of view. Bromine has a similar usage to chlorine for water disinfection. Silver bromide is used as a light-sensitive substance in photographic emulsions. A quarter of all bromine used finds its way down into boreholes in oilfields, where calcium and zinc bromide solutions are used as drilling fluids. In high concentrations, the liquids are heavy and exert a high hydrostatic pressure that prevents the very disturbing “blow-out” situations.

50.4.4
Iodine

Iodine has different medical uses. The antiseptic tincture of iodine (3% iodine and 2.5% potassium iodide in alcohol) has been known since 1828. PVPI is a modern disinfectant with 1–3% iodine, bound in a complex way to polyvinylpyrrolidone. It is applied to the skin before surgical operations. Iodine is used as an alternative to chlorine for disinfection of drinking water. Even in such small concentrations as 1 ppm, iodine has a positive effect and is without the negative secondary effects characteristic of chlorine.

In industry iodine is utilized as a catalyst for several organic chemical processes, such as for instance the production of acetic acid and rubber, both butadiene and isoprene.

The iodine atom has a pronounced ability to scatter X-ray radiation, and soluble iodine compounds are utilized as X-ray contrast media.

A very special lithium battery has iodine as anode material. The battery is used for the running of pacemakers (Chapter 12 Lithium).

Small additions of iodine and bromine are used in halogen lamps. The bulbs are small and made of quartz. Vaporized tungsten from the filament forms tungsten iodide/bromide with the gas and this compound reacts with the filament and redeposit tungsten on it. In these types of lamps the filament can have a much higher temperature than in conventional incandescent lamps, 3200 K compared to 2700 K.

50.5
Halogens and Health

50.5.1
Fluorine – Skeleton and Teeth

Fluoride ions are found everywhere in nature. The content of fluorine in groundwater depends on which minerals and rocks the water is in contact with. In spring water there may be 0.1–40 mg of fluorine per liter. In the oceans the content is 1 mg/l.

Fluorine is one of the vital elements. Its content in skeleton and teeth is especially high, and the element is important for the durability of dental enamel. In regions with high fluorine content in the drinking water, the incidence of dental caries is low. This is the reason for the regular rinsing of teeth with water, containing sodium fluoride, especially for people living in a region with a low content of fluorine in the drinking water. Toothpaste may be enriched in fluorine for a similar reason.

The historical background to knowledge about teeth and fluorine is described in the *New York State Dental Journal*, 1964, **30**, p. 373:

> The dental caries–fluorine relationship probably begins with the discovery of fluorine in a fossilized elephant tooth by Morichini in 1803. In 1874, Erhardt suggested the systemic use of fluoride (as potassium fluoride) by children and women during pregnancy to harden enamel and protect teeth against caries. Crighton-Browne (1892) in England postulated that a deficiency of fluorine, caused by the refinement of wheat for bread making, was responsible for an increase in dental caries in that country. Several years later, Hempel and Schaffler (1899) reported a greater concentration of fluorine in sound than in carious teeth.

50.5.2
Chlorine – Vital Yet Highly Dangerous

Chlorine is one of our most essential elements. In spite of that, it has become the target of serious criticism and is looked upon as one of the most harmful among the elements. Both opinions are true.

Perhaps it was in seawater with its chloride milieu that life began. The element is present in considerable concentrations as sodium chloride in all cells and body fluids. Even though it does not take part directly in many biochemical reactions, it is important for ionic balance, as it provides the negative charges that neutralize the positive metal cations.

On the contrary, elemental chlorine is dangerous – so toxic that it was used for gaseous warfare in World War I. Also, in times of peace, chlorine has found dangerous applications as chlorinated hydrocarbons. *DDT* (Figure 50.3) is dichlorodiphenyltrichloroethane, thus a diphenylethane in which five hydrogen atoms are replaced by chlorine. In 1962 *Rachel Carson* (1907–1964) in the USA published her book *Silent Spring*. Farmers had an effective means to combat noxious insects, but the chemicals also poisoned birds. When dead birds and non-hatched eggs were analyzed, it was found that they contained DDT and mercury. Rachel Carson was extremely disturbed by and fearful of the profligate use of synthetic chemical pesticides, and decided to warn the public about the long-term effects of misusing them. The "silent spring" alluded to a world in which all the songbirds have been poisoned. In her book she challenged agricultural scientists and governments to protect human health and the environment.

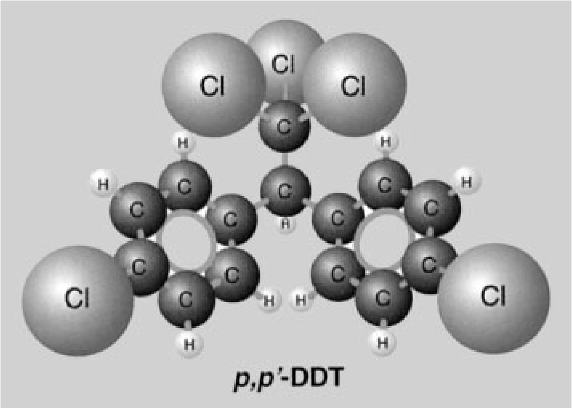

Figure 50.3 The insecticide DDT. (Reprinted from ref. [50.6], with permission.)

Although DDT was first prepared in 1873, its effectiveness as an insecticide was not discovered until 1939, by Paul Müller in Switzerland. The effectiveness of DDT against mosquitoes and lice, spreading malaria and typhus, and its ability to protect crops as well, made the insecticide appreciated. In all the justified criticism against DDT, it should be remembered that the World Health Organization estimated that, during the period of its use, approximately 25 million lives were saved. Paul Müller was also awarded the Nobel Prize for medicine and physiology in 1948. The substance however has a fatal characteristic in common with other chlorinated hydrocarbons, namely its fat solubility. DDT is also a stable substance and stays in the food chain. It is metabolized very slowly by animals and is stored in the fatty tissues.

Polychlorinated biphenyl (PCB) (Figure 50.4) is another chlorinated hydrocarbon, but one that is not used at all as an insecticide. Instead, the substance was utilized in electrical condensers and in transformers. Its insulating properties and durability at high temperatures were very much appreciated. Furthermore, it was used as an additive in PVC plastics, paints, copying papers and glues. During the chlorination, different biphenyls are formed, and many have been detected in commercial PCB samples.

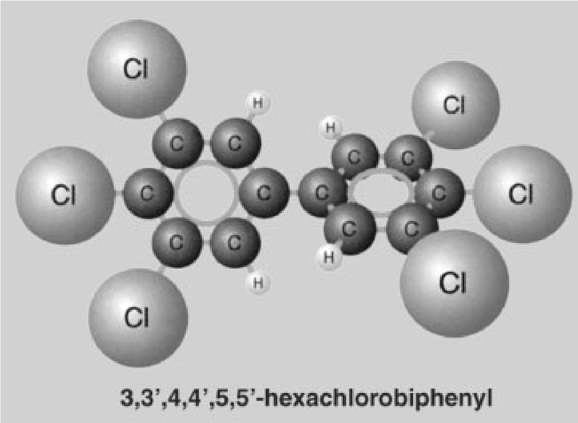

Figure 50.4 Hexachlorobiphenyl, a PCB. (Reprinted from ref. [50.6], with permission.)

There was no intention to spread PCBs in nature. Nevertheless, it was discovered, after many years' detective work, that harmful effects were being caused to white-tailed eagles and other birds due to residues of PCB distributed in the environment by waste disposal. Because of its high fat solubility, fish can absorb it, so that the PCB content can be 100 000 times higher in fish tissues than the PCB content in the surrounding water. This is the reason for its *bioaccumulation* and *biomagnification* in birds and fishes (Figure 50.5). Chlorinated hydrocarbons (represented by black dots in the figure) are slowly degrading substances and their concentrations eventually become far higher in the predator than in its prey.

Investigations with chromatography by Sören Jensen and his colleagues at the University of Stockholm resulted in this discovery. A report of theirs in *Nature* in 1969 about the very high PCB contents in birds and fish in the Baltic region caused scientists in many places to analyze samples from animals in different environments. They found PCBs almost everywhere.

Bleaching processes within the pulp industry earlier caused huge volumes of effluent of chlorinated hydrocarbons. Other substances for bleaching have changed the routines, which has led to a drastic reduction in the quantity of chlorine released to the environment. An important contributory factor to abandoning the old bleaching methods was the discovery that toxic *dioxins* (Figure 50.6) could be formed during chlorine bleaching.

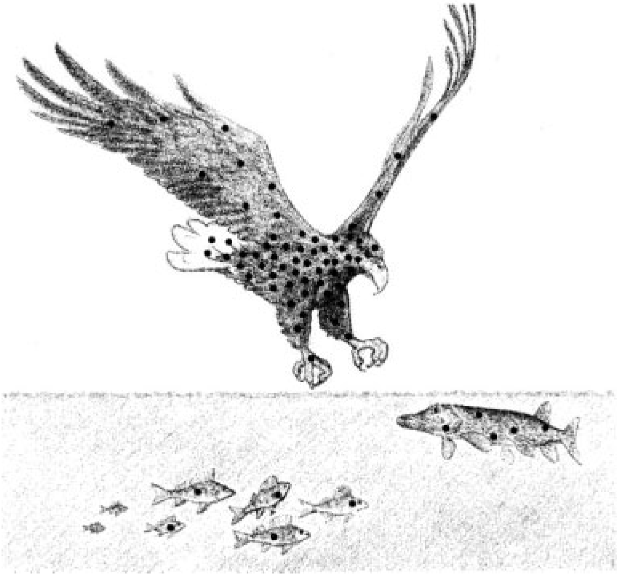

Figure 50.5 Biomagnification or concentration through a food chain – a drawing by Johan Wihlke. (Reprinted from ref. [50.6], with permission.)

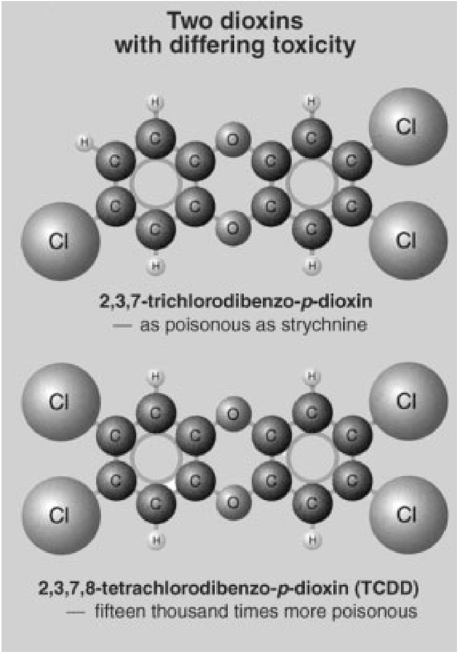

Figure 50.6 Two different polychlorinated dioxins, one as toxic as strychnine, the other 15 000 times more so. (Reprinted from ref. [50.6], with permission.)

Dioxins have never been produced intentionally by mankind (other than for research purposes). However, they may be formed in the burning of chlorine-containing components, especially if the burning occurs at low temperature. Incineration of products containing chlorine is for that reason the largest source of dioxins in modern society.

50.5.3

Bromine – Medicines and Drugs

Bromine became well known as a depressant some years after the discovery of the element. "Take bromine to calm down" became a saying in the 19th century – not bromine itself, but potassium bromide. Bromine medicines inhibit cerebral processes and were earlier used also for the treatment of epilepsy. The side-effects however are serious, and the conventional bromine compounds are no longer used. Bromides are still used in the synthesis of some modern drugs.

50.5.4

Iodine – Thyroid Gland

Essential trace elements with their functions in enzymes and hormones are distributed in different parts of the body. Iodine is special. Some 75% of the total iodine content in the human body (about 14 mg) is found in the thyroid gland, a small organ in the neck. There, it participates in the formation of the important thyroid hormone, *thyroxine*. This is vital for normal mental and physical development and for regulating the body's metabolism. A recommended daily intake is 100–200 µg. Deficiency of iodine will cause goitre. This has to be treated by additional potassium iodide or iodine casein. In developed countries, iodine deficiencies are now rare because iodine is added to table salt.

Radioactive iodine isotopes are spread as a result of nuclear power plant disasters. Especially important is ^{131}I with a half-life of eight days. When this iodine isotope is taken up by the thyroid gland, it causes cancer. People living and working near a nuclear power station are therefore recommended to have iodine tablets available and to use them in an emergency situation. The tablet's content of normal iodine is taken up by the thyroid gland and saturates it. This blocks the uptake of radioactive iodine. After the Chernobyl catastrophe, the intake of dairy products enriched with iodine is of particular importance for the population of Ukraine's western regions.

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51
Noble Gases

The noble gases are helium, neon, argon, krypton, xenon and radon. The first five are described in this chapter. The radioactive element radon is treated in Chapter 52 Radioactive Elements.

The elements have a full outer electron shell (containing two electrons for helium, and eight for the others), and they do not easily form chemical compounds. The noble gases were previously referred to as the “inert gases”. However, the heavier atoms, lower down in the series, are a little more reactive, and xenon forms compounds with fluorine and oxygen.

51.1 He
Facts about Helium

51.1.1 He
The Element

Symbol:	He
Atomic number:	2
Atomic weight:	4.003
Ground state electron configuration:	$1s^2$
Crystal structure:	Cubic fcc with $a = 4.24$ Å

Encyclopedia of the Elements. Per Enghag

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51.1.2 He
Discovery and Occurrence

Discovery: The French astronomer P. J. C. Janssen found a yellow line in the solar spectrum in 1868. As it did not belong to sodium, hydrogen or any other known element, a new element had been discovered. It was named *helium* due to its origin in the sun. In 1895 Ramsay in England as well as Cleve and Langlet in Sweden discovered helium in the mineral cleveite, a uraninite with high content of rare earth metals.

Important raw materials: Helium is the second most abundant element in the universe after hydrogen. The earth's atmosphere however contains only about 5 ppm by volume. Natural gas, with an average of 0.4% helium, is the major commercial source of helium in the USA. Its origin is traced to the decay of radioactive elements in rocks.

Ranking in order of abundance in earth crust:	72
Mean content in earth crust:	0.008 ppm (g/tonne)
Mean content in oceans:	$7 \cdot 10^{-6}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

51.1.3 He
Chemical Characterization

Helium is an inert, colorless and odorless noble gas. As it is non-combustible, helium is preferred to hydrogen as the lifting gas in military and meteorological balloons and blimps. Helium is also used as a pressure gas to force liquid hydrogen into rocket engines. Helium is ideal for this purpose because it remains a gas even at the low temperature of liquid hydrogen. A more ordinary use is as an inert gas in arc welding. Helium protects heated parts such as aluminum and titanium from attack by air. Quite another application is the mixture of helium and oxygen as a breathing gas for deep-sea diving. Due to its low density it streams easily through the lungs. Unlike nitrogen, helium is not dissolved in the blood plasma, so "the bends" are avoided on ascent.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
–	$He(g) \rightarrow He^+(g) + e^-$	2372	$He(g) + e^- \rightarrow He^-(g)$
	$He^+(g) \rightarrow He^{2+}(g) + e^-$	5251	–

Standard reduction potential: –

Electronegativity (Pauling): –

Radii of atoms and ions:	Atomic:	–
(WebElements™)	Covalent:	32 pm
	Van de Waals	140 pm
	No ionic radii are known for helium	

51.1.4 He
Physical Properties

Density (at 273 K)	**Relative density (air = 1)**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
0.1785 kg m^{-3} 0.179 g/l	0.137	0.95 K –272.2 °C	4.22 K –268.93 °C	5193 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

73 K	**173 K**	**273 K**	**373 K**	**1273 K**
0.0595	0.1045	0.1422	0.1777	0.419

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K)

a	**b**	**c**
20.786	0	0

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.66

Solubility in water m^3 gas at STP per m^3 water

273 K	**293 K**	**303 K**	**333 K**	**353 K**	**373 K**
0.0098	0.0086	0.0084	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K $-5.9 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Diamagnetic (as susceptibility is negative)

Critical point:
T_c 5.2 K
P_c 0.229 MPa

51.1.5 He
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	0.021 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	0.083 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	0 $kJmol^{-1}$
Entropy S^0 at 298 K	126.15 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
20.786	20.786	20.786	20.786	20.786	20.786

51.1.6 He

Nuclear Properties and X-ray

Isotope range, natural and artificial 3–10

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{3}He	Stable	0.0001	1/2+	–2.128
^{4}He	Stable	99.9999	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{3}He
Reference compound	He-gas
Frequency MHz (^{1}H = 100 MHz)	76.179
Receptivity D^{P} relative to ^{1}H = 1.00	$6.06 \cdot 10^{-7}$
Receptivity D^{C} relative to ^{13}C = 1.00	$3.56 \cdot 10^{-3}$
Magnetogyric ratio, radT^{-1}s^{-1}	$-20.380 \cdot 10^{7}$
Nuclear quadropole moment, barn	–

Characteristic X-radiation

Z	Element	Kα_2 keV
–	–	–
–	–	–

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	0.292
17.37 keV (MoKα_2)	0.202

Neutron absorption **Thermal neutron capture cross section** 0.007 barns

51.1 Ne
Facts about Neon

51.1.1 Ne
The Element

Symbol:	Ne
Atomic number:	10
Atomic weight:	20.18
Ground state electron configuration:	$[He]2s^2 2p^6$
Crystal structure:	Cubic fcc with $a = 4.43$ Å.

51.1.2 Ne
Discovery and Occurrence

Discovery: Shortly after their discovery of the element krypton in 1898, William Ramsay and Morris M. Travers in England also found neon. Its name has the meaning "new" after the Greek *neos*.

Important raw materials: Liquid air. Neon is, after argon, the most abundant noble gas in the earth's atmosphere. Its content is 18 ppm by volume.

Ranking in order of abundance in earth crust:	73–74
Mean content in earth crust:	0.005 ppm (g/tonne)
Mean content in oceans:	$1.2 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

51.1.3 Ne

Chemical Characterization

Neon is a colorless, odorless noble gas. In a vacuum discharge tube, neon glows reddish orange. Of all the rare gases, the discharge of neon is the most intense at ordinary voltages and currents. The term “neon light” is often incorrectly applied to discharge tubes filled with gases other than neon. Liquid neon is used as a cryogenic refrigerant.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
–	$Ne(g) \rightarrow Ne^+(g) + e^-$	2081	$Ne(g) + e^- \rightarrow Ne^-(g)$
	$Ne^+(g) \rightarrow Ne^{2+}(g) + e^-$	3952	–
	$Ne^{2+}(g) \rightarrow Ne^{3+}(g) + e^-$	6122	
	$Ne^{3+}(g) \rightarrow Ne^{4+}(g) + e^-$	9371	

Standard reduction potential: –

Electronegativity (Pauling): –

Radii of atoms and ions:	Atomic:	–
(WebElements™)	Covalent:	69 pm
	Van de Waals	154 pm
	No ionic radii are known for neon	

51.1.4 Ne
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
0.9002 kg m^{-3} 0.900 g/l	0.70	24.48 K –248.67 °C	27.10 K –246.05 °C	1030 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

73 K	173 K	273 K	373 K	1273 K
0.0174	0.0337	0.0465	0.0566	0.128

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K)

a	b	c
20.786	0	0

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.64

Solubility in water m^3 gas at STP per m^3 water

273 K	293 K	313 K	333 K	353 K	373 K
0.014	0.010	–	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-4.2 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)
Critical point:	T_c 44.4 K P_c 2.72 MPa

51.1.5 Ne
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	0.34 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	1.75 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	0 $kJmol^{-1}$
Entropy S^0 at 298 K	146.33 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
20.786	20.786	20.786	20.786	20.786	20.786

51.1.6 Ne
Nuclear Properties and X-ray

Isotope range, natural and artificial 16–29

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{20}Ne	Stable	90.48	0+	–
^{21}Ne	Stable	0.27	3/2+	−0.6618
^{22}Ne	Stable	9.25	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{21}Ne
Reference compound	Ne-gas
Frequency MHz (^{1}H = 100 MHz)	7.894
Receptivity D^P relative to ^{1}H = 1.00	$6.65 \cdot 10^{-6}$
Receptivity D^C relative to ^{13}C = 1.00	0.039
Magnetogyric ratio, radT^{-1}s^{-1}	$-2.113 \cdot 10^7$
Nuclear quadropole moment, barn	0.10

Characteristic X-radiation

Z	Element	Kα_2 keV
9	F	0.677
10	Ne	0.848
11	Na	1.041

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	23.0
17.37 keV (MoKα_2)	2.37

Neutron absorption **Thermal neutron capture cross section** 0.040 barns

51.1 Ar
Facts about Argon

51.1.1 Ar
The Element

Symbol:	Ar
Atomic number:	18
Atomic weight:	39.95
Ground state electron configuration:	$[Ne]3s^23p^6$
Crystal structure:	Cubic fcc with $a = 5.26$ Å

51.1.2 Ar
Discovery and Occurrence

Discovery: Lord Rayleigh and Sir William Ramsay removed nitrogen and oxygen from air. On examination of the gas residue in a spectroscope, they observed, in 1894, red and green lines from an element never seen before. They named it argon after the Greek word *argos*, meaning tardy or idle.

Important raw materials: Liquid air. Argon is the third most abundant gas, with a content of 0.93% (by volume), in the earth's atmosphere.

Ranking in order of abundance in earth crust:	43–44
Mean content in earth crust:	3.5 ppm (g/tonne)
Mean content in oceans:	0.45 ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

51.1.3 Ar
Chemical Characterization

Argon is an inert, colorless and odorless noble gas. It is used to fill electric light bulbs in order to prevent the evaporation of tungsten in the filament at the high temperature of operation. Argon is also used to protect metals from oxidation in arc welding and heat treatment of alloys.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
–	$Ar(g) \rightarrow Ar^+(g) + e^-$	1521	$Ar(g) + e^- \rightarrow Ar^-(g)$
	$Ar^+(g) \rightarrow Ar^{2+}(g) + e^-$	2666	–
	$Ar^{2+}(g) \rightarrow Ar^{3+}(g) + e^-$	3931	
	$Ar^{3+}(g) \rightarrow Ar^{4+}(g) + e^-$	5771	

Standard reduction potential: –

Electronegativity (Pauling): –

Radii of atoms and ions:	Atomic:	–
(WebElements™)	Covalent:	97 pm
	Van de Waals	188 pm
	No ionic radii are known for argon	

51.1.4 Ar
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
1.784 kg m^{-3} 1.78 g/l	1.38	84.0 K –189.2 °C	87.3 K –185.9 °C	520 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

73 K	173 K	273 K	373 K	1273 K
–	0.0109	0.0163	0.0212	0.05

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K)

a	b	c
20.786	0	0

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.667

Solubility in water m^3 gas at STP per m^3 water

273 K	293 K	313 K	333 K	353 K	373 K
0.0537	0.0340	0.0251	0.0206	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-6.16 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)
Critical point:	T_c 150.8 K P_c 4.86 MPa

51.1.5 Ar
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	1.19 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	6.51 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	0 kJmol^{-1}
Entropy S^0 at 298 K	154.84 J$K^{-1}$$mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	20.786	20.786	20.786	20.786	20.786	20.786

51.1.6 Ar

Nuclear Properties and X-ray

Isotope range, natural and artificial 30–47

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{36}Ar	Stable	0.337	0+	–
^{38}Ar	Stable	0.063	0+	–
^{40}Ar	Stable	99.60	0+	–

Characteristic X-radiation

Z	Element	Kα_2 keV
17	Cl	2.620
18	Ar	2.956
19	K	3.311

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	117
17.37 keV (MoKα_2)	13.0

Neutron absorption **Thermal neutron capture cross section** 0.65 barns

51.1 Kr
Facts about Krypton

51.1.1 Kr
The Element

Symbol:	Kr
Atomic number:	36
Atomic weight:	83.80
Ground state electron configuration:	$[Ar]3d^{10}4s^24p^6$
Crystal structure:	Cubic fcc with a = 5.71 Å

51.1.2 Kr
Discovery and Occurrence

Discovery: William Ramsay and Morris W. Travers in England discovered krypton in 1898 while studying liquefied air. They looked for an element between helium and argon, with an expected atomic weight about 20. In fact they found a hidden gas (hidden = *kryptos* in Greek). On examination they got the atomic weight 84. They had found a new element but not the one that they had searched for.

Important raw materials: Liquid air. Krypton is present in the atmosphere to a small extent, 1.14 ppm by volume.

Ranking in order of abundance in earth crust:	82
Mean content in earth crust:	$1 \cdot 10^{-4}$ ppm (g/tonne)
Mean content in oceans:	$2.1 \cdot 10^{-4}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

51.1.3 Kr
Chemical Characterization

Krypton is a colorless and odorless noble gas. It is characterized by its brilliant green and orange-red spectral lines and is used, together with argon and other noble gases, in electric discharge tubes and in incandescent bulbs. Krypton is also used in certain photographic flash lamps for high-speed photography. Between 1960 and 1983 the length of the meter was defined in terms of the orange-red spectral line of the krypton–86 isotope. From 1983 the meter has been defined as the distance the light from a helium–neon laser passes in specified time.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Kr^{II} as in KrF_2	$Kr(g) \rightarrow Kr^+(g) + e^-$	1351	$Kr(g) + e^- \rightarrow Kr^-(g)$
	$Kr^+(g) \rightarrow Kr^{2+}(g) + e^-$	2350	–
	$Kr^{2+}(g) \rightarrow Kr^{3+}(g) + e^-$	3565	
	$Kr^{3+}(g) \rightarrow Kr^{4+}(g) + e^-$	5070	

Standard reduction potential: –

Electronegativity (Pauling): 3.00

Radii of atoms and ions:	Atomic:	–
(WebElements™)	Covalent:	110 pm
	Van de Waals	202 pm
	No ionic radii are known for krypton	

51.1.4 Kr
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
3.735 kg m^{-3} 3.74 g/l	2.89	116.6 K –156.6 °C	120.9 K –152.3 °C	248 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$ 73 K	173 K	273 K	373 K	1273 K
–	0.0057	0.0087	0.0115	0.029

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K) a	b	c
20.786	0	0

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.68

Solubility in water m^3 gas at STP per m^3 water 273 K	293 K	303 K	333 K	353 K	373 K
0.099	0.059	0.049	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K $-4.32 \cdot 10^{-9}$ m^3 kg^{-1}

Magnetic characterization Diamagnetic (as susceptibility is negative)

Critical point: T_c 209.2 K
P_c 5.50 MPa

51.1.5 Kr
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p. 1.64 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p. 9.03 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K 0 $kJmol^{-1}$
Entropy S^0 at 298 K 164.08 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$	100 K	298 K	600 K	1000 K	2000 K	2500 K
	31.6 (solid)	20.786 (gas)	20.786	20.786	20.786	20.786

51.1.6 Kr
Nuclear Properties and X-ray

Isotope range, natural and artificial 71–95

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ
^{78}Kr	Stable	0.35	0+	–
^{80}Kr	Stable	2.25	0+	–
^{82}Kr	Stable	11.6	0+	–
^{83}Kr	Stable	11.5	9/2+	–0.9707
^{84}Kr	Stable	57.0	0+	–
^{86}Kr	Stable	17.3	0+	–

Nuclear magnetic resonance NMR (WebElements™)

Isotope	^{83}Kr
Reference compound	Kr-gas
Frequency MHz (^{1}H = 100 MHz)	3.85
Receptivity D^{P} relative to ^{1}H = 1.00	$2.19 \cdot 10^{-4}$
Receptivity D^{C} relative to ^{13}C = 1.00	1.25
Magnetogyric ratio, radT^{-1}s^{-1}	$-1.033 \cdot 10^{7}$
Nuclear quadropole moment, barn	0.25

Characteristic X-radiation

Z	Element	Kα_2 keV
35	Br	11.878
36	Kr	12.598
37	Rb	13.336

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	95.6
17.37 keV (MoKα_2)	80.2

Neutron absorption **Thermal neutron capture cross section** 24 barns

51.1 Xe
Facts about Xenon

51.1.1 Xe
The Element

Symbol: Xe
Atomic number: 54
Atomic weight: 131.29
Ground state electron configuration: $[Kr]4d^{10}5s^25p^6$
Crystal structure: Cubic fcc with $a = 6.20$ Å

51.1.2 Xe
Eiscovery and Occurrence

Discovery: William Ramsay and Morris W. Travers in England discovered xenon in 1898. They extracted krypton from liquid air, and on fractional distillation of this gas they found a new element, heavier than krypton. Its blue glow and characteristic spectrum identified it. It was named xenon, *the stranger*.

Important raw materials: Liquid air. Xenon is present in the atmosphere to a small extent, 0.086 ppm by volume.

Ranking in order of abundance in earth crust: 83

Mean content in earth crust: $3 \cdot 10^{-5}$ ppm (g/tonne)
Mean content in oceans: $5 \cdot 10^{-5}$ ppm (g/tonne)
Residence time in oceans: –
Mean content in an adult human body: –
Content in a man's body (weight 70 kg): –

51.1.3 Xe

Chemical Characterization

Xenon is a noble gas without color and odor. Since 1962 several compounds, especially fluorides, have been prepared, although xenon, as a noble gas, ought to be completely inert. In fact the highly explosive xenon trioxide, XeO_3, is known. In modern cars high-intensity discharge lighting is more and more used. The tubes contain xenon and small amounts of other noble gases. As the headlamps have no tungsten filaments they run at lower temperatures and use less electrical energy than traditional halogen lamps.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Xe^{II} as in XeF_2	$Xe(g) \rightarrow Xe^+(g) + e^-$	1170	$Xe(g) + e^- \rightarrow Xe^-(g)$
Xe^{IV} as in XeF_4	$Xe^+(g) \rightarrow Xe^{2+}(g) + e^-$	2046	–
Xe^{VI} as in XeF_6 and XeO_3	$Xe^{2+}(g) \rightarrow Xe^{3+}(g) + e^-$	3099	
Xe^{VIII} as in XeO_4 and XeO_3F_2			

Standard reduction potential:	$XeF_2(s) + 2e^- \rightarrow Xe(g) + 2F^-$	$E^0 = +2.32$ V
	$XeO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Xe(g) + 3H_2O(l)$	$E^0 = +2.12$ V
Electronegativity (Pauling):	2.6	
Radii of atoms and ions:	Atomic:	–
	Covalent:	130 pm
	Van der Waals	216 pm
	Xe^{8+} (4-coordinate, tetrahedral):	54 pm
	Xe^{8+} (6-coordinate, octahedral):	62 pm

51.1.4 Xe
Physical Properties

Density (at 273 K)	Relative density (air = 1)	Melting point	Boiling point	Specific heat c_p at 298 K
5.887 kg m^{-3} 5.89 g/l	4.53	161.3 K –111.9 °C	166.1 K –107.1 °C	158 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

73 K	173 K	273 K	373 K	1273 K
–	0.0034	0.0052	0.007	0.019

Heat capacity coefficients in $C_p = a + bT + cT^{-2}$ (valid 298–2000 K)

a	b	c
20.786	0	0

Ratio C_p/C_v (ideal gas = 5/3 = 1.667) 1.666

Solubility in water m^3 gas at STP per m^3 water

273 K	293 K	303 K	333 K	353 K	373 K
0.203	0.108	0.085	–	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$-4.20 \cdot 10^{-9}$ m^3 kg^{-1}
Magnetic characterization	Diamagnetic (as susceptibility is negative)
Critical point:	T_c 289.7 K P_c 5.84 MPa

51.1.5 Xe
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	2.30 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	12.64 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	0 $kJmol^{-1}$
Entropy S^0 at 298 K	169.68 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	298 K	600 K	1000 K	2000 K	2500 K
	28.2 (solid)	20.786 (gas)	20.786	20.786	20.786	20.786

51.1.6 Xe

Nuclear Properties and X-ray

Isotope range, natural and artificial 110–145

Naturally occurring isotopes

Nuclide	Type	Abundance %	Nuclear spin	Magnetic moment μ	Half-life	Decay mode	Decay energy Q
^{126}Xe	Stable	0.09	0+	–	–	–	–
^{128}Xe	Stable	1.91	0+	–	–	–	–
^{129}Xe	Stable	26.4	1/2+	−0.7768	–	–	–
^{130}Xe	Stable	4.1	0+	–	–	–	–
^{131}Xe	Stable	21.2	3/2+	0.6919	–	–	–
^{132}Xe	Stable	26.9	0+	–	–	–	–
^{134}Xe	Stable	10.4	0+	–	–	–	–
^{124}Xe	Active	0.10	0+	–	$1.6 \cdot 10^{14}$ y	EC or β^+	–
^{136}Xe	Active	8.9	0+	–	$2.4 \cdot 10^{21}$ y	–	–

Nuclear magnetic resonance NMR

Isotope	^{129}Xe	^{131}Xe
Reference compound	$XeOF_4$+C_6D_6	
Frequency MHz (^{1}H = 100 MHz)	27.809	8.244
Receptivity D^P relative to ^{1}H = 1.00	$5.71 \cdot 10^{-3}$	$5.97 \cdot 10^{-4}$
Receptivity D^C relative to ^{13}C = 1.00	32.6	3.41
Magnetogyric ratio, radT^{-1}s^{-1}	$-7.452 \cdot 10^7$	$2.209 \cdot 10^7$
Nuclear quadropole moment, barn	−0.393	−0.114

Characteristic X-radiation

Z	Element	Kα_2 keV
53	I	28.317
54	Xe	29.459
55	Cs	30.625

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	301
17.37 keV (MoKα_2)	38.7

Neutron absorption **Thermal neutron capture cross section** 25 barns

51.2
The Discovery of Argon

51.2.1A
Hundred-Year-Long "Sleep"

At the beginning of the 1890s, the main outlines of the periodic table of the elements were formulated and well known. But gaps remained to be filled, and the elements awaiting discovery were certainly thought to be of metallic character. Chemists were convinced that the chemistry of the atmosphere was elucidated, and to search for new elements there was quite pointless. However, a one-hundred-year-old observation by Henry Cavendish had fallen into oblivion, otherwise they would certainly not have been so convinced.

Henry Cavendish (1731–1810), well known in the history of the discovery of the elements (see Chapter 9 Hydrogen) is also well known within geophysics for the *Cavendish experiment*. In this, he determined, with simple means, the average density of the earth to be 5.45 times that of water, an astoundingly good result compared to the value of today, 5.5268.

In 1785 he performed advanced experiments with electrical discharges in a mixture of oxygen and common air. Nitrogen was oxidized to nitrogen oxide, which was absorbed by lye (a strong alkaline solution), also present in the reaction vessel. The excess of oxygen became a residue. Cavendish found that the volume of this residue was too large. He thought that one part of the phlogiston-rich air (the nitrogen) had not been dephlogistated (oxidized). He estimated that the quantity of gas that behaved in this mysterious way amounted to 1/120, thus 0.83%, of the air volume in the experiment. Today we know that air contains 0.93% noble gases, mainly argon. Thus Cavendish had in fact observed gaseous strangers in air already in 1785. But, as mentioned above, his experiment was forgotten for many years.

51.2.2
The Awakening

Henry Cavendish's important achievements in science during the second half of the 18th century were recognized in the naming of the Cavendish Laboratory in Cambridge, one of the most famous scientific institutions in the world. Its founding was made possible by a donation in 1870 from William Cavendish, seventh Duke of Devonshire. In 1871 James Clerk Maxwell, known for the electromagnetic theory, became the first professor of experimental physics at Cambridge. When he died in 1879, Lord Rayleigh became his successor. He reawakened Henry Cavendish's observation from its hundred-year-long slumber and prepared the way for the discovery of the noble gases.

John William Strutt (1842–1919), the third *Baron Rayleigh* in the county of Essex, entered Trinity College, Cambridge, in October, 1861. He became professor of physics at Cambridge University and at the Royal Institution. His work was performed in the domains of acoustics, optics, electricity and thermodynamics. He is perhaps best known for *Rayleigh's formula*, dealing with light dispersion in the atmosphere. It gave for the first time an explanation of why the sky is blue. Physically it expresses the energy in the spectrum as a function of wavelength. This typical physicist also played a great role in the discovery of the element argon. Lord Rayleigh's interest in the physics of gases was stimulated by *Prout's hypothesis*1).

If Prout's hypothesis were correct, the density relation between oxygen and hydrogen could be expected to be exactly 16:1. In 1888 Rayleigh published results showing a ratio of 15.882:1. This result prepared for the coming discoveries of neutrons and isotopes. In his examination of nitrogen, Rayleigh found that there is a difference between "atmospheric" nitrogen (1) and "chemical" nitrogen (2):

- (1) nitrogen, prepared by removing of oxygen, carbon dioxide and moisture from air;
- (2) nitrogen, prepared by decomposition of ammonia and removal of hydrogen.

His experimental work was meticulous. He determined the weight of one liter of "atmospheric" nitrogen (1) to be 1.2572 g, while one liter of "chemical" nitrogen (2) weighed 1.2505 g. The density of (1) was thus 0.54% higher than that of (2). In corresponding investigations of oxygen gas, prepared in different ways, he always got the same density values. Had he made some mistakes in his experiments? He himself imagined four possibilities:

- The nitrogen he had prepared from air contains residues of oxygen.
- The nitrogen he had prepared from ammonia contains residues of hydrogen.
- The atmospheric nitrogen contains N_3 molecules, analogous to ozone O_3.
- Some of the nitrogen molecules had been split into atoms in the decomposition of ammonia, which would lead to a lower value of the gas density.

The different explanations were all eliminated by further experiments. But then, what was so special with the nitrogen? Was there an unknown gas as contamination? Lord Rayleigh had reawakened Cavendish's observation.

51.2.3
A Scotsman Intervenes

Sir William Ramsay (1852–1916) was a Scottish chemist and physicist. He studied in Glasgow, his native town, and in Tübingen and Heidelberg in Germany. On his return to Glasgow in 1872 he became a teacher of chemistry there. In 1880 he was appointed Principal and Professor of Chemistry at University College in Bristol, and moved on in 1887 to the Chair of Inorganic Chemistry at University College, London, a post that he held until his retirement in 1913. He carried on research within the

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1) *William Prout* (1785–1850), English physician and chemist, formulated in 1815 the hypothesis that the atomic weights of all elements are integral multiples of that of hydrogen. Thus hydrogen should be the primary substance of which all matter is built. The hypothesis does not square with experimental results, mainly because the atoms of almost all elements are mixtures of isotopes with different atomic weights.

field of gaseous chemistry and physics, and was recognized as very clever in handling small gas volumes. As early as 1885–1890 he published several notable papers on the oxides of nitrogen.

Ramsay was informed about Lord Rayleigh's problems with nitrogen density and cooperation was established. Different experiments were carried out in order to isolate the stranger in the atmosphere.

- A strong electrical spark discharge was sent through a mixture of air and oxygen. Potassium hydroxide was present in the reaction vessel. Nitrogen oxides were formed and absorbed in the hydroxide solution. The discharge continued until the gas volume (oxygen plus unknown gas) became constant. The oxygen was then absorbed in potassium pyrogallate. The gaseous residue had to be the gas searched for, or at least a gas mixture enriched in the unknown gas.
- Air was led over white-hot copper, a process in which oxygen was removed from the air. Nitrogen was removed from the gas residue by hot magnesium, binding nitrogen as magnesium nitride Mg_3N_2. The gas residue ought to contain the unknown gas, pure or highly enriched.

On examination of the gas residues in a spectroscope, indications of oxygen and nitrogen were of course found, but above all groups of red and green lines, never before observed in a gas spectrum. *Sir William Crookes* (1832–1919), professor at the Royal College of Chemistry and a pioneer in spectroscopy, was contacted in order to get a more extensive examination. He observed almost two hundred lines. Could that bear witness to a new element?

51.2.4
Assiduous Scientists and an Idle Element

Rayleigh and Ramsay worked in their separate laboratories but communicated their results almost daily. During May–August, 1894, they agreed that they had in fact discovered and isolated a new gaseous element, although in a very small quantity. They decided to announce their discovery at the August, 1894, meeting of the British Association. The new element was named *argon* after the Greek word αργος (*argos*) meaning "tardy or idle". In the name the most characteristic property of the new element was expressed, its unreadiness to react. One hundred years later this property became very much appreciated when the element was utilized as a protection gas during welding and heat treatment processes.

News of the discovery of a gaseous element, not previously known, came like a bombshell in the scientific world. After 1870 several elements had been discovered, the existence of which had been anticipated by Mendeleev in his periodic system. The discovery of argon was not facilitated by an empty place in the periodic table, waiting to be filled in. Instead, scientists of the day were bold enough to foresee a quite new group, the noble gas group, in the periodic table. The periodic system contains, as is well known, six finished periods. In a modified system, a noble gas element ought to finish *every* period. One was known, argon, but six could be expected. During the short time until the start of the 1900s, the remaining five elements, helium, neon, krypton, xenon and radon, were discovered.

51.3
The Discovery of the Other Noble Gases

51.3.1
Helium

51.3.1.1 In the Sun

As mentioned, argon was the first noble gas to be discovered, but helium was in fact known 26 years before the discovery of argon. The French astronomer *Pierre J. C. Janssen* (1824–1907) studied a total solar eclipse in India in 1868. A yellow line D_3, not coincident with sodium's doublet, was observed. Neither did the line emanate from hydrogen or any other known element, as was proved by the British astronomer *Sir Norman Lockyer* (1836–1920). Thus there was an element in the sun that was not known on earth. It was named *helium* due to its origin in the sun. Many spectrum analysts did not accept the new solar element. However, in 1876, *John W. Draper*, the first president of the American Chemical Society, made an inspired statement [51.1]:

> And now, while we have accomplished only a most imperfect examination of objects that we find on the earth, see how, on a sudden, through the vista that has been opened by the spectroscope, what a prospect lies beyond us in the heavens! I often look at the bright yellow ray emitted from the chromosphere of the sun, by that unknown element, Helium. As the astronomers have ventured to call it. It seems trembling with excitement to tell its story, and how many unseen companions it has. And if this be the case with the sun, what shall we say of the magnificent hosts of the stars? May not every one of them have special elements of its own? Is not each a chemical laboratory in itself?

51.3.1.2 On Earth

About 1890 the American mineralogist and chemist W. F. Hildebrand observed that, when the mineral *uraninite* (pitchblende) was dissolved in acid, an inert gas was given off. He thought it was nitrogen. Ramsay read the report about that and called Hildebrand's conclusion into question. He repeated the experiment in 1895 but used the mineral *cleveite*. It is a uraninite with a high content of rare earth metals. On acid treatment an inert gas was set free, which was found to be a mixture of nitrogen, argon and an unknown gas. In his own, not too advanced, spectroscope, Ramsay examined the gas mixture and observed unknown lines. For a more careful analysis, he again made contact with Sir William Crookes and gave him a sample. The two Sir Williams had found the solar element helium on earth. A summary of the investigation is found in a letter that Ramsay sent to his wife, Lady Ramsay, on March 24, 1895 [51.2]:

> Let's take the biggest piece of news first. I bottled the new gas in a vacuum tube, and arranged so that I could see its spectrum and that of argon in the same spectroscope at the same time. There is argon in the gas; but there was a magnificent yellow line, brilliantly bright, not coincident with, but very close to the sodium yellow line. I was puzzled but began to smell a rat. I told Crookes, and on Saturday morning when Harley, Shields, and I were looking at the spectrum in the darkroom, a telegram came from Crookes. He had sent a copy here and I enclose that copy. You may wonder what it means. Helium is a name given to a line in the solar spectrum, known to belong to an element, but that element has hitherto been unknown on the earth … 587.49 is the wave-length of the brilliant line. It is quite overwhelming and beats argon. I telegraphed to Berthelot at once yesterday: Gas obtained by me cleveite mixture argon helium. Crookes identifies spectrum …

This was the most important part of his letter to his wife. What followed after this? The history of science is silent on that point.

> In Sweden the eagerness to find new elements had not been reduced. A. E. Nordenskiöld (1832–1901), born in Finland, and known for the discovery of the North-East Passage, was in exile in Sweden from 1857 after a struggle with the Russian authorities in his homeland. In Stockholm, at the age of 26, he became the superintendent of the Mineralogical Department of the Swedish Royal Museum. Nordenskiöld held the office until his death. He found the uranium mineral cleveite, mentioned above, and named it in honor of Professor P. T. Cleve, the discoverer in 1878 of the rare earth element holmium.

At the same time as Ramsay worked with cleveite in England, a young scientist, Nils Abraham Langlet (1868–1936), in Cleve's department at the University of Uppsala, examined the same mineral. He isolated, like Ramsay, the unknown gas helium in the mineral. He showed, at age 27, that it is monatomic and determined its atomic weight with great precision. Both Ramsay/Crookes and Cleve/Langlet have the credit for the discovery of helium in 1895.

In the pioneering work with noble gases, Rayleigh and Ramsay had very good support from William Crookes and his knowledge of and equipment for spectral analysis. Cleve and Langlet were in a similar situation. In Uppsala *Robert Thalén* (1827–1895) had succeeded Anders Ångström (Chapter 10 Blowpipe and Spectroscope) as professor of physics and he continued his fundamental investigations on spectroscopy.

51.3.2
Krypton

The two noble gases known from 1895 had the atomic weights 4 (He) and 40 (Ar). Ramsay concluded that there should exist a gas in between, with an atomic weight about 20. He now cooperated with Morris William Travers (1872–1961), 20 years younger than himself, and an authority on glass technology. The two scientists started a project in order to find that element.

They obtained a large quantity of liquid air and subjected it to fractional distillation to remove the bulk of the nitrogen and oxygen. From the residue, hot copper and magnesium removed the traces of oxygen and nitrogen. Spectral analysis of the least volatile fraction revealed the presence of a new element. It showed one yellow and one brilliant green line, which did not coincide with the lines in the spectra of helium, argon or any other known element. They discovered this element on May 30, 1898, and named it *krypton* after the Greek word meaning "hidden". They had found a new noble gas but not the element for which they were searching – not lighter but heavier than argon. When they determined its density and calculated the atomic weight, they were astonished. It had the value 84 and not about 20 as they had been expecting.

51.3.3
Neon

The lighter gas they had searched for had certainly been vaporized together with oxygen/nitrogen in the first part of their experiment (see Table 51.1). They were aware of that and planned a new investigation. In this, they placed a vessel, containing liquid argon, in liquid air, reduced the pressure and let argon vaporize. The first fraction was saved. There the elusive gas, the gas with an atomic weight of about 20, ought to be present. They passed an electrical arc through this fraction, in order to make a spectral analysis of it. The gas in the test tube shone with a beautiful crimson-red color. It was a sight they would never forget. They were fascinated and thought that they had received good remuneration for all their hard work. In our present time we do not go into ecstasies over red neon tubes. But it is something quite different to make the discovery and see the phenomenon for the very first time.

Eventually they forced themselves to examine the spectrum of the new element. They observed many characteristic lines in the visible wavelength region. A new gas had been discovered. A name? Ramsay asked his thirteen-year-old son for a proposal. He answered promptly: *novum* because it is new. The proposal fell onto fertile ground, but the name was changed to *neon*, also meaning "new" but more adapted to the names argon and krypton. The discovery was made in June, 1898. They were satisfied with its atomic weight – the value was 20.

51.3.4
Xenon

With the discoveries made up to mid-1898, the group of noble gases was complete for periods 1–4. Helium finished period 1, in which hydrogen had been alone. Periods 2–4 had got their own right-hand ends with the element pairs *fluorine–neon*, *chlorine–argon* and *bromine–krypton*. However, in period 5 iodine stood alone as the right termination. So it was reasonable to search for and find a noble gas even there. For their further research Ramsay and Travers needed larger and larger volumes of the already known gases. When they got access to equipment for liquefying huge quantities of air, they could produce large quantities of liquid krypton. In July, 1898, only one month after the discovery of neon, they discovered a new noble gas, a heavier one. They named it *xenon*, the stranger. This element was also found to have a characteristic spectrum.

The year of the xenon discovery, 1898, also was the year in which radium was discovered in Paris by Marie and Pierre Curie. The last noble gas, radon, could be detected in the atmosphere around the new radioactive element. It is treated in Chapter 52 Radioactive Elements.

51.3.5
Nobel Prizes for the Discoverers

The achievement of finding a quite new group of elements was impressive. The Nobel Foundation also thought so, and in 1904 awarded the Nobel prize for physics to Lord Rayleigh and that for chemistry to Sir William Ramsay.

51.4
Manufacture of the Noble Gases

51.4.1
Helium From Natural Gas

Helium is the most common element in the universe, next to hydrogen. On earth, however, it is rare, but it is present at a level of 5 ppm in the atmosphere. Owing to the production of α-radiation by radioactive decay in the earth's crust, helium is continuously produced there, and this can give rise to a rather high content of helium in natural gas.

Natural gas suitable for the commercial production of helium is available, especially in the USA. Winning is economically attractive from a helium level of 0.3%. The hydrocarbons of the natural gas are liquefied in a heat exchanger. The remaining gas, in equilibrium with the liquid, is enriched in helium but highly contaminated by nitrogen. The helium concentration is increased in several purifying steps. Eventually the gas, at a temperature corresponding to liquid nitrogen, passes over a bed of active carbon that adsorbs all the gases but helium. The helium gas now has a content of 99.997% He.

51.4.2
Other Noble Gases From Liquid Air

Air is also the raw material for the manufacture of noble gases other than helium. Of special importance is argon, the content of which in the atmosphere is 0.93%. The conditions of separation by fractional distillation of liquid air are determined by the differences in the boiling points of the various components (Table 51.1).

Table 51.1 Components in air: boiling points and concentrations

Gas	Boiling point °C	Content in the atmosphere[a)]	
		Percentage	ppm
Helium	–268.9		5.2
Neon	–246.1		18.2
Nitrogen	–195.8	78.1	
Argon	–185.9	0.93	9340
Oxygen	–183.0	20.9	
Krypton	–152.3		1.14
Xenon	–107.1		0.086

a) By volume, at sea level.

The availability of the noble gases has increased considerably because liquefied air has been so important for the production of oxygen on a large scale. It was the need for oxygen in the modern steel industry that caused this development. As a consequence, neon, argon, krypton and xenon are won as byproducts in large quantities and at rather low cost.

51.5
The Uses of the Noble Gases

51.5.1
Signs, Lasers and Lighting

Neon is used in advertising signs. These signs are made of long, vacuum-tight glass tubes, often bent into all sorts of shapes. The tubes have electrodes at both ends and are filled with neon gas (and a little argon) to a pressure of 6 mbar (0.006 atm). When a high voltage, up to 4000 V, is applied across the electrodes, a discharge through the gas occurs and an intense orange-red light is emitted. A small addition of mercury changes the color to blue. Mercury is nowadays substituted by xenon. If tubes that normally emit blue light are made of yellow glass, then the radiation passing through the glass is green.

The helium–neon laser is common and inexpensive. It can be constructed to produce laser action in the green visible region of the spectrum at 543.5 nm and in the infrared at 1523 nm. The light emitted from xenon lamps is used to power ruby lasers.

Electric-discharge tubes, containing krypton, emit a red-orange light that penetrates fog and haze. The main use of krypton is however for filling in candescent lamps, krypton lamps. Due to the high atomic weight of the element, the gas is a bad transporter of heat by convection and the temperature of the tungsten wire can be increased up to 2500°C. It then emits a sparkling white light with very high intensity. Even when working with a lower wattage, the output of luminous flux is acceptable and the lamp may last for 3000 hours. Krypton lamps also save energy by emitting less heat. Krypton is also used in some types of photographic flashes used in high-speed photography. Some fluorescent light bulbs are filled with a mixture of krypton and argon gases. Krypton gas is also combined with other gases to make luminous signs that glow with a greenish-yellow light.

In modern cars, high-intensity discharge (HID) lighting is used more and more. The tubes contain xenon and small amounts of other noble gases. As the headlamps have no tungsten filaments, they run at lower temperatures and use less electrical energy than traditional halogen lamps.

51.5.2
Some Very Special Applications

Between 1960 and 1983 the length of the meter was defined in terms of the orange-red spectral line of the krypton-86 isotope. From 1983, the meter has been defined as the distance the light from a helium–neon laser passes in specified time.

Liquid helium is used in superconducting magnet applications, including magnetic resonance imaging (MRI) within medicine.

Liquid helium is also used to attain the temperatures needed to study the low-temperature properties of matter, e.g. superconductivity. Use within low-temperature physics and cryogenics accounts for 30% of helium consumption.

51.5.3
Protection or Shielding Gases

Helium and argon are utilized as protection gases in the bright annealing of special steels and other alloys. The noble gas atmosphere prevents the metallic surface from oxidation at the high temperature of the process.

Helium and argon are also used as carrier gases in gas chromatography and for processes that require shielding from other atmospheric gases. The latter could be the growing of semiconductor crystals and welding, for example.

Noble gases fulfill a very important protection function in connection with *gas metal arc welding* (GMAW), frequently referred to as *MIG welding* (Figure 51.1a). Wire is continuously fed from a spool. It melts and forms the weld, together with the base material. The shielding gases used are argon and argon/helium. The gas protects the material against oxidation but also has other functions. It stabilizes the arc and allows the smooth transfer of metal from the weld wire to the molten weld pool.

In *gas tungsten arc welding* (GTAW), or *TIG welding* (Figure 51.1b), an arc is formed between a non-consumable tungsten electrode and the metal being welded. The filler material is added separately as a special TIG wire. Shielding gases are argon or mixtures of argon and helium.

The shielding gases for welding applications are, as mentioned, helium or argon or their mixtures. In the United States, helium gas is preferred due to the accessibility of natural gas rich in helium, which makes the use of helium economic. In other

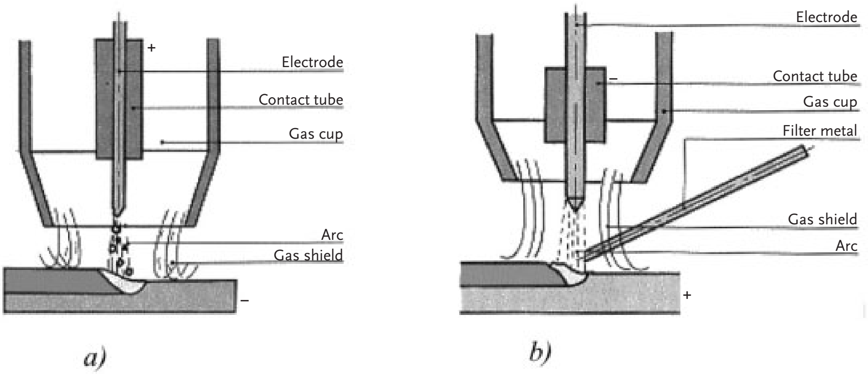

Figure 51.1 The principles of a) MIG welding and b) TIG welding. (Reprinted from ref. [51.3] with permission.)

parts of the world, helium is too expensive and argon, manufactured by fractional distillation of liquid air, is preferred.

Great quantities of argon are used in the production of stainless steels with the AOD (argon–oxygen–decarburization) process, treated in Chapter 8 Iron.

51.5.4
Noble Gases in Plasma Coating

Once upon a time, we learned the following two “truths”:

- Noble gases cannot be ionized, just because they *are* noble.
- Matter is built up in three different states: *solid*, *liquid* and *gas*.

Neither statement is now correct.

With very strong electron acceptors such as fluorine, the noble gas elements can form compounds, in which the positive ions of the various noble gas elements exist.

When an electric arc is forced through argon (or another gas), its electrically neutral atoms split, to some extent, into positively charged ions and negatively charged free electrons. Such a mixture of atomic nuclei and electrons is called a *plasma*. A plasma is thus an ionized gas and is said to be the *fourth state of matter*. Plasma makes up 99% of all the visible matter in the universe but is not present naturally on earth. The generation of a plasma, its use in coating and its temperature distribution are schematically described in Figures 51.2 and 51.3.

The very high temperatures that it is possible to reach in a plasma are utilized in nuclear fusion processes (Chapter 52 Radioactive Elements) but also for solving more “normal” technical problems. This can be exemplified by the material situation in aero engines. Nickel alloys are utilized to withstand the high working temperatures, but special materials problems arise in those parts of the engine which are exposed to thermal shock or to extreme wear due to oxidation, hot corrosion (salt and sulfur) and erosion (from desert sand and other particles). For such situations, the nickel alloys are protected by *plasma coating*. Layers of, for example, zirconium oxide ZrO_2 or magnesium zirconate $MgZrO_3$ are applied.

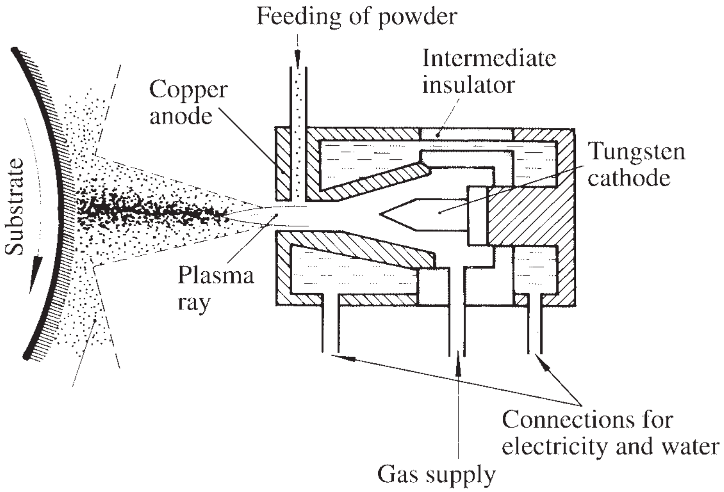

Figure 51.2[1] Generation of a plasma and its use in plasma coating. An arc passes from the tungsten cathode to the water-cooled copper anode. Argon is forced through the arc and is ionized. On recombination beyond the outlet, the ionization energy is returned and the temperature increases considerably. The feed powder particles melt and are thrown against the substrate surface. In the zone in which the powder is fed, the temperature is higher than the melting points of all the coating materials used.

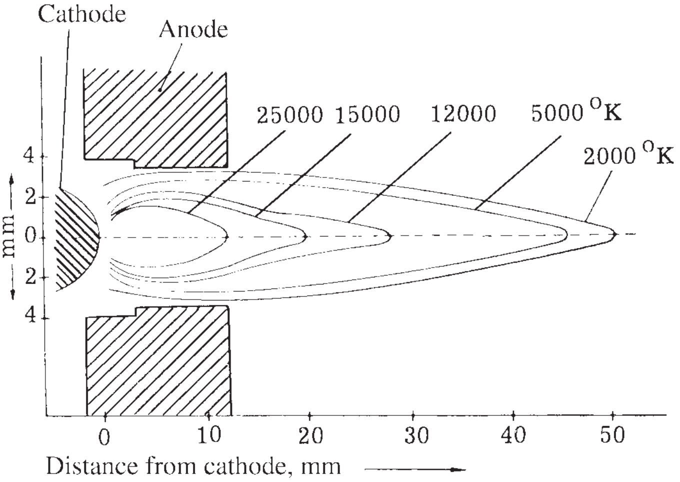

Figure 51.3[1] The temperature distribution in a plasma.

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[1] From IVF-report 77604 with permission (Swedish Research Institute for Engineering Mechanics)

51.5.5
Pressure Medium and Safe Balloon Filling

Helium is used as the pressure medium to open and close the valves in the fuel tanks for space rockets. If the fuel is liquid hydrogen, helium is the sole alternative as no other substance is gaseous at these low temperatures. Another application for helium is as the lifting gas for military and meteorological balloons and blimps. The helium consumption for this purpose is small but important. The loss of 7% in the aerodynamic lifting force, compared to hydrogen, is compensated by the great safety gain due to the fact that, unlike hydrogen, helium gas is not combustible and explosive.

51.5.6
Medical Use

Mixtures of helium and oxygen are used as a breathing gas for deep-sea diving. Due to its low density, this mixture streams easily through the lungs. Unlike nitrogen, helium is not dissolved in the blood plasma, and thus caisson disease (also known as decompression sickness, and the bends) is avoided on ascent.

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52
Radioactive Elements

Most of the elements found in nature have several isotopes. Elements with atomic number 83 (bismuth) and lower have at least one stable isotope, although some are also radioactive and unstable. From element number 84 (polonium) and upwards, all the elements lack stable isotopes. The nine elements 84–92 are called “naturally occurring” radioactive elements. They are polonium, astatine, radon, francium, radium, actinium, thorium, protactinium and uranium. They are all treated in this chapter. There are also an additional two radioactive elements, number 43 technetium and 61 promethium. However, they have been described in Chapter 28 Technetium and Chapter 17 Rare earths, respectively.

Two of the nine radioactive elements described in this chapter, uranium and thorium, were known before the discovery of radioactivity itself. In addition, polonium and radium were discovered in 1898, actinium in 1899, and the other four became known in the 20th century. The synthetic transuranium elements are treated in section 52.16–17 of this chapter.

52.1 Po
Facts about Polonium

52.1.1 Po
The Element

Symbol:	Po
Atomic number:	84
Atomic weight:	209
Ground state electron configuration:	[Xe]$4f^{14}5d^{10}6s^{2}6p^{4}$
Crystal structure:	Cubic with a = 3.36 Å. At 36°C it changes to rhombohedral with a = 3.37 Å and α = 98.2°

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52.1.2 Po
Discovery and Occurrence

Discovery: Polonium was discovered in connection with the investigation of the ore pitchblende by the French scientists Marie and Pierre Curie in 1898. They discovered that the ore was more radioactive than its principal component, uranium, and they separated the ore into many chemical fractions in order to isolate the unknown sources of radioactivity. One fraction, isolated by use of bismuth sulfide, contained a strongly radioactive substance that the Curies showed was a new element. They named it polonium after Poland.

Most important mineral: Polonium is present in pitchblende but in small quantities. The content may be 0.1 mg of polonium in a tonne of ore. It is more usual to obtain polonium through the neutron bombardment of ^{209}Bi.

Ranking in order of abundance in earth crust:	87
Mean content in earth crust:	$2 \cdot 10^{-10}$ ppm (g/tonne)
Mean content in oceans:	$1.5 \cdot 10^{-14}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 Po
Chemical Characterization

Polonium is a rare, radioactive silver-gray metal that dissolves readily in dilute acids, but is only slightly soluble in alkalis. Because most polonium isotopes disintegrate by emitting alpha particles, the element is a source of pure alpha radiation.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Po^{II} as in PoO	$Po(g) \rightarrow Po^+(g) + e^-$	812	$Po(g) + e^- \rightarrow Po^-(g)$
Po^{IV} as in PoO_2			–188

Standard reduction potential:	$PoO_2(s) + 4H^+(aq) + 2e^- \rightarrow Po^{2+}(aq) + 2H_2O(l)$	$E^0 = +1.1$ V
	$Po^{2+}(aq) + 2e^- \rightarrow Po(s)$	$E^0 = +0.37$ V

Electronegativity (Pauling): 2.0

Radii of atoms and ions:	Atomic:	190 pm
(WebElements™)	Po^{4+} (6-coordinate, octahedral):	108 pm
	Po^{4+} (8-coordinate):	122 pm
	Po^{6+} (6-coordinate, octahedral):	81 pm

52.1.4 Po
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
9320 kg m^{-3} 9.32 g cm^{-3}	22.4 cm^3	527 K 254 °C	1235 K 962 °C	(125) J K^{-1} kg^{-1}

Thermal conductivity at 298 K	20 W m^{-1} K^{-1}
Coefficient of linear expansion at 298 K	$23 \cdot 10^{-6}$ K^{-1}
Resistivity at 298 K	420 nΩm

52.1.5 Po
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	13 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	100 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	142 kJmol^{-1}
Entropy S^0 at 298 K	–
Molar heat capacity Cp at 298 K	–

52.1.6 Po
Nuclear Properties and X-ray

Isotope range, all nuclides radioactive	190–218

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{209}Po	102 y	–	1/2-	0.77	α	$^{209}\mathrm{Po}\rightarrow{}^{205}\mathrm{Pb}$	4.979 MeV
					EC or β^+	$^{209}\mathrm{Po}\rightarrow{}^{209}\mathrm{Bi}$	1.893 MeV
^{208}Po	2.898 y	–	0+	–	α	$^{208}\mathrm{Po}\rightarrow{}^{204}\mathrm{Pb}$	5.216 MeV
					EC or β^+	$^{208}\mathrm{Po}\rightarrow{}^{208}\mathrm{Bi}$	1.401 MeV
^{210}Po	138.4 d	N	0+	–	α	$^{210}\mathrm{Po}\rightarrow{}^{206}\mathrm{Pb}$	5.407 MeV
^{206}Po	8.8 d	–	0+	–	EC or β^+	$^{206}\mathrm{Po}\rightarrow{}^{206}\mathrm{Bi}$	1.847 MeV
					α	$^{206}\mathrm{Po}\rightarrow{}^{202}\mathrm{Pb}$	5.327 MeV
^{207}Po	5.80 d	–	5/2-	0.79	EC or β^+	$^{207}\mathrm{Po}\rightarrow{}^{207}\mathrm{Bi}$	2.909 MeV
					α	$^{207}\mathrm{Po}\rightarrow{}^{203}\mathrm{Pb}$	5.216 MeV

Characteristic X-radiation Z	 Element	 Kα_2 keV
83	Bi	74.815
84	Po	76.863
85	At	78.943

X-ray radiation absorbed by the element Incoming radiation energy	 Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	247
17.37 keV (MoKα_2)	133

Neutron absorption **Thermal neutron capture cross section** –

52.1 At
Facts about Astatine

52.1.1 At
The Element

Symbol:	At
Atomic number:	85
Atomic weight:	210
Ground state electron configuration:	[Xe]4f^{14}5d^{10}6s^{2}6p^5
Crystal structure:	–

52.1.2 At
Discovery and Occurrence

Discovery: When, in 1940, D. Corson, K. MacKenzie and E. Segrè used the Berkeley 60-inch cyclotron and bombarded bismuth ^{209}Bi with energetic helium ions, the element number 85 was formed

Most important mineral: Some isotopes of astatine are present in uranium and thorium minerals as part of their radioactive decay series. Astatine belongs to the most rare elements of all. Its total amount in the earth's crust is estimated to be less than 30 grams.

Ranking in order of abundance in earth crust:	89–92
Mean content in earth crust:	–
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 At
Chemical Characterization

Astatine is the heaviest of the halogens. There are about 20 isotopes known, all of which are radioactive. The element name, from Greek *astatos*, "unstable", also indicates this fact. The longest-lived isotope, ^{210}At, has a half-life of 8.1 hours. Astatine behaves chemically very much like iodine. People in contact with this very rare element would probably accumulate it in their thyroid gland.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**	**Electron affinity (kJ mol^{-1}):**
At^{-I} as in HAt At^{V} as in $[AtO_3]^-$ There is also an inconclusive indication of oxoastatine(VII).	$At(g) \rightarrow At^+(g) + e^-$ 920	$At(g) + e^- \rightarrow At^-(g)$ –270

Standard reduction potential: $At_2(s) + 2e^- \rightarrow 2At^-(aq)$ $E^0 = +0.2$ V

Electronegativity (Pauling): 2.2

Radii of atoms and ions: (WebElements™)		
	Atomic	–
	Covalent:	–
	Van der Waals:	–
	At^{7+} (6-coordinate, octahedral):	76 pm

52.1.4 At
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
–	–	575 K 302 °C	610 K 337 °C	(140) J K^{-1} kg^{-1}

Thermal conductivity at 298 K	1.7 W m^{-1} K^{-1}
Coefficient of linear expansion at 298 K	–
Resistivity at 298 K	–

52.1.5 At
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	(15) kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	30 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	–
Entropy S^0 at 298 K	–
Molar heat capacity Cp at 298 K	–

52.1.6 At

Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 193–223

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{210}At	8.1 h	–	5+	–	EC or β^+	$^{210}\text{At}\rightarrow{}^{210}\text{Po}$	3.981 MeV
					α	$^{210}\text{At}\rightarrow{}^{206}\text{Bi}$	5.631 MeV
^{211}At	7.21 h	–	9/2-	–	α	$^{211}\text{At}\rightarrow{}^{207}\text{Bi}$	5.982 MeV
					EC or β^+	$^{211}\text{At}\rightarrow{}^{211}\text{Po}$	0.786 MeV
^{209}At	5.41 h	–	9/2-	–	EC or β^+	$^{209}\text{At}\rightarrow{}^{209}\text{Po}$	3.486 MeV
					α	$^{209}\text{At}\rightarrow{}^{205}\text{Bi}$	5.757 MeV
^{207}At	1.80 h	–	9/2-	–	EC or β^+	$^{207}\text{At}\rightarrow{}^{207}\text{Po}$	3.910 MeV
					α	$^{207}\text{At}\rightarrow{}^{203}\text{Bi}$	5.873 MeV
^{208}At	1.63 h	–	6+	–	EC or β^+	$^{208}\text{At}\rightarrow{}^{208}\text{Po}$	4.985 MeV
					α	$^{208}\text{At}\rightarrow{}^{204}\text{Bi}$	5.751 MeV

Characteristic X-radiation

Z	Element	Kα_2 keV
84	Po	76.863
85	At	78.943
86	Rn	81.065

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	258
17.37 keV (MoKα_2)	120

Neutron absorption **Thermal neutron capture cross section** –

52.1 Rn
Facts about Radon

52.1.1 Rn
The Element

Symbol:	Rn
Atomic number:	86
Atomic weight:	222
Ground state electron configuration:	[Xe]$4f^{14}5d^{10}6s^{2}6p^{6}$
Crystal structure:	–

52.1.2 Rn
Discovery and Occurrence

Discovery: F. E. Dorn in Halle, Germany, is frequently credited with the discovery in 1900, but actually Rutherford and Soddy were the first to isolate radon and also the first to really understand the nature of radon. It occurred in the first decade of 1900 at McGill University in Montreal, Canada.

Most important mineral: Small quantities of radon, formed by decay of uranium minerals, are found in rock and soil, and radon makes up most normal background radioactivity. Radon is present as a dissolved gas in some spring waters.

Ranking in order of abundance in earth crust:	88
Mean content in earth crust:	$4 \cdot 10^{-13}$
Mean content in oceans:	$6 \cdot 10^{-16}$
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 Rn
Chemical Characterization

Radon is a colorless, odorless and radioactive gas, the heaviest of all gases. ^{222}Rn, the most abundant isotope of radon, has a half-life of 3.8 days and decays into an isotope of the element polonium. After inhalation of radon, this radionuclide stays locked in the tissues, e.g. in the lungs. Because of that, radon from the surrounding soil and rocks has become a safety issue around the world.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**	**Electron affinity (kJ mol^{-1}):**
As a noble gas, radon ought not to react with other elements. Fluorine is however an exception. The compound RnF_2 has been formed.	$Rn(g) \rightarrow Rn^+(g) + e^-$ 1037	$Rn(g) + e^- \rightarrow Rn^-(g)$ –

Standard reduction potential: –

Electronegativity (Pauling): –

Radii of atoms and ions:	Atomic:	–
(WebElements™)	Covalent:	145
	No ionic radii are known for Rn	

52.1.4 Rn
Physical Properties

Density (at 273 K)	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
9.73 kg m^{-3} 9.73 g/l	50.5 cm^3 (at 211 K)	202.0 K –71.2 °C	211.4 K –61.8 °C	94 J K^{-1} kg^{-1}

Thermal conductivity at 298 K $3.6 \cdot 10^{-3}$ W m^{-1} K^{-1}

52.1.5 Rn
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	2.9 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	17 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	0 kJmol^{-1}
Entropy S^0 at 298 K	176,1 JK^{-1}mol^{-1}
Molar heat capacity Cp at 298 K	20.786 JK^{-1}mol^{-1}

52.1.6 Rn
Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 196–228

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{222}Rn	3.82 d	N	0+	–	α	^{222}Rn→^{218}Po	5.590 MeV
^{211}Rn	14.6 h	–	1/2-	0.60	EC or β+	^{211}Rn→^{211}At	2.892 MeV
					α	^{211}Rn→^{207}Po	5.965 MeV
^{210}Rn	2.4 h	–	0+	–	α	^{210}Rn→^{206}Po	6.159 MeV
					EC or β+	^{210}Rn→^{210}At	2.374 MeV
^{221}Rn	25 m	–	7/2+	–	β−	^{221}Rn→^{221}Fr	1.130 MeV
					α	^{221}Rn→^{217}Po	6.146 MeV

Characteristic X-radiation

Z	Element	Kα$_2$ keV
85	At	78.943
86	Rn	81.065
87	Fr	82.231

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα$_2$)	255
17.37 keV (MoKα$_2$)	118

Neutron absorption **Thermal neutron capture cross section** 0.7 barns (^{222}Rn)

52.1 Fr
Facts about Francium

52.1.1 Fr
The Element

Symbol:	Fr
Atomic number:	87
Atomic weight:	223
Ground state electron configuration:	[Rn]$7s^1$
Crystal structure:	–

52.1.2 Fr
Discovery and Occurrence

Discovery: Marguerite Perey discovered the element in 1939. She worked at the Curie Laboratory of the Radium Institute in Paris.

Most important mineral: Francium is formed when the radioactive element actinium disintegrates. Because of that, very small amounts of francium are found in uranium ores. The element can also be made artificially by bombarding thorium with protons. No weighable quantity of the element has been prepared or isolated.

Ranking in order of abundance in earth crust:	89–92
Mean content in earth crust:	–
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man’s body (weight 70 kg):	–

52.1.3 Fr
Chemical Characterization

Francium is the heaviest of the alkali metals and the most electropositive of all elements. Chemically, it closely resembles cesium. Francium is naturally radioactive. It is the most unstable of the first 101 elements. Only two isotopes, ^{221}Fr and ^{223}Fr, are naturally occurring; all others are artificial. ^{223}Fr is the longest-lived isotope with a half-life of 22 minutes.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**	**Electron affinity (kJ mol^{-1}):**
Fr^{I} as in Fr^+	$Fr(g) \rightarrow Fr^+(g) + e^-$ 380	$Fr(g) + e^- \rightarrow Fr^-(g)$ –

Standard reduction potential:	$Fr^+(aq) + e^- \rightarrow Fr(s)$ $E^{\ominus} = -2.92$ V	
Electronegativity (Pauling):	0.7	
Radii of atoms and ions: (Web Elements™)	Atomic: Fr^+ (6-coordinate, octahedral):	– 194 pm

52.1.4 Fr
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
(2410) kg m^{-3} (2.41) g cm^{-3}	–	(300) K (27) °C	(930) K (657) °C	–

Thermal conductivity at 298 K	(15) W m^{-1} K^{-1}
Coefficient of linear expansion at 298 K	–
Resistivity at 298 K	–

52.1.5 Fr
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	(2) kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	(65) kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	(64) kJmol^{-1}
Entropy S^0 at 298 K	95.4 JK^{-1}mol^{-1}
Molar heat capacity Cp at 298 K	–

52.1.6 Fr

Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 200–232

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{223}Fr	21.8 m	N	3/2–	1.17	β^-	$^{223}\text{Fr}\rightarrow{}^{223}\text{Ra}$	1.149 MeV
					α	$^{223}\text{Fr}\rightarrow{}^{219}\text{At}$	5.432 MeV
^{212}Fr	20.0 m	–	5+	4.6	EC or β^+	$^{212}\text{Fr}\rightarrow{}^{212}\text{Rn}$	5.129 MeV
					α	$^{212}\text{Fr}\rightarrow{}^{208}\text{At}$	6.529 MeV
^{222}Fr	14.2 m	–	2–	0.63	β^-	$^{222}\text{Fr}\rightarrow{}^{222}\text{Ra}$	2.033 MeV
^{221}Fr	4.9 m	N	5/2–	1.58	α	$^{221}\text{Fr}\rightarrow{}^{217}\text{At}$	6.458 MeV
^{225}Fr	4.0 m	–	3/2–	1.07	β^-	$^{225}\text{Fr}\rightarrow{}^{225}\text{Ra}$	1.865 MeV

Characteristic X-radiation

Z	Element	Kα_2 keV
86	Rn	81.065
87	Fr	82.231
88	Ra	85.434

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	266
17.37 keV (MoKα_2)	88.7

Neutron absorption **Thermal neutron capture cross section** –

52.1 Ra
Facts about Radium

52.1.1 Ra
The Element

Symbol:	Ra
Atomic number:	88
Atomic weight:	226.02
Ground state electron configuration:	$[Rn]7s^2$
Crystal structure:	Cubic bcc with $a = 5.15$ Å

52.1.2 Ra
Discovery and Occurrence

Discovery: Radium was discovered in connection with the investigation of the ore pitchblende by the French scientists Marie and Pierre Curie in 1898. They discovered that the ore was more radioactive than its principal component, uranium, and they separated the ore into many chemical fractions in order to isolate the unknown sources of radioactivity. In a highly radioactive barium chloride fraction they found a new element, which they named radium, the "radiator".

Most important mineral: Radium is formed by the radioactive disintegration of uranium and is consequently found in all uranium ores. One tonne of pitchblende might contain 0.3 g of radium. Ores containing radium are found in Zaire, Australia, Canada and the USA (New Mexico, Utah and Colorado).

Ranking in order of abundance in earth crust:	85
Mean content in earth crust:	$9 \cdot 10^{-7}$ ppm (g/tonne)
Mean content in oceans:	$8.9 \cdot 10^{-11}$ ppm (g/tonne)
Residence time in oceans:	$4 \cdot 10^{6}$ years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 Ra
Chemical Characterization

Radium is a white metal, but blackens on exposure to air. The chemical properties of the element are similar to those of barium. Like other heavy elements of group 2 radium salts impart a characteristic color (a carmine red) to a flame. Radium is radioactive, over a million times more radioactive than the same quantity of uranium. It emits α, β and γ rays as well as radioactive radon gas. When a radium salt is mixed with a substance such as zinc sulfide, the substance glows in the dark. Small amounts of this mixture was used in the mid-1900s to paint the hands and numbers of watches. Exposure to radium can cause cancer. On the contrary "ordinary" cancerous cells may be "killed" by directed radium radiation. This treatment is nowadays utilized for only a few kinds of cancer.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ra^{II} as in RaO, $Ra(OH)_2$	$Ra(g) \rightarrow Ra^+(g) + e^-$	509	$Ra(g) + e^- \rightarrow Ra^-(g)$
and $RaCl_2$	$Ra^+(g) \rightarrow Ra^{2+}(g) + e^-$	979	–

Standard reduction potential:	$Ra^{2+}(aq) + 2e^- \rightarrow Ra(s)$	$E^0 = -2.916$ V
Electronegativity (Pauling):	0.9	
Radii of atoms and ions:	Atomic:	215 pm
	Ra^{2+}(8-coordinate):	162 pm

52.1.4 Ra
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
5000 kg m^{-3} 5.0 g cm^{-3}	45.2 cm^3	973 K 700 °C	1413 K 1140 °C	119 J K^{-1} kg^{-1}

Thermal conductivity at 298 K	18.6 W m^{-1} K^{-1}
Coefficient of linear expansion at 298 K	$20.2 \cdot 10^{-6}$ K^{-1}
Resistivity at 298 K	1000 nΩm

52.1.5 Ra
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	8.37 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	136.8 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	159 $kJmol^{-1}$
Entropy S^0 at 298 K	71 $JK^{-1}mol^{-1}$
Molar heat capacity Cp at 298 K	27.0 $JK^{-1}mol^{-1}$

52.1.6 Ra
Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 202–234

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{226}Ra	1600 y	N	0+	–	α	$^{226}Ra \rightarrow {}^{222}Rn$	4.871 MeV
^{228}Ra	5.75 y	N	0+	–	β^-	$^{228}Ra \rightarrow {}^{228}Ac$	0.046 MeV
^{225}Ra	14.9 d	N	1/2+	−0.734	β^-	$^{225}Ra \rightarrow {}^{225}Ac$	0.358 MeV
^{223}Ra	11.435 d	N	3/2+	0.271	α	$^{223}Ra \rightarrow {}^{219}Rn$	5.979 MeV
^{224}Ra	3.66 d	N	0+	–	α	$^{224}Ra \rightarrow {}^{220}Rn$	5.789 MeV
^{227}Ra	42.2 m	–	3/2+	−0.404	β^-	$^{227}Ra \rightarrow {}^{227}Ac$	1.326 MeV

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
87	Fr	82.231
88	Ra	85.434
89	Ac	87.675

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	274
17.37 keV ($MoK\alpha_2$)	91.6

Neutron absorption **Thermal neutron capture cross section** –

52.1 Ac
Facts about Actinium

52.1.1 Ac
The Element

Symbol:	Ac
Atomic number:	89
Atomic weight:	227.03
Ground state electron configuration:	$[Rn]6d^17s^2$
Crystal structure:	Cubic fcc with $a = 5.67$ Å

52.1.2 Ac
Discovery and Occurrence

Discovery: Actinium was discovered in connection with the investigation of the ore pitchblende by the French scientists Marie and Pierre Curie in 1898. They discovered that the ore was more radioactive than its principal component, uranium, and they separated the ore into many chemical fractions in order to isolate the unknown sources of radioactivity. In one fraction André Debierne, a colleague of the Curies, and a specialist in chemistry, discovered a new, strongly radioactive element that was given the name actinium. The discovery year was 1899.

Most important mineral: Actinium is a decay product of ^{235}U and is found naturally in uranium ores.

Ranking in order of abundance in earth crust:	86
Mean content in earth crust:	$5.5 \cdot 10^{-10}$ ppm (g/tonne). In uranium ores 0.2 ppm
Mean content in oceans:	–
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 Ac
Chemical Characterization

Chemically actinium is similar to the rare earth metals, especially lanthanum. Actinium is 150 times more radioactive than radium and for that reason it is a very dangerous element.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Ac^{III} as in Ac_2O_3 and $AcCl_3$	$Ac(g) \rightarrow Ac^+(g) + e^-$	499	$Ac(g) + e^- \rightarrow Ac^-(g)$
	$Ac^+(g) \rightarrow Ac^{2+}(g) + e^-$	1170	–

Standard reduction potential:	$Ac^{3+}(aq)+e^- \rightarrow Ac^{2+}((aq)$	$E^{\ominus} = -4.9$ V
	$Ac^{2+}(aq) + 2\,e^- \rightarrow Ac(s)$	$E^{\ominus} = -0.7$ V
	$Ac^{3+}(aq) + 3e^- \rightarrow Ac(s)$	$E^{\ominus} = -2.13$ V
Electronegativity (Pauling):	1.1	
Radii of atoms and ions:	Atomic:	195 pm
(WebElements™)	Ac^{3+} (6-coordinate, octahedral):	126 pm

52.1.4 Ac
Physical Properties

Density	**Molar volume**	**Melting point**	**Boiling point**	**Specific heat c_p at 298 K**
10 070 kg m^{-3} 10.07 g cm^{-3}	22.6 cm^3	1324 K 1051 °C	3473 K 3200°C	120 J K^{-1} kg^{-1}

Thermal conductivity at 298 K	12 W m^{-1} K^{-1}
Coefficient of linear expansion at 298 K	$14.9 \cdot 10^{-6}$ K^{-1}
Resistivity at 298 K	–

52.1.5 Ac
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	14 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	400 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	406 kJmol^{-1}
Entropy S^0 at 298 K	56.5 JK^{-1}mol^{-1}
Molar heat capacity Cp at 298 K	27.2 JK^{-1}mol^{-1}

52.1.6 Ac

Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 206–234

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{227}Ac	21.77 y	N	3/2–	1.1	β^-	${}^{227}\mathrm{Ac} \rightarrow {}^{227}\mathrm{Th}$	0.045 MeV
					α	${}^{227}\mathrm{Ac} \rightarrow {}^{223}\mathrm{Fr}$	5.042 MeV
^{225}Ac	10.0 d	N	3/2–	–	α	${}^{225}\mathrm{Ac} \rightarrow {}^{221}\mathrm{Fr}$	5.935 MeV
^{226}Ac	29.37 h	–	(1)	–	β^-	${}^{226}\mathrm{Ac} \rightarrow {}^{226}\mathrm{Th}$	1.117 MeV
					EC or β^+	${}^{226}\mathrm{Ac} \rightarrow {}^{226}\mathrm{Ra}$	0.640 MeV
					α	${}^{226}\mathrm{Ac} \rightarrow {}^{222}\mathrm{Fr}$	5.536 MeV
^{228}Ac	6.15 h	N	3+	–	β^-	${}^{228}\mathrm{Ac} \rightarrow {}^{228}\mathrm{Th}$	2.127 MeV
^{224}Ac	2.78 h	–	0-	–	EC or β^+	${}^{224}\mathrm{Ac} \rightarrow {}^{224}\mathrm{Ra}$	1.403 MeV
					α	${}^{224}\mathrm{Ac} \rightarrow {}^{220}\mathrm{Fr}$	6.327 MeV
					β^-	${}^{224}\mathrm{Ac} \rightarrow {}^{224}\mathrm{Th}$	0.232 MeV

Characteristic X-radiation

Z	Element	Kα_2 keV
88	Ra	85.434
89	Ac	87.675
90	Th	89.952

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (CuKα_2)	285
17.37 keV (MoKα_2)	95.4

Neutron absorption **Thermal neutron capture cross section** 880 barns (^{227}Ac)

52.1 Th
Facts about Thorium

52.1.1 Th
The Element

Symbol:	Th
Atomic number:	90
Atomic weight:	232.04
Ground state electron configuration:	[Rn]$6d^2 7s^2$
Crystal structure:	Cubic fcc with a = 5.08 Å

52.1.2 Th
Discovery and Occurrence

Discovery: J. J. Berzelius discovered thorium in Stockholm in 1829. The element name was selected from Norse mythology: *Thor* was the god of thunder.

Most important mineral: Thorite $ThSiO_4$ (Figure M24) and thorianite ThO_2. The primary source of thorium is monazite (Figure M25).

Ranking in order of abundance in earth crust:	38
Mean content in earth crust:	9.6 ppm (g/tonne).
Mean content in oceans:	$1 \cdot 10^{-6}$
Residence time in oceans:	100 years
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 Th

Chemical Characterization

When pure, thorium is a silvery white metal. In air, it tarnishes slowly, becoming gray and finally black. Thorium has isotopes ranging in mass number from 210 to 237, all isotopes being radioactive. Much of the internal heat in the earth's crust has been attributed to thorium (and uranium).Thorium is a potential atomic fuel source, because bombardment of ^{232}Th with slow neutrons yields the fissile isotope ^{233}U. There is probably more energy available for use from thorium in the minerals of the earth's crust than from combined uranium and fossil fuel sources.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
Th^{IV} as in ThO_2 and ThI_4	$Th(g) \rightarrow Th^+(g) + e^-$	587	$Th(g) + e^- \rightarrow Th^-(g)$
	$Th^+(g) \rightarrow Th^{2+}(g) + e^-$	1110	–
	$Th^{2+}(g) \rightarrow Th^{3+}(g) + e^-$	1930	
	$Th^{3+}(g) \rightarrow Th^{4+}(g) + e^-$	2780	

Standard reduction potential:	$Th^{4+}(aq) + 4e^- \rightarrow Th(s)$ $E^0 = -1.83$ V	
Electronegativity (Pauling):	1.3	
Radii of atoms and ions:	Atomic:	180 pm
(WebElements™)	Th^{4+} (6-coordinate, octahedral):	108 pm
	Th^{4+} (8-coordinate):	119 pm

52.1.4 Th
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
11 720 kg m^{-3} 11.72 g cm^{-3}	19.80 cm^3	2023 K 1750 °C	5061 K 4788 °C	118 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
55	54	54	56	58

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
–	$11 \cdot 10^{-6}$	–	–

Resistivity nΩm

78 K	298 K	373 K	573 K	973 K	1473 K
39	130	208	325	536	680

Mass magnetic susceptibility χ_{mass} at 293 K	$+7.2 \cdot 10^{-9}$ m^3kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Youngs modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
79 GPa	31 GPa	58 GPa	0.27

52.1.5 Th
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	16 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	543.9 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	598.3 $kJmol^{-1}$
Entropy S^0 at 298 K	53.39 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

	100 K	**298 K**	**600 K**	**1000 K**	**2000 K**	**2500 K**
	22.69	27.32	28.83	32.39	39.60	46.00

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	**298 K**	**500 K**	**1000 K**	**1500 K**	**2000 K**
$Th+O_2 \rightarrow ThO_2$	–1169	–1132	–1045	–955	–862

52.1.6 Th
Nuclear Properties and X-ray

Isotope range, natural and artificial 210–237

Naturally occurring isotopes

Nuclide	Half-life	Abundance %[1]	Nuclear spin	Magnetic moment μ	Decay mode	Decay energy Q
^{232}Th	$1.405 \cdot 10^{10}$ y	100	0+	–	α	4.083 MeV
^{230}Th	$7.538 \cdot 10^{4}$ y	N	0+	–	α	4.770 MeV
^{229}Th	7340 y	N	5/2+	0.46	α	5.168 MeV
^{228}Th	1.912 y	N	0+	–	α	5.520 MeV
^{234}Th	24.10 d	N	0+	–	β^-	0.273 MeV

[1] N = naturally occurring trace

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
89	Ac	87.675
90	Th	89.952
91	Pa	92.287

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	291
17.37 keV ($MoK\alpha_2$)	97.6

Neutron absorption	**Thermal neutron capture cross section**	7.4 barns

52.1 Pa
Facts about Protactinium

52.1.1 Pa
The Element

Symbol:	Pa
Atomic number:	91
Atomic weight:	231.04
Ground state electron configuration:	$[Rn]5f^2 6d^1 7s^2$
Crystal structure:	Tetragonal with $a = b = 3.925$ Å, $c = 3.24$ Å

52.1.2 Pa
Discovery and Occurrence

Discovery: Protactinium was identified by Fajans and Göhring in Karlsruhe in 1913, who named the new element *brevium*. They had discovered the isotope ^{234}Pa with a half-life of 6.70 h. Lise Meitner at the Kaiser-Wilhelm Institute for Chemistry in Berlin separated the oxide of a more long-lived isotope from pitchblende (mixed with tantalum oxide). She published the news in 1918 together with Otto Hahn. The new element was discovered independently in the same year by F. Soddy, J. A. Cranston and A. Fleck in Glasgow. The name protactinium was selected because it was recognized as the prototype for actinium. The element was first isolated by Aristid V. Grosse in 1934. He prepared 2 mg of the metal.

Most important mineral: Protactinium is one of the rarest and most expensive naturally occurring elements, found in pitchblende.

Ranking in order of abundance in earth crust:	84
Mean content in earth crust:	$1.4 \cdot 10^{-6}$ ppm (g/tonne)
Mean content in oceans:	$5 \cdot 10^{-11}$ ppm (g/tonne)
Residence time in oceans:	–
Mean content in an adult human body:	–
Content in a man's body (weight 70 kg):	–

52.1.3 Pa
Chemical Characterization

Isotopes of protactinium ranging in mass number from 212 to 238 are known. ^{231}Pa is the most long-lived isotope with a half-life of 32 760 years.

Oxidation states:	Ionization energy (kJ mol^{-1}):	Electron affinity (kJ mol^{-1}):
Pa^{IV} as in PaO_2 and PaF_4 Pa^{V} as in Pa_2O_5 and $PaCl_5$ Pa^{III} exists but is of secondary importance	$Pa(g) \rightarrow Pa^+(g) + e^-$ 568	$Pa(g) + e^- \rightarrow Pa^-(g)$ –

Standard reduction potential:	$Pa^{4+}(aq) + 4e^- \rightarrow Pa(s)$ $E^0 = -1.47$ V
Electronegativity (Pauling):	1.5

Radii of atoms and ions: (WebElements™)		
	Atomic:	180 pm
	Pa^{3+} (6-coordinate, octahedral):	118 pm
	Pa^{4+} (6-coordinate, octahedral):	104 pm
	Pa^{4+} (8-coordinate):	115 pm
	Pa^{5+} (6-coordinate, octahedral):	92 pm
	Pa^{5+} (8-coordinate):	105 pm

52.1.4 Pa
Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
15 370 kg m^{-3} 15.37 g cm^{-3}	15.0 cm^3	(1840) K (1567) °C	(4500) K (4227) °C	120 J K^{-1} kg^{-1}

Thermal conductivity at 298 K	47 W m^{-1} K^{-1}
Coefficient of linear expansion at 298 K	–
Resistivity at 298 K	180 nΩm

52.1.5 Pa
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	15 kJmol^{-1}
Enthalpy of vaporization ΔH_{vap} at b.p.	480 kJmol^{-1}
Enthalpy of atomization ΔH_{at} at 298 K	607 kJmol^{-1}
Entropy S^0 at 298 K	51.9 JK^{-1}mol^{-1}
Molar heat capacity Cp at 298 K	28 JK^{-1}mol^{-1}

52.1.6 Pa

Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 212–238

Most long-lived

Nuclide	Half-life	Natural (N/–)	Nuclear spin	Magnetic moment μ	Decay mode	Decay reaction	Decay energy Q
^{231}Pa	32 760 y	N	3/2-	2.01	α	^{231}Pa→^{227}Ac	5.150 MeV
^{233}Pa	27.0 d	–	3/2-	4.0	β⁻	^{233}Pa→^{233}U	0.570 MeV
^{230}Pa	17.4 d	–	(2-)	2.0	EC or β⁺	^{230}Pa→^{230}Th	1.310 MeV
					β⁻	^{230}Pa→^{230}U	0.564 MeV
					α	^{230}Pa→^{226}Ac	5.439 MeV
^{229}Pa	1.50 d	–	(5/2+)	–	EC or β⁺	^{229}Pa→^{229}Th	0.310 MeV
					α	^{229}Pa→^{225}Ac	5.836 MeV
^{232}Pa	1.31 d	–	(2-)	–	β⁻	^{232}Pa→^{232}U	1.337 MeV
					EC or β⁺	^{232}Pa→^{232}Th	0.495 MeV

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
90	Th	89.952
91	Pa	92.287
92	U	94.659

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV (Cu$K\alpha_2$)	305
17.37 keV (Mo$K\alpha_2$)	102

Neutron absorption **Thermal neutron capture cross section** 200 barns (^{231}Pa)

52.1 U
Facts about Uranium

52.1.1 U
The Element

Symbol:	U
Atomic number:	92
Atomic weight:	238.03
Ground state electron configuration:	$[\mathrm{Rn}]5f^3 6d^1 7s^2$
Crystal structure:	Orthorombic with $a = 2.85$ Å, $b = 5.87$ Å, $c = 4.95$ Å

52.1.2 U
Discovery and Occurrence

Discovery: M. H. Klaproth in Berlin discovered a new element in pitchblende in 1789. He named the new element *uranium* after *Uranus*, the father of the gods in Greek mythology.

Most important mineral: Pitchblende and uraninite, essentially UO_2, but usually partly oxidized to U_3O_8 (both in Figure M76). The uranium minerals *carnotite* and *coffinite* are also important.

Ranking in order of abundance in earth crust:	49
Mean content in earth crust:	2.7 ppm (g/tonne).
Mean content in oceans:	$3.2 \cdot 10^{-3}$ ppm (g/tonne)
Residence time in oceans:	$2.5 \cdot 10^{6}$ years
Mean content in an adult human body:	0.001 ppm
Content in a man's body (weight 70 kg):	0.07 mg

52.1.3 U
Chemical Characterization

Uranium is a silvery metal. As it is chemically reactive, it tarnishes in air. It is attacked by steam and acids but not by alkalis. Due to its radioactivity and accessibility, the element is the main fuel in nuclear reactors. Natural uranium consists of 99.3% of the isotope ^{238}U and 0.7% of the fissile isotope ^{235}U.

Oxidation states:	**Ionization energy (kJ mol^{-1}):**		**Electron affinity (kJ mol^{-1}):**
U^{III} as in UCl_3	$U(g) \rightarrow U^+(g) + e^-$	584	$U(g) + e^- \rightarrow U^-(g)$
U^{IV} as in UO_2 and $[UCl_6]^{2-}$	$U^+(g) \rightarrow U^{2+}(g) + e^-$	1420	–
U^V as in $[UF_6]^-$			
U^{VI} as in UO_3, UF_6, UCl_6 and $UO_2(NO_3)_2$			

Standard reduction potential:

$[UO_2]^{2+}(aq) + 4H^+(aq) + 2e^- \rightarrow U^{4+}(aq) + 2H_2O(l)$ $E^0 = +0.27$ V

$U^{4+}(aq) + 4e^- \rightarrow U(s)$ $E^0 = -1.38$ V

Electronegativity (Pauling): 1.38

Radii of atoms and ions:
(WebElements™)

Atomic:	175 pm
Van der Waals:	186 pm
U^{3+} (6-coordinate, octahedral):	116.5 pm
U^{4+} (6-coordinate, octahedral):	103 pm
U^{4+}(8-coordinate):	114 pm
U^{5+} (6-coordinate, octahedral):	90 pm
U^{6+} (6-coordinate, octahedral):	87 pm
U^{6+} (4-coordinate, tetrahedral):	66 pm
U^{6+} (8-coordinate):	100 pm

52.1.4 U

Physical Properties

Density	Molar volume	Melting point	Boiling point	Specific heat c_p at 298 K
18 950 kg m^{-3} 18.95 g cm^{-3}	12.56 cm^3	1405.5 K 1132.3 °C	(4100) K (3827) °C	116 J K^{-1} kg^{-1}

Thermal conductivity $Wm^{-1}K^{-1}$

173 K	273 K	373 K	573 K	973 K
24	27	29	33	43

Coefficient of linear expansion K^{-1}

100 K	293 K	500 K	800 K
$10 \cdot 10^{-6}$	$13.9 \cdot 10^{-6}$	$16.9 \cdot 10^{-6}$	$24.3 \cdot 10^{-6}$

Resistivity nΩm

78 K	273 K	373 K	573 K	973 K	1473 K
110	280	350	470	–	–

Mass magnetic susceptibility χ_{mass} at 293 K	$+21.6 \cdot 10^{-9}$ m^3kg^{-1}
Magnetic characterization	Paramagnetic (as susceptibility is positive)

Elastic properties

Youngs modulus E	Shear modulus G	Bulk modulus K	Poissons ratio ν
180 GPa	72 GPa	120 GPa	0.25

52.1.5 U
Thermodynamic Properties

Enthalpy of fusion ΔH_{fus} at m.p.	15.48 $kJmol^{-1}$
Enthalpy of vaporization ΔH_{vap} at b.p.	420 $kJmol^{-1}$
Enthalpy of atomization ΔH_{at} at 298 K	535.6 $kJmol^{-1}$
Entropy S^0 at 298 K	50.21 $JK^{-1}mol^{-1}$

Molar heat capacity Cp at temperature K. $JK^{-1}mol^{-1}$

100 K	298 K	600 K	1000 K	2000 K	2500 K
22.24	27.665	34.65	42.40	49.125	20.555

Standard free energy ΔG^0 of oxide formation kJ/mol O_2

Reaction	298 K	500 K	1000 K	1500 K	2000 K
$U+O_2 \rightarrow UO_2$	–1032	–997	–912	–826	–741
$2/3U+O_2 \rightarrow 2/3\ UO_3$	–764	–729	–647	–	–

52.1.6 U
Nuclear Properties and X-ray

Isotope range, all nuclides radioactive 218–242

Most long-lived

Nuclide	Half-life	Abundance %[1]	Nuclear spin	Magnetic moment μ	Decay mode	Decay energy Q
^{238}U	$4.468 \cdot 10^9$ y	99.274	0+	–	α	4.270 MeV
^{235}U	$7.038 \cdot 10^8$ y	0.720	7/2-	–0.35	α	4.679 MeV
^{236}U	$2.342 \cdot 10^7$ y	–	0+	–	α	4.572 MeV
^{234}U	$2.455 \cdot 10^5$ y	0.006	0+	–	α	4.859 MeV
^{233}U	$1.592 \cdot 10^5$ y	–	5/2+	0.59	α	4.909 MeV

1) – = not naturally occuring

Characteristic X-radiation

Z	Element	$K\alpha_2$ keV
91	Pa	92.287
92	U	94.659
93	Np	97.077

X-ray radiation absorbed by the element

Incoming radiation energy	Absorption coefficient μ (cm^2/g)
8.028 keV ($CuK\alpha_2$)	308
17.37 keV ($MoK\alpha_2$)	104

Neutron absorption	**Thermal neutron capture cross section**	7.6 barns

52.2
Elements Known Before Radioactivity Was Discovered

52.2.1
Uranus – The Father of the Gods in Greek Mythology

Martin Heinrich Klaproth (1743–1817) grew up in a family of tailors in Harz, Germany. He became an apprentice in a pharmacy and acquired deep knowledge of chemistry mostly by studying alone. In spite of his apprenticeship and later work with his own pharmacy, he was the foremost chemist of his time regarding the analysis of minerals and ores. In 1810, at the age of 67, he became the first holder of the newly established professorship in chemistry at the University of Berlin. He worked there until his death in 1817. We met him in Chapter 18, regarding the discovery of titanium.

In 1789 Klaproth obtained a sample of pitchblende for investigation. In the mineral he found the oxide of a metal that had not been described earlier. He named the new element *uranium*. There are various reasons mentioned for why he used that name. The astronomer, telescope-builder and organist William Herschel (1738–1822) in London had discovered a new planet in 1781 and given it the name *Uranus* after the father of the gods in Greek mythology. Did Klaproth select the element name after the new planet or after the Greek god? The latter seems to have been the case, because, as he himself says, six years later, in connection with the discovery of titanium:

> As the case was at the naming of uranium I take the designation titanium from mythology.

Klaproth reduced the new oxide with carbon at high temperature. His reaction product consisted of gray, lustrous grains, which he regarded as uranium metal. Probably they consisted of uranium carbide to a large extent. The pure metal was prepared in 1842 by E. M. Péligot in France. He reduced uranium tetrachloride with potassium metal.

52.2.2
Thor – The God of Thunder in Norse Mythology

52.2.2.1 A Day of the Week – Why Not Also an Element?

In 1815 Berzelius examined a mineral from Falun, in which he thought he had found a new element. He intended to use the element-naming philosophy utilized by Klaproth for uranium and titanium, and of his own former student Ekeberg for tantalum (Chapter 23). But why not use a god from Norse mythology? The name of the Norse god Thor had been used in the naming of numerous places and had also given its name to a day of the week, Thor's day. Why not also an element name? However, Berzelius had to change his mind when he found that the "new" element was not new. The mineral was an yttrium phosphate. But in 1829 it *was* time for an element discovery, beyond dispute.

52.2.2.2 The Reverend Finds a Mineral and Berzelius Has His New Element

At this time Professor Jens Esmark was active at the University of Christiania (Oslo) in Norway. He was a leading Norwegian geologist and is remembered for his initial discoveries about ice ages. In 1824 he concluded that glaciers had once covered much of Norway and the adjacent sea floor. A son of his became a clergyman. He had inherited his father's interest in stones and became known as a clever mineral collector with an extensive correspondence with mineralogists in other countries. He discovered a black mineral near Brevig in Norway. He thought it was gadolinite, but his father did not agree. As he could not identify it, he sent a specimen to Berzelius for examination. The latter examined it and established that it contained 60% of a new "earth". He named the new oxide *thoria,* the mineral in which it was obtained *thorite* (Figure M24) and the new element *thorium* [52.1]. He also isolated the metal by reduction of potassium thorium fluoride with metallic potassium. The discovery of thorium was announced by Berzelius in *Annalen der Physik und Chemie* (Poggendorf) **16** (1829).

52.3
Radioactivity

52.3.1
Measuring Radioactivity – The Becquerel

Since the Chernobyl disaster in 1986, we have become accustomed to the concept of the becquerel (Bq) as a means to describe radioactivity in the environment and in food (Figure 52.1). But what is a becquerel?

The answer to that question is as follows: the becquerel (Bq) is the unit used to measure the amount of radiation that radioactive substances emit. The number of

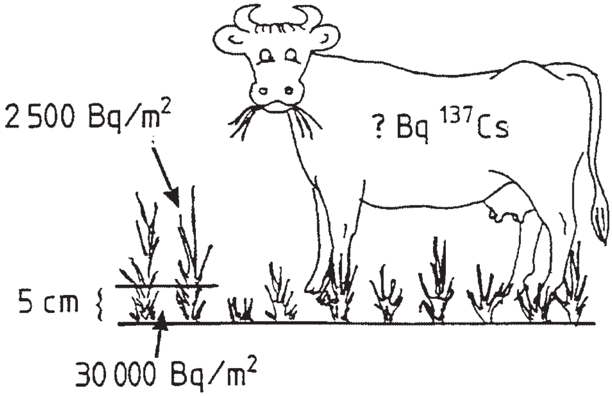

Figure 52.1 As a result of the Chernobyl nuclear reactor accident, grass became radioactive, cattle ate it and the meat became unfit for human consumption. (Reprinted from ref. [52.2] with permission.)

becquerels is the number of disintegrations per second. An older unit is the curie (Ci), which corresponds to the rate of decay of 1 g radium, i.e. 37 billion disintegrations per second. Thus 1 Ci = $37 \cdot 10^9$ Bq. Several attendant questions arise. What is radioactivity? What is it that disintegrates? Why is the decay injurious to the human and other organisms?

52.3.2
What Is Radioactivity?

The atomic nucleus consists of two types of nucleons, protons (positively charged) and neutrons (uncharged). Neutrons provide a special nuclear force that binds protons and neutrons together into stable units. Otherwise, the nucleus would disintegrate due to the repulsive electrostatic forces between the positively charged protons. A condition for a stable nucleus is that the number Z of protons (atomic number) has a certain relation to the number N of neutrons.

In light atoms, $N/Z=1$. The nuclide ^{12}C, for instance, has six protons and six neutrons in its nucleus. The combination of a pair of protons with a pair of neutrons has particularly high stability. That group corresponds to the stable helium nucleus, which also remains after some radioactive decays and is emitted as alpha (α) particles. When radium disintegrates, α particles are emitted. Electrons from the environment are added to the helium nuclei and neutral helium atoms are formed. That is the reason why helium was discovered in uraninite.

In heavier atoms, the repulsive forces between the protons are very high, and $N/Z>1$ is a condition that must be fulfilled if the nucleus is to be stable. The most usual lead isotope ^{208}Pb has 82 protons and 126 neutrons in its nucleus. The N/Z ratio is thus 1.54 and the isotope is stable. Above atomic number 83, all nuclei are unstable, no matter how many neutrons are present.

52.3.3
Radioactive Decay

The naturally occurring radioactive substances disintegrate in different ways, as outlined below.

52.3.3.1 Alpha Particle Emission (Alpha or α Radiation)

A stable helium nucleus (an α particle), thus a bundle of two protons and two neutrons, may be emitted in a decay process. For example:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

Both Z and N decrease by two units, and the mass number A (number of protons plus number of neutrons, $A=Z+N$) is four units lower than the mass number of the mother nuclide. Thus a new element located two steps to the left in the periodic table has been formed.

52.3.3.2 Beta Particle Emission (Beta-minus or β^- Radiation)

An electron may be emitted in a nuclear decay process. For example:

$$^{234}_{90}\mathrm{Th} \rightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\beta$$

The process can be regarded as the emission of an electron from a neutron, which is then changed to a proton. The atomic number increases by one unit. A new element has been formed but the mass number is unchanged.

52.3.3.3 Positron Emission (Beta-plus or β^+ Radiation)

Emission of a positron can also occur in a nuclear decay process. For example:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta$$

The process can be regarded as a transition of a proton to a neutron. Also in this case a new element has been formed, one with a lower atomic number. The emitted positron is rapidly annihilated on collision with an electron. Gamma (γ) radiation is formed (see below).

52.3.3.4 Electron Capture (EC)

Electron capture is a process that achieves the same effect as positron emission. An electron from a shell is absorbed by the nucleus. A proton in the nucleus is changed to a neutron, and the new element formed has decreased the atomic number by one unit.

52.3.3.5 Gamma Rays (Gamma or γ Radiation)

Gamma rays are physically of the same character as X-rays with a great ability to penetrate matter. The injurious effects of radioactivity are connected with this type of radiation. Immediately after a decay of α or β type, the daughter nuclei are excited. They have energy in excess, which leads to a regrouping of the nucleons and the emission of electromagnetic radiation with short wavelength. This can be regarded as an echo of the material processes in the atomic nucleus, which are associated with radioactive decay.

52.3.4
Activity and Dose

The unit becquerel (Bq) measures the *activity* of the radiation. It gives no direct information about its injurious effect. A radioactive substance with high Bq value may be harmless if its distance is 100 m but highly dangerous if people eat it. To assess the health hazard, a different unit is needed, expressing the radiation energy that is absorbed by the tissues of the body. To evaluate the risk, the absorbed radiation in J/kg is multiplied by a *quality factor* Q (relative biological effectiveness): Q is 1 for γ, X and β^- radiation, while it is 20 for α radiation. The multiplication gives the *equivalent dose*, which is expressed in sievert (Sv) or millisievert (mSv).

The Swede Rolf Sievert was a pioneer within international radiation protection research. He took an active part in the foundation in 1928 of the International Commission of Radiological Protection (ICRP) and was its chairman from 1956 to 1962.

52.3.5
Radioactive Decay Series

If radioactive elements disintegrate, how is it possible that they still remain in the earth's crust after 4.5 billion years, which is estimated to be the age of the earth? Yet, some are not left – the exciting story about the search for element 43, technetium, tells us that (Chapter 28 Technetium). It is the same story for the rare earth element 61, promethium (Chapter 17 Rare earths). These elements may be found after reactions in a nuclear reactor, but they are short-lived. The most long-lived technetium isotope has a half-life of 4 million years; the most long-lived promethium isotope only 17.7 years. If they had been present at the creation of the earth, they would have disappeared long ago.

Other short-lived isotopes can, however, still be detected in nature. The element number 86, radon (Rn), has several isotopes, the most long-lived of which has a half-life of only 3.8 days. How is it then possible that we have radon problems in our mines and our houses? The answer is that radon certainly disintegrates rapidly but is also being formed continuously. Radon is part of the *radioactive uranium decay series*[1]:

$$^{238}\mathrm{U} \rightarrow {}^{234}\mathrm{Th} \rightarrow {}^{234}\mathrm{Pa} \rightarrow {}^{234}\mathrm{U} \rightarrow {}^{230}\mathrm{Th} \rightarrow {}^{226}\mathrm{Ra} \rightarrow {}^{222}\mathrm{Rn} \rightarrow {}^{218}\mathrm{Po} \rightarrow {}^{214}\mathrm{Pb} \rightarrow$$
$$^{214}\mathrm{Bi} \rightarrow {}^{214}\mathrm{Po} \rightarrow {}^{210}\mathrm{Pb} \rightarrow {}^{210}\mathrm{Bi} \rightarrow {}^{210}\mathrm{Po} \rightarrow {}^{206}\mathrm{Pb}\ \text{(stable)}$$

Uranium-238 (^{238}U) has a half-life of 4.5 billion years. This value is of the same magnitude as the age of the earth. Thus for ^{238}U only one half-life has passed. Referring to our radon example, ^{226}Ra emits α particles and forms ^{222}Rn, which also disintegrates with the emission of α particles and forms ^{218}Po.

Other natural decay series originate with thorium and actinium. Radon is also an intermediate link in the former, the *radioactive thorium decay series*[1]:

$$^{232}\mathrm{Th} \rightarrow {}^{228}\mathrm{Ra} \rightarrow {}^{228}\mathrm{Ac} \rightarrow {}^{228}\mathrm{Th} \rightarrow {}^{224}\mathrm{Ra} \rightarrow {}^{220}\mathrm{Rn} \rightarrow {}^{216}\mathrm{Po} \rightarrow {}^{212}\mathrm{Pb} \rightarrow {}^{212}\mathrm{Bi} \rightarrow$$
$$^{208}\mathrm{Tl} \rightarrow {}^{208}\mathrm{Pb}\ \text{(stable)}$$

The starting element ^{232}Th is very long-lived. Its half-life is 14 billion years.

---

1) In three positions of the uranium series and two of the thorium series, alternative decay pathways are possible.

52.4
Henri Becquerel Discovers Radioactivity

Just before the start of the 20th century, several important discoveries were made within physics and chemistry. Two dealt with radiation.

52.4.1
X-rays

Wilhelm Roentgen (1845–1923) worked in the Physical Institution at the Julius-Maximilian University in Würzburg, Germany. As many other scientists at this time, he investigated the radiation emitted from a cathode ray tube. In November, 1895, he made a remarkable discovery. Outside the tube he had placed a paper coated with barium platinocyanide. It fluoresced while the tube was in operation. He tried to stop the radiation with black paper round the tube. The platinum compound glowed in spite of that. Nor could lead stop the radiation. Wilhelm Roentgen had seen what no man had observed before: the effect of X-ray radiation. The discoverer himself coined the term "X-ray", and this designation is still used in many countries. On December 28 he published his discovery in the university's own journal, and before the New Year he made an X-ray picture of his wife's hand. The bones in it were clearly visible. The picture was sent to a colleague in Vienna and the innovation was soon known even outside the circle of physicists. On January 5, 1896, the newspaper *Die Presse* made it known that it was now possible to look through a man. The novelty was spread over the world. In 1901 Wilhelm Roentgen became the first winner of the Nobel Prize for physics.

The principle of the X-ray tube is shown in Figure 52.2. It consists of a glass vacuum tube in which X-rays are generated. Electrons are accelerated from the hot cath-

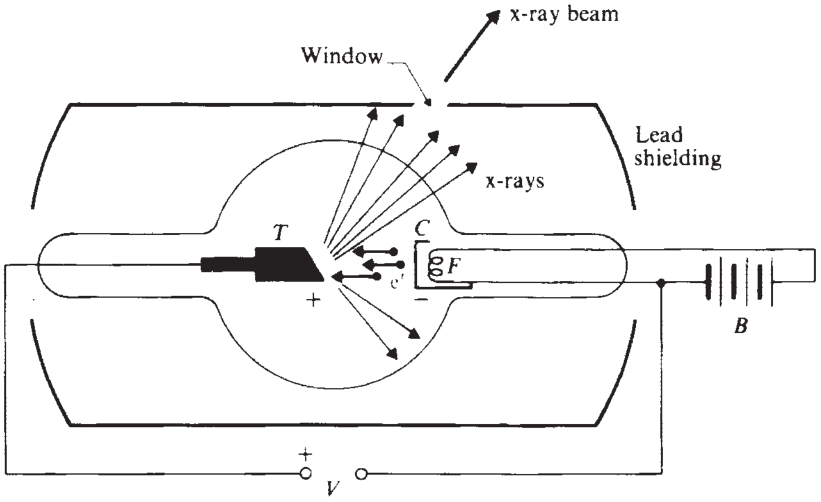

Figure 52.2 X-ray tube. (Reprinted from ref. [52.3].)

ode filament F towards the anode surface T, where X-rays are produced. A window allows the produced X-rays to escape from the tube housing.

52.4.2

Uranium Radiation

Henri Becquerel (1852–1908) grew up in Paris. His father Alexandre-Edmond Becquerel was a professor of applied physics and had done research on solar radiation and on luminescence[2]. Henri studied at the Polytechnic from 1872. In 1892 he was appointed Professor of Applied Physics in the Department of Natural History at the Paris Museum. He became a professor at the Polytechnic in 1895.

In 1889, still very young, Henri Becquerel was elected a member of the *Académie des Sciences de France*. His membership there came to be important in connection with the discovery of uranium radiation. The Becquerel family, Henri's father Alexandre-Edmond and also his grandfather Antoine-Edmond, had been passionately interested in luminescence. Henri himself had, for his father's investigations, prepared beautiful crystals of potassium uranyl sulfate, a substance with fluorescing properties. In his earliest scientific work he also was concerned with the phenomenon of phosphorescence and with the absorption of light by crystals (the subject of his doctoral thesis).

When, in early 1896, Henri heard about Roentgen's discovery, he was excited. Could the X-rays be a special form of fluorescence? As Becquerel himself tells it [52.4]:

> The idea of examining whether bodies could emit an invisible and penetrating radiation was suggested to me by the announcement of the first experiments of Roentgen. Poincaré[3] showed the first radiographs of Roentgen at the Academy of Sciences in Paris on January 20th, 1896, and in an answer to a question from me [Becquerel] stated that the source of the rays was the luminous spot on the wall of the glass tube, which received the cathode stream. I immediately thought of examining whether this new emission was caused by the vibratory movement, which gave rise to the phosphorescence, and whether all phosphorescent bodies could emit similar rays. At this epoch no one imagined … that it was natural to suppose that a transportation of energy must be going on.

---

[2] *Phosphorescence* is one type of *luminescence* (from the Latin *lumen* meaning "light"). Another is *fluorescence*. When certain materials absorb energy (from sunshine or from a UV lamp), the electrons become excited and jump from the inner orbits of the atoms to the outer ones. When an electron falls back to its original state, a photon of light is emitted. The interval between the two steps may be short or long. If the interval is short, the process is called *fluorescence*. It means that the emission of light ceases as soon as the primary source, such as the UV lamp, is switched off. If the interval is long and the emission continues after the source has been switched off, the process is called *phosphorescence*. When yellow phosphorus oxidizes in air, emitting green radiation, this is neither phosphorescence nor fluorescence but another type of luminescence called *chemiluminescence*.

[3] Jules Henri Poincaré became Professor of Mathematical Physics and Mechanics at the University of Paris in 1885. In 1887, two years before Becquerel, he was elected a member of the Académie des Sciences.

Just 10 days later Poincaré wrote an article on Roentgen rays in *Revue Générale des Sciences*, in which he said:

> Thus it is the glass which emits the rays, and it emits them by becoming fluorescent. May we ask, therefore, whether all bodies whose fluorescence is sufficiently intense may not emit, beside luminous rays, the X-rays of Roentgen, whatever may be the cause of their fluorescence? These phenomena would then be no more connected by an electric stimulus. It may not be very probable, but it is possible, and doubtless easy enough to verify.

In those days of 1896 science stood at the crossroads. Roentgen's rays were a new hard fact. The radiation due to luminescence was well known and had been studied for a long time. We must remember that radioactivity was quite unknown. It was discovered in those days during experiments intended for quite other purposes. What Becquerel wanted to verify was the connection between the two phenomena, X-rays and fluorescence. Uranium compounds had good fluorescing properties and could be suitable to use. He had prepared, 15 years earlier, crystals of potassium uranyl sulfate for his father's investigations and he now utilized them for his own experiments. He knew very well that they phosphoresce on exposure to light. When the salts were placed near to a photographic plate, the effect was indeed confusing. Even if the plate was covered with opaque paper, the plate was fogged (Figure 52.3).

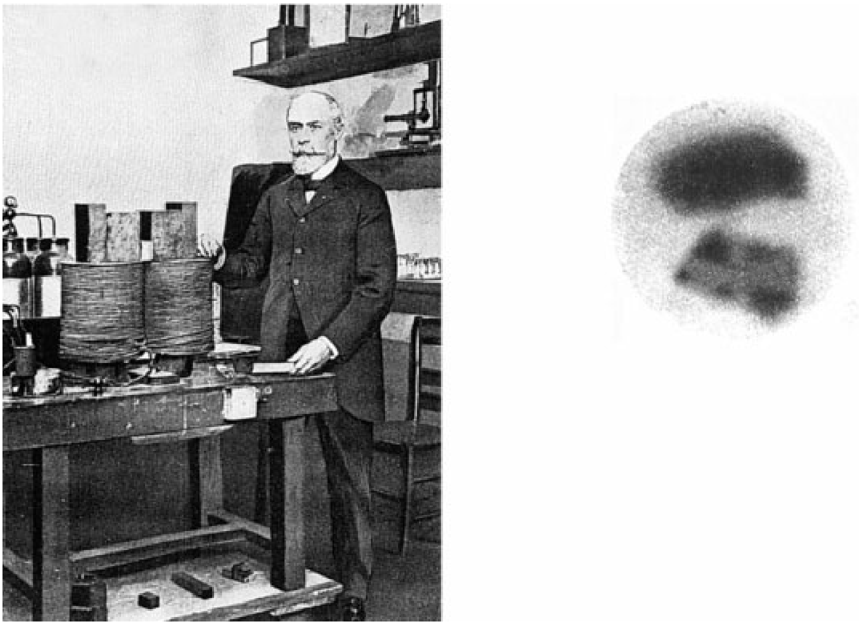

Figure 52.3 Henri Becquerel (1852–1908) discovered the radiation from uranium. In 1896 he placed small pieces of a uranium salt on a photographic plate. The plate was exposed, as shown in the figure on the right. This was the first indication of the decay of atoms. (Reprinted from ref. [52.5].)

Becquerel had carried out his experiments during the last days of February, 1896, and on March 2, 1896, he reported the results to the French Academy of Sciences. His very important report had the title "On the invisible rays emitted by phosphorescent bodies". The translation by C. Giunta [52.6] is quoted here:

> In the previous session, I summarized the experiments which I had been led to make in order to detect the invisible rays emitted by certain phosphorescent bodies, rays which pass through various bodies that are opaque to light.
>
> I was able to extend these observations, and although I intend to continue and to elaborate upon the study of these phenomena, their outcome leads me to announce as early as today the first results I obtained.
>
> The experiments which I shall report were done with the rays emitted by crystalline crusts of the double sulfate of uranyl and potassium [$SO^4(UO)K+H^2O$], a substance whose phosphorescence is very vivid and persists for less than 1/100th of a second. The characteristics of the luminous rays emitted by this material have been studied previously by my father, and in the meantime I have had occasion to point out some interesting peculiarities which these luminous rays manifest.
>
> One can confirm very simply that the rays emitted by this substance, when it is exposed to sunlight or to diffuse daylight, pass through not only sheets of black paper but also various metals, for example a plate of aluminium and a thin sheet of copper. In particular, I performed the following experiment:
>
> A Lumière plate with a silver bromide emulsion was enclosed in an opaque case of black cloth, bounded on one side by a plate of aluminium; if one exposed the case to full sunlight, even for a whole day, the photographic plate would not become clouded; but, if one came to attach a crust of the uranium salt to the exterior of the aluminium plate, which one could do, for example, by fastening it with strips of paper, one would recognize, after developing the photographic plate in the usual way, that the silhouette of the crystalline crust appears in black on the sensitive plate and that the silver salt facing the phosphorescent crust had been reduced. If the layer of aluminium is a bit thick, then the intensity of the effect is less than that through two sheets of black paper.
>
> If one places between the crust of the uranium salt and the layer of aluminium or black paper a screen formed of a sheet of copper about 0.10 mm thick, in the form of a cross for example, then one sees in the image the silhouette of that cross, a bit fainter yet with a darkness indicative nonetheless that the rays passed through the sheet of copper. In another experiment, a thinner sheet of copper (0.04 mm) attenuated the active rays much less.
>
> Phosphorescence induced no longer by the direct rays of the sun, but by solar radiation reflected in a metallic mirror of a heliostat, then refracted by a prism and a quartz lens, gave rise to the same phenomena.
>
> I will insist particularly upon the following fact, which seems to me quite important and beyond the phenomena which one could expect to observe: The same crystalline crusts, arranged the same way with respect to the photographic plates, in the same conditions and through the same screens, but sheltered from the excitation of incident rays and kept in darkness, still produce the same photographic images. Here is how I was led to make this observation: among the preceding experiments, some had been prepared on

> Wednesday the 26th and Thursday the 27th of February, and since the sun was out only intermittently on these days, I kept the apparatuses prepared and returned the cases to the darkness of a bureau drawer, leaving in place the crusts of the uranium salt. Since the sun did not come out in the following days, I developed the photographic plates on the 1st of March, expecting to find the images very weak. Instead the silhouettes appeared with great intensity. I immediately thought that the action had to continue in darkness, and I arranged the following experiment:
>
> At the bottom of a box of opaque cardboard I placed a photographic plate; then, on the sensitive side I put a crust of the uranium salt, a convex crust which only touched the bromide emulsion at a few points; then, alongside, I placed on the same plate another crust of the same salt but separated from the bromide emulsion by a thin pane of glass; this operation was carried out in the darkroom, then the box was shut, then enclosed in another cardboard box, and finally put in a drawer.
>
> I did the same with the case closed by a plate of aluminium in which I put a photographic plate and then on the outside a crust of the uranium salt. The whole was enclosed in an opaque box, and then in a drawer. After five hours, I developed the plates, and the silhouettes of the crystalline crusts appeared in black as in the previous experiments and as if they had been rendered phosphorescent by light. For the crust placed directly on the emulsion, there was scarcely a difference in effect between the points of contact and the parts of the crust which remained about a millimetre away from the emulsion; the difference can be attributed to the different distance from the source of the active rays. The effect from the crust placed on a pane of glass was very slightly attenuated, but the shape of the crust was very well reproduced. Finally, through the sheet of aluminium, the effect was considerably weaker, but nonetheless very clear.
>
> It is important to observe that it appears this phenomenon must not be attributed to the luminous radiation emitted by phosphorescence, since at the end of 1/100th of a second this radiation becomes so weak that it is hardly perceptible any more.
>
> One hypothesis which presents itself to the mind naturally enough would be to suppose that these rays, whose effects have a great similarity to the effects produced by the rays studied by M. Lenard and W. Röntgen, are invisible rays emitted by phosphorescence and persisting infinitely longer than the duration of the luminous rays emitted by these bodies. However, the present experiments, without being contrary to this hypothesis, do not warrant this conclusion. I hope that the experiments which I am pursuing at the moment will be able to bring some clarification to this new class of phenomena.

His report awakened very little interest from the Academy members. The blackened plates were put into the shade by the X-rays. Six reports on the X-ray theme were read at the March 2 meeting and a further six were announced to the next.

The consequence of Becquerel's results was however that the observed uranium phenomena were not caused by phosphorescence. Instead it was a question of a fundamentally new fact, the emission of radiation not earlier observed. The phenomenon was found to be common to all uranium salts, and was concluded to be a property of the uranium atom. Gradually it obtained the designation *uranium radiation*. Becquerel had discovered “radioactivity”, but Marie Curie was the first to use that designation.

Becquerel made an additional important discovery about his uranium radiation. A gold leaf electroscope was charged and the leaves separated. Different substances, placed in its vicinity, had no effect on the position of the gold leaves. Under the influence of a uranium salt, the leaves however fell down. The gold leaf electroscope is not an instrument of precision, nor is it very sensitive. The experiment however demonstrated that uranium radiation cooperates with electricity. This property made it possible for Pierre Curie to develop equipment for quantitative radiation measurement.

The radiation that Becquerel had discovered was a powerful tool in the coming search for atomic structure. It gradually also became utilized in medicine and for generating energy to an extent beyond previous comprehension. But people were unaware of these things when Becquerel made his first experiments and reported the results to the Academy, listening with absent-mindedness, in Paris on March 2, 1896. Nor was the listener aware of the coming fission of uranium atoms.

There were in fact good reasons for the lack of interest. Uranium salts had been known for more than one hundred years. M. H. Klaproth had discovered the element in Berlin in 1789. He named it after Uranus, the very first of the Greek gods, the father of them all. That had been over-ambitious. The insignificant metal had, during that hundred years, existed only in a remote corner of the element family. Its oxide U_3O_8 had a certain use for coloring glass yellow and green. That was all.

Becquerel was systematic, as can be expected of a professor of physics. He questioned whether the radiation he had discovered was related just to the uranium salts he had investigated, or whether it might also emanate from uranium in an ore. He obtained such ore from Joachimsthal, situated in the Bohemian part of Erzgebirge [52.7]. There an ore was won that contained *pitchblende* (Figure M76), a uranium oxide. It could be expected that uranium in an ore acted in the same way as uranium in a salt. The photographic effect ought however to be reduced, due to the lower content of uranium. The investigation became a great surprise. The ore from Bohemia had a much greater effect on the photographic plate than could be expected from its content of uranium. Why? Is there any substance in the ore that influences a photographic plate more than uranium itself? It must be investigated!

In France, Becquerel was almost alone in the research on uranium radiation. At the University of Sorbonne, a young Polish woman, Marie Sklodowska, studied and worked. She had been married for one year to a Frenchman, the physicist Pierre Curie. Professor Becquerel had observed her. She seemed to be clever and skilled in experimental work. He told her about his findings and put a straight question to her. Would she work with uranium radiation? The answer was yes.

52.5
Marie Sklodowska-Curie (1867–1934)

52.5.1
A Young Girl Fights for Herself and Her People

The teacher and principal *Wladyslaw Sklodowski* was about the same age as Mendeleev. He had studied science in St Petersburg in the middle of the 19th century, when also Dimitri Mendeleev was active there. He returned to Poland and in 1868 was a teacher of physics at a high school in Warsaw. The year before, his youngest child Marie was born. His wife Bronsitwa Boguska had been working as the headmistress of a girls' school but got tuberculosis and died when Marie was 11. The father now had to take responsibility, not only for teaching and duties as a principal, but also for the care of Marie and her three sisters and one brother.

Three fields in Marie's education were important to her: Polish literature, poetry and prose; the political liberation of Poland; and – due to her father's influence – science. At this time Poland's independence was lost. Russia had captured Warsaw in 1831, Poland's constitution was abolished, and Polish independence was ended for more than a century. All teaching was fulfilled in the Russian language, and Polish was not allowed. About 1885, when Marie and her young Polish comrades were 15–20 years of age, the situation for education and liberation was bad, especially for young women.

In the last decades of the 19th century, Europe experienced a great enthusiasm for technology and science. Considerable progress was made within physics and chemistry. Industry and communications experienced quite new conditions as a result of the development of electricity. The influence of all this also reached Poland. Education, especially in science, was the key to this fascinating world, but women in Poland did not have access to higher education. Marie and her sister Bronya joined other friends in attending the "Floating University". It had this name because its classes met in changing locations, in order to avoid the watchful eyes of the Czarist authorities. The fact that education was given in Polish, and also that new political theories were treated, was dangerous.

Paris was at this time a center of attraction regarding both science and striving for political liberty. Many Polish insurgents had emigrated, and several young people had gone to Paris for their studies. Marie's sister Bronya had done so to study medicine. Marie wished to follow her. She still lacked real laboratory experience, however, and she hoped to gain some before her departure. The Museum of Industry and Agriculture in Warsaw presented the opportunity. It was a laboratory aimed at training Polish scientists. Marie's cousin Joseph Boguski helped her. He was responsible for the laboratory and arranged for Marie to have an intensive chemistry course on Sundays and evenings. Joseph had been an assistant to Dimitri Mendeleev and could certainly convey lots of direct information that could fill his young student with enthusiasm.

Finally, in the fall of 1891, at the age of 24, Maria Sklodowska set out for Paris. Some very hard and laborious years followed.

It is told by Jaffe [52.7] that Marie should have met Mendeleev during this preparatory time in Warsaw. The fact that his former assistant Boguski ran the Museum of Industry makes it probable that Mendeleev paid a visit there in connection with some journey. And he would have found Marie Sklodowska, daughter of the old Petersburger Wladyslaw Sklodowski, working in the laboratory. Obviously the girl had impressed him favorably. Mendeleev had encouraged her and predicted a bright future if she stayed with chemistry. Even if she took his words just as an expression of kindness from the nice old man, the speech was certainly significant for the young girl. Considering the elements that Mendeleev had anticipated before their discovery, he has been called a prophet of science. His talk to Marie Sklodowska at the end of the 1880s – if it really took place – also contained a prophecy that was fulfilled. Mendeleev lived to see Marie Sklodowska discover the elements *polonium* and *radium* in 1898 and be awarded the Nobel Prize in 1903.

52.5.2
First Degrees and a Happy Time

In the fall of 1891 Marie enrolled at the Sorbonne. She had to live somewhere – at first in the home of her sister Bronya; after some time in a small garret, cold in winter, hot in summertime, but nearer the Sorbonne. Paris offered the possibility for studies and perhaps ... perhaps a career within science. That was an unrealistic dream. Science was something for men. The young Polish woman was however obsessed by her will to succeed. Had not her father, whom she admired so much, believed in her? And who, among the self-confident French students just on the point of going into the Sorbonne, had a personal exhortation of the great Mendeleev to study chemistry. None! But she had.

And her diligence paid off. In 1893 and 1894 she undertook her first degrees in physics and mathematics. Her economic situation however was a permanent concern. Then she received information from Warsaw that she had been awarded the *Alexandrowitch scholarship* intended for Polish students abroad. A miracle! The amount, 600 roubles, was enough for her to live for 15 months.

In Paris at this time existed the *École de Physique et de Chimie Industrielle*. There Pierre Curie (1859–1906) worked on research on the magnetic properties of materials. He had identified a temperature above which a material's magnetic properties disappear. It is still known as the *Curie point*. By 1880 he and his brother Jacques had discovered *piezoelectricity*, showing that a pressure applied to some special crystals resulted in the creation of an electric potential.

In 1894, Marie met the eight years older Pierre. They became friends and colleagues in materials research. And still more. The year after they met, they married. Marie's father arrived from Warsaw for the simple wedding celebration. After the wedding they continued their assignments. Marie completed her studies and did some work at the *École Industrielle*. One day Professor Henri Becquerel paid a visit to Madame Curie and asked if she would examine pitchblende. Marie and her husband Pierre realized that research on uranium radiation could be an excellent field for

Marie's further studies towards gaining a doctor's degree. So Marie answered "yes". That decision was the start of something very important in the history of science.

52.6
Marie Curie's Work for Her Doctor's Degree

52.6.1
A Simple Problem Analysis

In 1897 Marie was preparing to continue her studies. The first degrees were completed, she was certificated as a teacher, and she had her first child, daughter Irène. It could be time to go further for her doctor's degree. Professor Becquerel's rays fascinated. Likewise the uranium mineral pitchblende that gave stronger radiation than pure uranium salts. It was a scientific mystery and a challenge. She also felt she had all the support she needed from her husband.

In Becquerel's first investigations, important observations had been made. From a scientific point of view, however, his method of measurement was unsatisfactory. The observations were only qualitative or possibly semi-quantitative. Results of the type "substance X blackens a photographic plate more than a substance Y" could not be a good basis for working through the subject field thoroughly. The doctoral candidate Marie, however, had a much better foundation from which to tackle this difficult problem. Her husband Pierre and his brother Jaques had developed new equipment, an *ionization chamber* (Figure 52.4), which made it possible to make quantitative measurements of the effect of so-called ionizing radiation. For research on Becquerel's radiation, this was of critical importance.

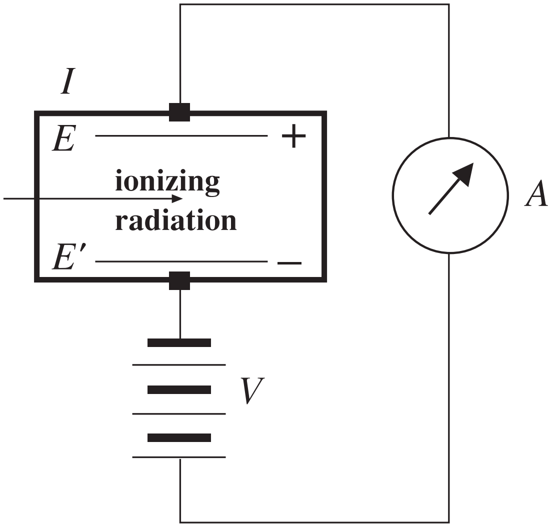

Figure 52.4 Principle of an ionization chamber.

An ionization chamber consists of a container, filled with gas at atmospheric pressure. Two electrodes, E and E′, in the container are given a high DC potential. Ionizing radiation entering the chamber removes electrons from the outer shells of the atoms in the chamber gas. The gas becomes conductive and a current pulse is recorded. (The Geiger counter for detecting radioactivity is a modern application of this principle.) With this equipment available, and with the assistance of her husband, Marie Curie could set to work with a systematic search. First she changed the designation "Becquerel radiation" to *radioactive radiation* and she discovered that not only uranium minerals but also thorium minerals give a radioactive radiation.

Marie Curie was the first to establish that radioactivity is an atomic property and independent of the origin and history of the radioactive element. Nor has chemical treatment or chemical binding any importance. For uranium radiation, Marie and Pierre made an important analysis of the problem: If the radioactivity of the ore in Joachimsthal is caused by uranium, the waste products after the uranium concentrate is produced should have no or low radioactivity. The reality was the contrary. The waste products were *more* radioactive than the ore. Thus one or more elements were hidden in the ore and did not follow uranium in the chemical treatment. Which elements were the carriers of this high radioactivity? Of the elements known at the turn of the century, not one had such high radioactivity that its presence in the ore could explain the strong radioactivity observed. The necessary consequence gave the scientists shudders of excitement. The radioactivity was the sign of the presence of one or more unknown elements with strong radioactivity.

52.6.2
Concentrated and Enriching Work

In the uranium mine at Joachimsthal in Bohemia, an ore with up to 15% U_3O_8 was won. With a dressing by hand, the gangue was removed and a concentrate with 65–70% U_3O_8 was obtained. It was roasted with soda and saltpeter at 800°C. The sodium uranate formed was leached out with sulfuric acid. From the solution, uranium oxide for sale was prepared. The residue after leaching, about one-third of the original ore weight, was waste. Some tonnes of this material, containing silicates, lead and calcium sulfate, aluminum and iron oxides, were placed at the Curies' disposal. The main components of this waste were of little interest. Nevertheless, the material was of utmost importance. Which trace elements did it hide?

The two scientists realized that there were small prospects of success by a random search for new elements in the huge amount of waste rock. Instead, they decided to dissolve a certain quantity in acid and examine the solution with the separation methods known from classical chemical analysis. The unknown elements would then be enriched in those fractions with which they have a chemical similarity. With the ionization chamber, they could measure the radioactivity of the different fractions. It was hard work in a damp room of a shed near Pierre's School of Physics, more like a barn or a potato-cellar than a laboratory.

The raw material was treated, of course manually, in batches of up to 20 kg. The fractions were saved and combined with the corresponding fractions from other batches, treated in the same way. The shed was filled with large receptacles, containing precipitates and solutions. It was a problem to keep the survey and to plan for the next step. The situation was also complicated by the fact that Marie and Pierre were physicists more than chemists. Because of that, they contacted a clever chemist, *André Debierne*, active in Professor Friedel's laboratory at the Sorbonne. From him they got a lot of good advice and he took an active part in the research.

52.6.3
The Discovery of Polonium

Mendeleev's eka-boron (scandium) had been discovered in 1879, eka-aluminum (gallium) in 1875, and eka-silicon (germanium) in 1886. In his book *Principles of Chemistry*, 1891, the Russian chemist continued his prophetic activity and anticipated an element with properties similar to those of tellurium and with an atomic weight of about 212. The element then would be in a position to the right of bismuth in the periodic table.

> In their hunt for new elements, Marie and Pierre Curie treated a batch of material with strong hydrochloric acid. Both the solution and the insoluble residue were radioactive. From the hydrochloric acid solution, sulfides were precipitated with hydrogen sulfide. The radioactivity followed bismuth. André Debierne introduced a modified technique. An iron foil was placed in the acid solution. Metals nobler than iron, thus copper, lead and bismuth, precipitated, at least partially. The radioactivity followed this metallic fraction. The precipitate was again dissolved in hydrochloric acid. Now a copper foil was introduced. A precipitate was obtained even now, but small and almost invisible – small, but the carrier of the whole activity. This precipitate was again dissolved in hydrochloric acid and something unknown in the solution was precipitated by addition of stannous chloride $SnCl_2$. When filtered off, it was shown that its radioactivity was 3500 times greater than that of pure uranium. A further purification was made by hydrogen sulfide precipitation, dissolution and finally electrolytic precipitation.

Some tonnes of raw material had been treated. The amount precipitated by electrolysis was 0.002 g, with an estimated quantity 0.0001 g of a new element. This new element was given the name *polonium* (Po) after Marie's native country. Polonium was the first element whose discovery was based on radioactive measurements. The isotope found in Curie's and Debierne's investigations was ^{210}Po with a half-life of 138 days. In nature polonium exists only in equilibrium with its mother substances in different decay series. If separated from its environment, it disintegrates to lead.

52.6.4
The Discovery of Radium

In their systematic investigation of how the radioactivity appeared in the different fractions, the Curies discovered that a radioactive element followed barium. After fractional crystallization of (a contaminated) barium chloride, they observed that the radioactivity increased in fractions with lower solubility. In the course of this investigation, they contacted *Eugène-Anatole Demarçay*. He worked in Paris with rare earth metals and discovered the element *europium* (see Chapter 17 Rare earths). He had great experience of fractional crystallization and he had also developed a special spectral analytical technique for identification of rare earth metals. With his new spectroscope, lines of a previously unknown element were observed in the less soluble barium chloride fractions. The crystallization was continued and the crystals were examined with spectral analysis and radioactivity measurements. Finally a substance was obtained with a spectrum clearly of the same type as that of the alkaline earth metals. Barium lines had disappeared and no lines from other known alkaline earth metals could be found. A new element had been discovered. Its chloride showed such strong radiation that it shone in darkness. Because of that, Marie and Pierre Curie named it *radium* (Ra). They calculated the atomic weight of the new element from the weight ratio between the radioactive chloride $RaCl_2$ and an equivalent amount silver chloride AgCl. From this ratio they got the atomic weight 225 for radium. In 1907 Marie Curie made new determinations, utilizing a greater sample quantity. Then she got the result 226.4. Today the accepted value is 226.02.

52.7
Marie Curie's Later Life ... and Death

52.7.1
Rewarded for Her Genius

In June, 1903, Marie Curie defended the thesis for her doctorate [52.8], based on the results she had obtained. It was a remarkable occasion, partly because she was the first woman to receive a doctorate in France, but above all for the content of the dissertation. It has been said that it certainly is the most important doctoral thesis ever.

Already in the same year, together with Pierre Curie and Henri Becquerel, she got the Nobel Prize for physics. The description of the further success and worldwide public attention is not a subject of this book. Few have been so exhaustively portrayed as Marie Curie (Figure 52.5). Her own daughter wrote a well-known biography [52.9].

Not surprisingly the Nobel Prize influenced Pierre and Marie's situation in France. Pierre Curie was appointed Professor of Physics at the Sorbonne and Marie, for the first time in her career, got both a title – Chief of Laboratory – and a university salary. Marie was satisfied but expressed that:

> ... it was not without regret that we left the School of Physics, where we had known such happy work days, despite their attendant difficulties.

Figure 52.5 Marie and Pierre Curie, portrayed on the cover of a French magazine. The year was 1904 and the scientists were already renowned for their discoveries. (Reprinted from ref. [52.5].)

52.7.2
The Tragedy of Death

On April 19, 1906, Pierre was on his way home from a meeting. Hurrying to cross a street, he was run over by a horse-drawn wagon with a heavy load. He was killed instantly. After this tragic event, Marie had to solve, alone, without her life companion, the many new, waiting assignments. Less than a month after the accident, the university offered her the chance to take up Pierre's academic post. By accepting, she hoped to honor the memory of Pierre. She started to create a scientific institution with better laboratory facilities than had been at Pierre's disposal.

52.7.3
Curie and Debierne Prepare Radium Metal

Metallic radium was prepared in 1910 by Marie Curie and André Debierne. They used 0.1 g of radium chloride and carried out an electrolytic reduction on a mercury cathode. When the liquid amalgam that had been formed was heated, mercury distilled off and elementary radium was isolated.

52.7.4
An Unprecedented Second Nobel Prize

In 1911 Marie Curie was awarded a second Nobel Prize, this time in chemistry. At the ceremony in Stockholm on December 10, 1911, the President of the Royal Swedish Academy of Sciences expressed the opinion that Marie Curie's achievements deserved an additional, and chemical, recognition:

> … for her services in the advancement of chemistry by the discovery of the elements radium and polonium, by the isolation of radium and the study of the nature and compounds of this remarkable element.

It was also a remarkable honor, as no other person, before or after, has been awarded the Nobel Prize in both physics and chemistry.

52.7.5
A Victim of Radioactivity

Radium metal has a bright luster and has many similarities with barium. And yet it is completely different. Its radioactivity is strong and dangerous. During Marie Curie's whole adult life, she was exposed to large radiation doses. When she died in 1934, at the age of 67, the cause of death was leukemia.

52.8
Radium – its Importance and Use

Radium has played a great role in the exploration of knowledge about the atom. By combination of the alpha radiator radium with beryllium, the first neutron source was created. During the first decades of the 20th century, radium had a large medical use for combating tumors and for treatment of rheumatic complaints. Radium institutes and "radium homes" were established in different parts of the world. They still existed in the 1950s. Today new medical techniques have been developed.

Radium was also utilized in self-luminous paints for watch, clock and instrument dials and for emission in automatic control systems. Safer radioisotopes for technical properties, such as cobalt-60 and cesium-137, can nowadays be tailored in nuclear reactors and have entirely replaced radium. This has released us from the need for radium, which is a great advantage, as radium is so difficult to handle from an environmental point of view. It forms gaseous radon, affecting its surroundings. And the problem remains for a long time, as the most usual radidum isotope, ^{226}Ra, has a half-life of 1600 years. Nowadays the use of radium has ceased. The annual amount manufactured is only round 100 g.

52.9
Two Other Key Radioactive Elements

52.9.1
Actinium

52.9.1.1 The Discovery of Actinium

It was mentioned above that the two Curies had called upon André Debierne for chemical support in the separation of the pitchblende residues. In that connection he made his own element discovery in 1899.

From a solution containing iron and some rare earth metals, Debierne precipitated a mixture of hydroxides. It was radioactive, an activity that could not have its origin in uranium, radium or polonium. A new element could be isolated by fractional crystallization of magnesium lanthanum nitrate. The element was named *actinium* after the Greek word *aktinos*, meaning "ray". Actinium metal has been prepared by the reduction of actinium fluoride with lithium vapor at about 1100 to 1300°C.

52.9.1.2 The Actinides

Element number 89, actinium, is chemically similar to number 57, lanthanum, which makes the placing of the element 89 in group 3 logical. In the 6th period we have met (Chapter 17) the element lanthanum and the 14 following lanthanides (58–71). In a corresponding way the followers of actinium in period 7 constitute the *actinides* (elements 90–103). The actinides among the "natural" elements up to number 92 are thorium (Th), protactinium (Pa) and uranium (U). The synthesizing of the actinides after uranium is treated in section 52.16.

52.9.2
Radon

52.9.2.1 Radioactive "Infection"

Marie and Pierre Curie examined the radiation emitted by radium. They found that all substances near the radiation source became radioactive themselves. The activity even remained some time after the removal of the emitting radium. It was questioned whether there is some "radioactive force" that was transferred with the radiation and was induced in the receiving substance. In 1900 *F. Dorn* in Halle, Germany, reported on a study of an isotope emanating from radium and, because of that, certainly incorrectly, was credited with the discovery of radon. In fact *Ernest Rutherford* (1871–1937) and *Frederick Soddy* (1877–1956) were the first to isolate radon and also the first to really understand the nature of radon. In the first decade of 1900 they worked at McGill University in Montreal, Canada, and carried out very comprehensive work on radioactivity [52.10]. They discovered that the *emanation* from radium was a gas of the same type as the noble gases. Ramsay at University College in London completed the spectral work. He showed that the spectrum of radon resembled that of xenon. He also showed that the formation of radon was accompanied by the simultaneous production of helium, as he also observed *its* spectrum. This observation by Ramsay was a key investigation in deciphering the structure of the atom. Rutherford and Soddy clearly realized how radium disintegrates into both radon and helium (α particles). They became the first to conclude that radioactivity is a phenomenon of natural and spontaneous transmutation of elements, involving atomic disintegration with the formation of new kinds of matter.

52.9.2.2 **Emanation – Niton – Radon**

The scientific world accepted the term *emanation*. However, in 1910 Ramsay suggested the name *niton* from a Greek word meaning “shining”. The reason was the appearance of the condensed, liquid element. However, the International Committee on Chemical Elements decided in 1923 in favor of the name *radon*, expressing its daughter relationship to radium.

52.9.2.3 **Radon Is Unstable**

In 1923 F. Aston searched for the new gas in common air. He let as much as 400 tonnes of air pass over a bed of charcoal for adsorption of radon. After that a mass spectrographic analysis was carried out. The result was negative, indicating that stable or very long-lived isotopes of radon do not exist. Considerations of nuclear physical character also suggest that radon should not have stable isotopes.

52.9.2.4 **Radon in Nature, Buildings and Mines**[4]

Radon is part of both the uranium and thorium decay series (see section 52.3.5). In the uranium series:

$$^{238}\mathrm{U} \rightarrow \ldots \rightarrow {}^{226}\mathrm{Ra} \rightarrow {}^{222}\mathrm{Rn} \rightarrow {}^{218}\mathrm{Po} \rightarrow \ldots$$

radon is formed from ^{226}Ra and disintegrates to ^{218}Po. The half-life of the main isotope ^{222}Rn is 3.8 days. Radon, as a gas, carries a radioactive “infection” from the original radiation source (a uranium ore, for instance) and may place it in the lungs of a man. There the disintegration process continues, now locked in the tissue. It may result in the formation of cancerous tumors.

The effects of radon were observed long before knowledge of radioactivity was established. Miners in the south of Germany died in the 16th century of *Bergkrankheit* (mine disease), which later became known as lung cancer.

Radon in houses began to be observed in the 1950s. A great Swedish epidemiological investigation showed that the injurious effect of radon depends on whether a person is a smoker or not. For smokers, the number of additional lung cancer cases, due to radon, was about 400 per year. For non-smokers, no significant increase could be detected.

The radon content we get in a house depends on the type and composition of the ground material and how permeable it is. If clay, the radon cannot move very far before it disintegrates. The house will not be a “radon house”. If the ground material instead is gravel or sand, the radon can migrate a long distance before it disintegrates.

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[4] The information in this section is taken mainly from ref. [52.2].

It can penetrate into the house and be a risk. If the building material itself contains uranium, it may also be a source of radon.

For dwellings and factory premises, radon contents are expressed in terms of the radiation it causes. A recommendation is to restrict the radiation to 200 Bq/m^2 while the maximum allowed value is 400 Bq/m^2. The situation for a "radon house" can be improved rather simply by installation of a radon fan that ventilates the earth below the foundations. Minimizing indoor radon content should be a conscious measure to take in connection with the construction and building of a new house.

The radon content of drinking water ought also to be observed. Surface water normally has a low radon content, corresponding to round 20 Bq/l. In water from deep-bored wells the radon content is higher, often corresponding to 30–400 Bq/l. Water with more than 1000 Bq/l is not allowed as drinking water.

52.10
The Periodic Table Becomes Complete

Mendeleev noted in 1871 that there is a gap between thorium and uranium in the element system. Investigations by Henry G. J. Moseley, before his too early decease in 1915, confirmed this and furthermore that still undiscovered elements might be expected between polonium and radon and between radon and radium. The situation around 1915 is described by Table 52.1.

Table 52.1 Known and unknown elements in 1915[a)]

Number	84	*85*	86	*87*	88	89	90	*91*	92
Element	Polonium	*Unknown*	Radon	*Unknown*	Radium	Actinium	Thorium	*Unknown*	Uranium

a) Further unknown elements were numbers 43 (became known as technetium) and 61 (became known as promethium). The discoveries of these unknown elements are described by Wahl and Bonner [52.11].

52.10.1
Number 91, Protactinium – Discovered in 1913–1918

It was a mystery that actinium exists in nature. Its most long-lived isotope, ^{227}Ac, has a half-life of 22 years. It must have a long-lived precursor, from which it is continuously formed. Otto Hahn and Lise Meitner, working at the Kaiser-Wilhelm Institute for Chemistry, Berlin, were aware of that and started an examination of the siliceous residues of pitchblende. While Otto Hahn was absent due to service in the army, in 1918 Lise Meitner succeeded, by utilizing tantalum pentoxide as a carrier, in detecting a long-lived alpha emitter that could be the mother of actinium. Although she had not separated the element itself, she (and Otto Hahn) had discovered the new element number 91.

Five years earlier, in 1913, K. Fajans and O. Göhring in Germany studied the decay of ^{234}Th and found a short-lived isotope. They named the nuclide *brevium*, a name later changed to UX$_2$. It is now known as a short-lived isotope of element number 91. In 1918, Fajans published a new report, indicating the discovery of element number 91.

In Great Britain, F. Soddy, J. Cranston and A Fleck independently discovered the element at about the same time as Hahn and Meitner. All three groups of scientists are credited for the discovery.

The name *protactinium* Pa (from the Greek *protos*, meaning "first") was selected because the element was recognized as the originator of actinium. Pitchblende ores contain about 200 mg per tonne of both radium and protactinium. Natural protactinium is almost entirely the isotope ^{231}Pa with a half-life of 32 800 years. The American chemist Aristid Grosse first isolated 2 mg of protactinium in 1934. In about 1960 a large quantity of 125 g of protactinium with 99.9% purity was prepared in Great Britain by the Atomic Energy Authority. The extraction was made from 60 tonnes of waste material.

52.10.2
Number 87, Francium – Discovered in 1939

Marguerite Perey worked on the investigation of very pure actinium in France in 1939. She found α particles and could show that these did not come from protactinium. Moreover, she could follow an element growing in the actinium sample, an element with β activity. After dissolving the sample she found that the element with β activity did not follow barium in precipitation of barium carbonate. Nor did it follow lead in lead sulfide or cerium in cerium(IV) hydroxide precipitation. However, it was carried by cesium when cesium perchlorate was precipitated. Element number 87 ought to be an alkali metal, a new element that Margeruite Perey had discovered. She named it *francium* after her native country.

52.10.3
Number 85, Astatine – Discovered in 1940

Moseley demonstrated clearly that there was a gap and a missed element between polonium and radon. A discovery of this element, number 85, was announced in 1931 by a group of scientists at Alabama Polytechnic Institute. They had dissolved monazite in aqua regia and claimed, after examination with a magneto-optic method [52.12], that the sought element was present in the solution at a concentration corresponding to 0.000 0001% of the monazite weight. The element was named *alabamium* Ab after Alabama. The claim could not be verified and the discovery was not approved.

In Bern, *Walter Minder* examined polonium in 1940. He found β radiation. If it originated from polonium, this element had been transformed to element number 85:

$${}_{84}\text{Po} \rightarrow {}_{85}(\text{Unknown}) + {}_{-1}\beta$$

Although the element was not directly detected, he gave it the name *Helvetium* Hv after Switzerland. Nor could this discovery be verified, and no element named after Switzerland exists.

In the USA the problem was solved at the same time, 1940. D. Corson, K. MacKenzie and E. Segrè used the Berkeley 60-inch cyclotron and bombarded bismuth ^{209}Bi with energetic helium ions. The scientists expected the reaction:

$${}_{83}\text{Bi} + {}_{2}\text{He} \rightarrow {}_{85}(\text{Unknown}) + 2\,{}_{0}\text{n}$$

A balance for the atomic masses:

$$209(\text{Bi}) + 4(\text{He}) = X(\text{unknown element}) + 2 \cdot 1(\text{n})$$

gives X=211 for the mass of the unknown element. Thus an isotope with the mass number 211 ought to be present in the surface region of the target material. The new element could also be distilled from the target by heating in air.

The discoverers named the new element *astatine* At from the Greek word *astatos*, meaning “unstable”. Astatine is the only member of the halogen family without stable isotopes. This highly radioactive halogen behaves chemically very much like iodine. It is however said to be more metallic and, like iodine, it probably accumulates in the thyroid gland.

Astatine belongs to the most rare elements of all. Its total amount in the earth’s crust is estimated to some 20–30 grams. The isotope ^{211}At, which Segrè and co-workers discovered, has a half-life of 7.2 hours. A little more long-lived, 8.1 hours, is the ^{210}At isotope.

52.10.4
A Complete Periodic Table

The actinide elements missing in 1915 were all discovered in the period 1917–1940. Number 43 technetium was also discovered in 1940, so now only one of the 92 elements on earth was missing. It was number 61, *promethium* Pm, one of the rare earth elements. Its discovery in 1945 was described in Chapter 17 Rare earths.

52.11
Thorium as a Technological Metal

52.11.1
Occurrence

In the earth's crust thorium is almost four times more common than uranium, and the radioactive decay of thorium generates a considerable part of the geothermal energy. The primary source of thorium is *monazite* (Figure M25), a yellow or reddish-brown rare-earth phosphate. Seashore deposits at Travancore in India contain very big quantities of monazite. The mineral formula is $(Ce,La,Nd,Th)PO_4$ and the thorium content in monazite ores is 5–10%. In 2001 the production of monazite concentrate in the world was 5710 tonnes [52.13], of which India accounted for 5000 tonnes or 88%. Other producers were Brazil and Malaysia.

Monazite is recovered mainly for its content of rare earth metals, and thorium has to be separated. This has led to an overproduction of thorium oxide. The excess is stored for potential use or disposed of as a radioactive waste. Most producers of rare earths have however switched to thorium-free raw materials due to the problems (and costs) of dealing with the radioactivity. This may change the situation for thorium supply. Other thorium minerals, besides monazite, are *thorite* $ThSiO_4$ (Figure M24) and *thorianite* ThO_2.

52.11.2
Manufacture

On the treatment of monazite with sulfuric acid, thorium and many other elements are dissolved. The separation occurs with liquid–liquid extraction. The fluoride ThF_4 is prepared from the thorium phase and reduced with magnesium. Fused salt electrolysis is also applied. The electrolyte is a mixture of equal parts of fused sodium and potassium chlorides, to which the double fluoride $ThF_4 \cdot KF$ is added. The process temperature is 800°C.

52.11.3
Uses

Practical interest in thorium metal and oxide lagged until 1884, when Auer von Welsbach developed and patented the incandescent gaslight mantle, in which thorium oxide was the essential ingredient (see Chapter 17 Rare Earths). Mantle production decreased and by 1925 thorium was relatively unimportant to commerce. Interest came back when thorium turned out to have a possible role in nuclear power plants (see section 52.14.2).

Thorium oxide ThO_2 has the highest melting point (3300°C) of all the binary oxides and has found some uses in special refractory applications.

52.12
Uranium as a Technological Metal

52.12.1
Occurrence

52.12.1.1 **Minerals**

Uranium occurs as oxide and vanadate. The uranium–oxygen system is complicated. During geological processes the oxide UO_2 is partly oxidized to a composition between $UO_{2.6}$ and $UO_{2.67}$. Uranium oxide is present in the brown to black mineral *pitchblende* (Figure M76). It may be expressed so that the oxide essentially is UO_2, but usually it is partly oxidized to U_3O_8. As mentioned earlier, it was in this mineral that radium and polonium were discovered. Besides the original locality, pitchblende was also found in *Port Radium* at Great Bear Lake in Canada. The deposit there was discovered in 1930 and was expropriated by the Canadian Government during World War II due to the importance of its uranium oxide for atomic energy. The mines were closed in 1960.

Uraninite (Figure M76) is a black or brown mineral with a composition similar to pitchblende. It is the chief mineral in uranium ores. It is strongly radioactive, and often contains impurities such as thorium and radium. When heated it emits helium.

Carnotite $K_2(UO_2)_2(VO_4)_2(H_2O)_3$ is a yellowish mineral, strongly radioactive. It is a constituent of uranium and vanadium ores and a source of radium.

Coffinite $U(SiO_4)_{1-x}(OH)_{4x}$ is a black mineral, important as a uranium ore. It occurs in sandstone deposits and hydrothermal veins.

52.12.1.2 **Some Geological Notes**

Acid magmas from the interior of the earth react with basic rocks and start to solidify. Uranium is enriched in the remaining melts. When these finally solidify, the uranium content may be 100 g/tonne (100 ppm, 0.01%). Compared to the mean content in the earth's crust, 2.7 ppm, this is a considerable geochemical enrichment. In addition, uranium is concentrated into phosphate minerals and coal, especially brown coal. This is the background to the fact that coal-fired power stations emit more uranium than nuclear power stations!

By hydrothermal leaching[5] of granitic rocks containing uranium and subsequent deposition, veins with uranium contents of several percent can be formed. This is the case in deposits at Joachimsthal in Bohemia, at Port Radium in Canada, and at Chingolobwe in Zaire (Congo Kinshasa).

On the weathering of pegmatites containing uranium, secondary concentrations are formed, in which uranium is oxidized to the hexavalent stage. Water-soluble uranyl complexes are enriched in clays and phosphates. In sandstones, uranyl-containing solutions may again be precipitated under reducing conditions and form

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[5] In hydrothermal processes, water, sometimes superheated, dissolves minerals at high pressure. Several minerals that normally are almost insoluble in water may be dissolved in the extreme conditions of hydrothermal processes.

minerals. One example is carnotite, found in the red and yellow sandstones of Arizona and Colorado, USA.

If the oxygen supply is limited, the weathered grains of uranium minerals are not oxidized and the uranium is not leached out. The grains are transported by the streaming water and are deposited in positions determined by their high density. The deposits in the Lake Superior region of Canada and at Witwatersrand in South Africa have been formed in that way. The two deposits are similar but the Canadian ore contains 0.1–0.3% uranium oxide, which is about 10 times more than the South African ore. On the other hand, the South African ore contains gold to such a great extent that uranium is obtained as a byproduct from gold winning.

Sweden has considerable uranium reserves, with low metal content, in the Cambrian schists in the middle part of the country. Canada stands out as the most important uranium country of the world. One of the richest uranium deposits known is situated at *Cigar Lake* in the Canadian province of Saskatchewan. High-grade uranium ores are mined there in underground work, using water jets to cut the rock. The annual production is more than 8000 tonnes of U_3O_8 from the rich eastern part of the ore body.

52.12.2
Production

The world production, counted as uranium, was about 36 000 tonnes in 2001. How the production was divided by country is shown in Table 52.2 [52.14].

Table 52.2 World production of uranium (tonne) in 2001

Country	Production tonnes	Percentage of total	Country	Production tonnes	Percentage of total
Canada	12520	34.4	South Africa	873	2.4
Australia	7756	21.3	Ukraine	750	2.1
Niger	2920	8.0	China	655	1.8
Russia	2500	6.9	Czech Republic	456	1.3
Namibia	2239	6.2	India	230	0.6
Kazakhstan	2050	5.6	France	195	0.5
Uzbekistan	1962	5.4	Other countries	249	0.7
USA	1011	2.8			
			Total	36366	100

Source: taken from ref. [52.14].

52.12.3
Manufacture of Uranium Metal and Isotope Separation

52.12.3.1 Preparation of Uranium Fluoride From Uranium Ore

The mined uranium ore is crushed and ground into a fine powder. After ore dressing, the concentrate is leached with sulfuric acid. The solution is treated in a liquid–liquid extraction, in which uranium is transferred to an organic phase. It is extracted from that with ammonia, and ammonium uranate is precipitated. At 1000°C it is decomposed to yellow uranium oxide UO_2. Uranium hexafluoride is prepared by treating the oxide with hydrogen fluoride to make uranium tetrafluoride. This in turn is treated with elemental fluorine to prepare the gaseous hexafluoride UF_6 (sublimation point 56°C).

52.12.3.2 Isotope Separation

It is the isotope ^{235}U, not ^{238}U, that can be utilized in conventional processes for fission by neutrons, and thus for energy generation (and for manufacturing atomic bombs). In natural uranium, only 0.7% of the nuclei are of the lighter isotope. The rest, 99.3%, consists of the heavier isotope ^{238}U. When uranium is to be used as a nuclear fuel, it generally needs to be enriched. In conventional reactors, a nuclear fuel with 3% ^{235}U is utilized[6]. That enriched uranium is obtained by diffusion processes originally developed in the so-called Manhattan Project.

> The classic method for isotope separation utilizes a gas diffusion method in cells. Each cell is divided into two parts, separated by a barrier, pierced with a lot of tiny holes. On one side of the barrier an under-pressure is maintained, on the other side an over-pressure. The fluoride is fed in to the part with over-pressure and diffuses through the barrier. The mean speed of the molecules of a gas is lower if the molecular weight is higher. It can be calculated that the diffusion speed for $^{235}UF_6$ is 1.0043 times higher than that for $^{238}UF_6$. When half of the gas volume has passed into the low-pressure part, a certain, very small, enrichment of the light isotope has occurred. That gas volume now is pumped to the high-pressure part of the next cell. The process is repeated with a lot of cells connected in a *cascade*. The light isotope moves "forward" in the process, the heavier "backward". When the ^{235}U content of the enriched fluoride has increased from 0.7% to 3.25%, the depleted fluoride has decreased its content to 0.2%. The process has fundamentally great similarities with fractional crystallization, described by figure 17.14 in chapter 17.

The diffusers work at a temperature of 80°C. The enriched hexafluoride is transformed to uranium oxide. The hydrofluoric acid is set free and re-used. The uranium oxide is pressed into small cylindrical pellets, 10 mm high and 10 mm in diameter. The pellets are filled into 4–5 m long tubes, made of zircaloy[7]. The tubes are filled with helium and welded. They are the fuel of the nuclear power stations.

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[6] An atom bomb needs to contain 90–100% fissionable material, since the chain reaction otherwise proceeds too slowly. Consequently, there is no possibility of nuclear fuel exploding.

[7] For more information about zircaloy, see Chapter 19 Zirconium.

> A modern variant of isotope separation is the *gas centrifuge*. In a very rapidly rotating cylinder, the heavier isotope is forced closer to the outer wall, while the lighter one stays nearer to the center. It is necessary to have many centrifuges, operating in cascade, to process large amounts of material. However the plant is more economic than diffusion equipment. A potential problem is that smaller and/or poorer nations may utilize the technique in order to produce their own nuclear weapons.
>
> A fundamentally different technique is *laser isotope separation* (LIS) or *atomic vapor laser isotope separation* (AVLIS). A laser beam is tuned to a wavelength that excites only one isotope of the material and ionizes those atoms preferentially. After the atom is ionized, it can be removed from the sample by applying an electric field.

As uranium has a density almost 70% higher than that of lead, ammunition made from this metal is an effective anti-tank weapon. When used in combat, the uranium in the bullet ignites upon impact and a cloud of uranium oxide dust is formed. To reduce the radiation risk, *depleted uranium* (DU) is used in weapon systems of this type. It is obtained as a residue when natural uranium has been enriched in respect of uranium-235. DU is a substance that is only about half as radioactive as natural uranium. But due to its radioactivity – even if it is low – the dust can cause internal injuries if it is inhaled or ingested.

52.13
Nuclear Fission

In 1939 the German scientists Otto Hahn (1879–1968), Lise Meitner (1878–1968) and Fritz Strassman (1902–1980) found that nuclear fission is possible. It was demonstrated in a paper in *Die Naturwissenschaften* in 1939. Lise Meitner, being both a woman and a Jew, did not have her name on the important paper. She had fled Berlin in July 1938 to escape Nazi persecution. However, in another paper in 1939, in *Nature*, together with Otto Frisch (1904–1979), she described the disintegration of uranium by neutrons and explained the theory of uranium fission.

The fission process will be described here for ^{235}U. If the nucleus of this atom captures a neutron, a very unstable nucleus ^{236}U is formed. Fission into two big fragments occurs spontaneously (Figure 52.6). Many different reactions are possible, one example of which is:

$$^{235}\mathrm{U} + {}^{1}\mathrm{n} \rightarrow {}^{139}\mathrm{Ba} + {}^{94}\mathrm{Kr} + 3\,{}^{1}\mathrm{n} + \text{energy}$$

The sum of the masses of the fragments is less than the original mass. This “missing” mass (about 0.1% of the original mass) has been converted into energy according to Einstein’s equation. Fission of 1 g uranium per day corresponds to a power of 1 MW.

It is important and noteworthy that one neutron is used and two or more free neutrons are generated. This makes a chain reaction possible. In the practical utilization

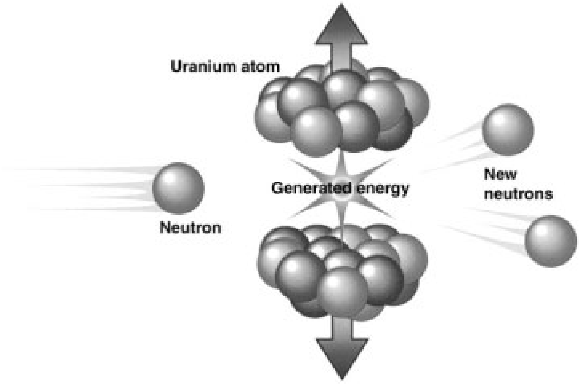

Figure 52.6 Fission of a uranium atom.

of nuclear fission for energy generation, the mean speed of the free neutrons has to be suitable for the capture process with new uranium atoms. A moderator reduces the speed to this level.

52.14
The Nuclear Reactor

52.14.1
With Enriched Uranium as the Fuel

Uranium is almost entirely used for energy production in nuclear power plants. The commercial nuclear era began with graphite-moderated reactors. The first plant for production of electricity (5 MW) was built at Obninsk near Moscow. In England, at Calder Hall, four reactors of this type, each with a power of 45 MW, were built in 1956. The Chernobyl reactors also were graphite-moderated.

New types of reactors utilize common water as moderator. Commercial nuclear power plants have *pressurized water reactors* (PWR) and *boiling water reactors* (BWR). A typical Swedish boiling water reactor is described in Figure 52.7.

In a modern reactor, almost 100 tubes with uranium oxide pellets are assembled into a fuel cluster, which in turn is placed in a casing, known as a fuel rod, prior to insertion into the reactor. A modern reactor contains several hundred of these fuel assemblies. Approximately one-fifth of the fuel is replaced each year. Control rods are used to start and stop the reaction and to regulate the power output. They contain substances, e.g. boron carbide, that have the ability to absorb neutrons.

In 1998, there were 434 power-generating nuclear reactors in operation in 31 countries and the total production amounted to about 2300 TWh[8], or approximately 16% of total electricity production.

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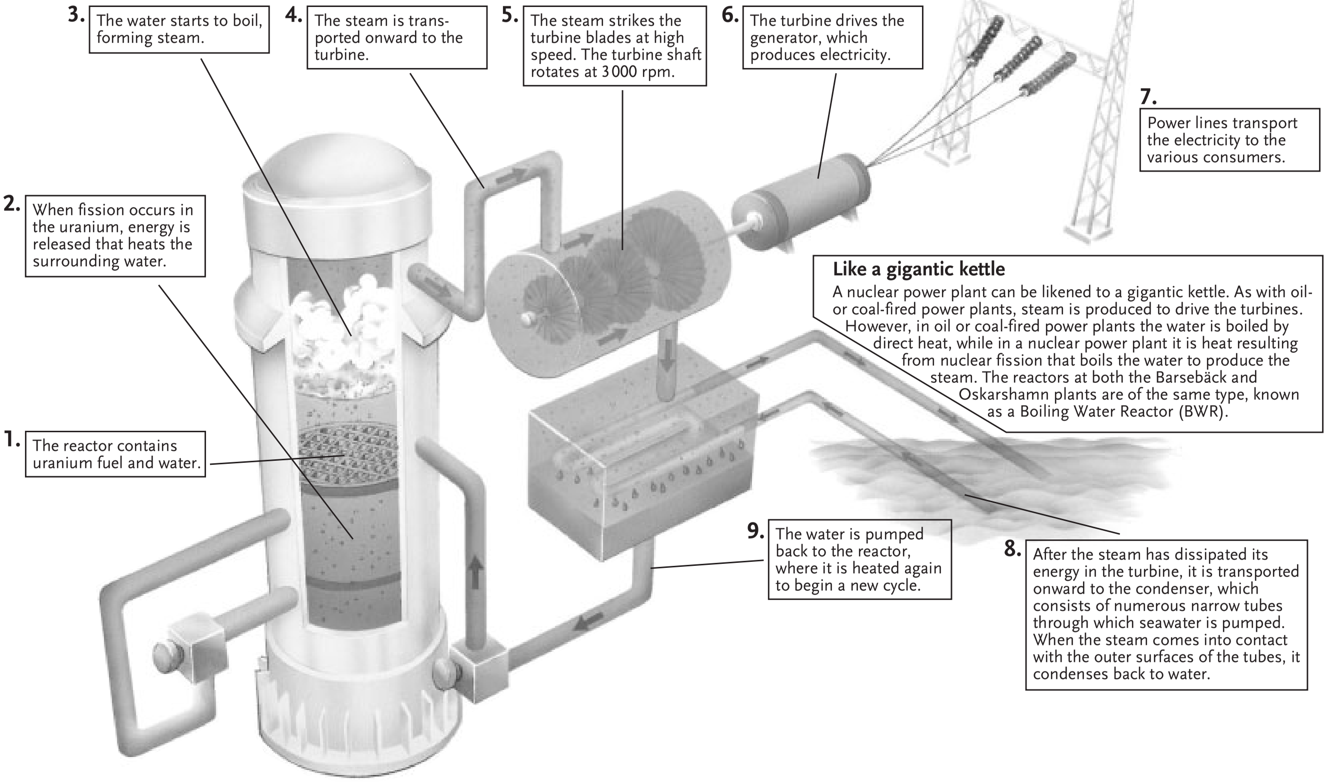
[8] 1 TWh (terawatt hour) = 1 billion kWh (kilowatt hours).



1. The reactor contains uranium fuel and water.

2. When fission occurs in the uranium, energy is released that heats the surrounding water.

3. The water starts to boil, forming steam.

4. The steam is transported onward to the turbine.

5. The steam strikes the turbine blades at high speed. The turbine shaft rotates at 3000 rpm.

6. The turbine drives the generator, which produces electricity.

7. Power lines transport the electricity to the various consumers.

8. After the steam has dissipated its energy in the turbine, it is transported onward to the condenser, which consists of numerous narrow tubes through which seawater is pumped. When the steam comes into contact with the outer surfaces of the tubes, it condenses back to water.

9. The water is pumped back to the reactor, where it is heated again to begin a new cycle.

Like a gigantic kettle

A nuclear power plant can be likened to a gigantic kettle. As with oil- or coal-fired power plants, steam is produced to drive the turbines. However, in oil or coal-fired power plants the water is boiled by direct heat, while in a nuclear power plant it is heat resulting from nuclear fission that boils the water to produce the steam. The reactors at both the Barsebäck and Oskarshamn plants are of the same type, known as a Boiling Water Reactor (BWR).

Twenty-five cubic meters of seawater per second

The water used in the condensers to cool the steam is drawn from the sea. At Barsebäck, each reactor unit uses 25 cubic meters of seawater per second, which is pumped into a channel leading into the power plant. When the cooling water is returned to the sea in the Öresund Strait, it is 10°C warmer than when it entered the plant. The seawater is pumped through the condenser in a special system of tubes. It never comes into contact with the steam produced by the reactor.

Figure 52.7 A boiling water reactor. (Reproduced by permission of Sydkraft, Sweden, and L+J AB.)

52.14.2
Breeder Reactors

A conventional nuclear reactor has a very low efficiency regarding uranium utilization. Unlike the lighter isotope, the heavy isotope (which is the major component) will never be utilized. A *breeder reactor* produces more fuel than it consumes. With molten sodium as a coolant, the main isotope in natural uranium, ^{238}U, absorbs neutrons and reacts according to the formulas given in Figure 52.9 (section 52.16.3).

The plutonium isotope is fissile and can produce energy. However, the handling of plutonium is a risk, as it can be used weapons. Super-Phenix, the first large-scale breeder reactor, was put into service in France in 1984.

The isotope ^{232}Th can also be used in a breeder reactor. A fissile substance ^{233}U is obtained in a chain reaction:

$$^{232}_{90}\mathrm{Th} \rightarrow {}^{233}_{90}\mathrm{Th} \rightarrow {}^{233}_{91}\mathrm{Pa} \rightarrow {}^{233}_{92}\mathrm{U}$$

These reactions can utilize the normal moderating and cooling system, and thus the reactions can occur in a conventional reactor, to which thorium is added.

52.15
Oklo – Nature's Own Reactor

Natural uranium has a content of 0.72% of the ^{235}U isotope. In Oklo, an African uranium deposit in Gabon, the ore has a lower content, only 0.44%. This indicates that a part of the lighter isotope has been consumed in a nuclear reactor, started and run by nature itself. Of course, there are discussions about this fantastic story. However this supposition is strongly confirmed by the results of mass spectroscopic examinations of disintegration products in the region of the deposit. The rare earth metal neodymium has been found to contain 2% of the isotope ^{142}Nd. In natural neodymium its content is 27% [52.15]. This is in agreement with the fact that neodymium, formed during fission of uranium in modern reactors, contains 1% of ^{142}Nd.

So nature's own reactor was perhaps active some 2000 million years ago. Water is thought to have been the moderator. Fission of ^{235}U started the process. In the actual period the content of ^{235}U (counted on total uranium) is estimated to have been 3%. This is one reason why the reactor started. With the ^{235}U content 0.72% of today a spontaneous reactor of Oklotype is not possible. The abundant access to ^{238}U made the formation of ^{239}Pu possible. Thus this natural reactor was a true breeder reactor.

52.16
More Than Just 92 Elements – The Transuranium Actinides

On earth there are 92 elements designated as “naturally occurring”. Hydrogen with atomic number 1 is the lightest, uranium with atomic number 92 the heaviest. The elements 43 technetium and 61 promethium are special and do not occur naturally. As described in Chapter 28 Technetium and Chapter 17 Rare earths, they are not present in detectable amounts on earth. They were discovered in fission products from atomic reactors.

The 14 elements following actinium (Z=89) are called the *actinides*. Up to 1940 only three of them, thorium, protactinium and uranium, were known. The question then was, would it be possible to find or synthesize the others?

52.16.1
The Situation in 1940

In the lanthanide series, the missing element number 61 was discovered in 1945, which made the lanthanide subgroup complete. The corresponding actinide group was almost empty, as shown in Figure 52.8. The squares 93–103 attracted great interest, typical for science, which in all times has endeavored to fill empty spaces.

6	58 Ce	59 Pr	60 Nd	**61**	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

(a)

7	90 Th	91 Pa	92 U	**93**	**94**	**95**	**96**	**97**	**98**	**99**	**100**	**101**	**102**	**103**

(b)

Figure 52.8 The a) lanthanides and b) actinides known in 1940.

52.16.2
Synthesis and Discovery

In 1940 E. McMillan and P. H. Abelson at the University of California, Berkeley, irradiated ^{238}U with neutrons; this led to the formation of element number 93, which they called *neptunium* [52.18]. What they did can be described by the first formulas in Table 52.3. Their successful result was the start of intensive work that led to the discovery of all the actinide elements. In fact neptunium and also plutonium occur in nature. Minute amounts of these elements are produced in the radioactive decay of uranium.

In the famous laboratory at Berkeley, E. O. Lawrence had developed the cyclotron. By irradiation with particles heavier than neutrons, accelerated in the cyclotron, several new transuranium elements could be produced, although in very small quantities. In 1940 G. T. Seaborg (1912–1999), E. M. McMillan, J. W. Kennedy and A. C. Wahl succeeded in preparing element 94, *plutonium*, by bombardment of uranium with deuterons, according to Table 52.3. Seaborg was co-discoverer of all the nine elements 94–102. Together with R. A. James, L. O. Morgan and A. Ghiorso, he prepared *americium* Am at the University of Chicago in 1944–1945. They irradiated plutonium with neutrons. The element 95 was formed in a three-stage process.

Curium, element 96, was also prepared by Seaborg's group at the University of Chicago. In 1944 they bombarded plutonium with helium ions and obtained the isotope ^{242}Cm.

Back in California, Seaborg synthesized the element 97 in a cooperation in 1949 with S. G. Thompson and A. Ghiorso. They used a method with bombardment of americium with helium ions. The new element got its name *berkelium* after its birthplace, the University of California, Berkeley.

Still six actinides remained to be discovered. On bombardment of curium in 1950 with helium ions, Seaborg's group obtained element 98 and called it *californium*.

After the thermonuclear explosion of 1952 at Enewetok Atoll in the Marshall Islands, in the Pacific Ocean, successive neutron captures and subsequent β^- decay was found to have changed ^{238}U to an isotope of the element 99. This was a big cooperative project between scientists at Berkeley, Argonne National Laboratory (Illinois) and Los Alamos Scientific Laboratory (New Mexico). The new element 99 got the name *einsteinium*.

In the debris from the Enewetok Atoll the combined scientific group also found, in 1953, the element 100 that was named *fermium*.

The new discoveries gave Seaborg and his colleague new targets for bombardment. Einsteinium was reacted with helium ions. The new element ^{101}Md, *mendelevium*, was formed, in 1955 at the University of California.

For the synthesis of the transfermium elements, thus elements with atomic number 101 or greater, it became usual to utilize projectile particles heavier than neutrons, deuterons or helium ions. Carbon, boron and oxygen were used. In Berkeley in 1958, J. R. Walton and G. T. Seaborg bombarded curium with carbon ions and got the element 102, *nobelium*. From the 1960s the Russian *Joint Institute for Nuclear Research* at Dubna became a new, important center for research regarding the transuranium elements. In 1964 E. D. Donets, V. A. Schegolev and V. A. Ermakov verified the formation of nobelium by bombardment of curium with carbon (see Table 52.3).

After nobelium had been discovered, only one actinide remained to be found, element number 103. A. E. Larsh and R. M. Latimer at Berkeley in 1961 and E. D. Donets, V. A. Schegolev and V. A. Ermakov at Dubna in 1965 bombarded californium isotopes with a mixture of boron-10 and boron-11 ions and were able to identify element 103. It was named *lawrencium*. Bombardment of americium with oxygen ions created another lawrencium isotope.

The properties of some isotopes of the transuranium actinides are collected in Table 52.4.

Table 52.3 The synthesis and discovery of the transuranium actinides

Synthesis/ discovery and year	Reaction(s)	Description
Neptunium 1940	${}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U}$ ${}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + \beta^-$	Neptunium-93 is synthesized from uranium-92 by neutron bombardment. The neptunium isotope obtained has a half-life of 2.36 days
Plutonium 1940	${}^{238}_{92}\mathrm{U} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{238}_{93}\mathrm{Np} + 2{}^{1}_{0}\mathrm{n}$ ${}^{238}_{93}\mathrm{Np} \rightarrow {}^{238}_{94}\mathrm{Pu} + \beta^-$	Plutonium-94 is synthesized from uranium-92 by deuteron bombardment. The isotope obtained has a half-life of 87.7 years
Americium 1944	${}^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{240}_{94}\mathrm{Pu}$ ${}^{240}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{241}_{94}\mathrm{Pu}$ ${}^{241}_{94}\mathrm{Pu} \rightarrow {}^{241}_{95}\mathrm{Am} + \beta^-$	Americium-95 is synthesized from plutonium-94 by neutron bombardment. The isotope obtained has a half-life of 432 years
Curium 1944	${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$	Curium-96 is obtained by bombardment of plutonium with helium ions. The isotope has a half-life of 163 days
Berkelium 1949	${}^{241}_{95}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{243}_{97}\mathrm{Bk} + 2{}^{1}_{0}\mathrm{n}$	Berkelium-97 is obtained by bombardment of americium with helium ions. The isotope obtained has a half-life of 4.5 hours
Californium 1950	${}^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{245}_{98}\mathrm{Cf} + {}^{1}_{0}\mathrm{n}$	Californium-98 is synthesized from curium-96 by bombardment with helium ions. The californium isotope obtained has a half-life of 45 min
Einsteinium 1952	Successive neutron captures by uranium-238 and β^- decay of the capture products resulted in ${}^{253}_{99}\mathrm{Es}$	Einsteinium-99 was found in the debris from the first thermonuclear explosion on November 1, 1952, at Enewetok Atoll. The einsteinium isotope obtained has a half-life of 20.5 days
Fermium 1953	Successive neutron captures by uranium-238 and β^- decay of the capture products resulted in ${}^{255}_{100}\mathrm{Fm}$	Fermium-100 was found in the debris from the first thermonuclear explosion at Enewetok Atoll on November 1, 1952. The fermium isotope obtained has a half-life of 20.1 hours
Mendelevium 1955	${}^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$	Mendelevium-101 is obtained by bombardment of einsteinium with helium ions. The mendelevium isotope obtained has a half-life of 1.3 hours
Nobelium 1958 and 1964	${}^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \rightarrow {}^{254}_{102}\mathrm{No} + 4{}^{1}_{0}\mathrm{n}$	Nobelium-102 is synthesized from curium-96 by bombardment with carbon ions. The isotope obtained has a half-life of 55 seconds
Lawrencium 1961–1965	${}^{250}_{98}\mathrm{Cf} + {}^{10}_{5}\mathrm{B} \rightarrow {}^{258}_{103}\mathrm{Lr} + 2{}^{1}_{0}\mathrm{n}$ ${}^{243}_{95}\mathrm{Am} + {}^{18}_{8}\mathrm{O} \rightarrow {}^{256}_{103}\mathrm{Lr} + 5{}^{1}_{0}\mathrm{n}$	Lawrencium-103 is synthesized from californium-98 by bombardment with boron and from americium by bombardment with oxygen. The isotopes ${}^{258}\mathrm{Lr}$ and ${}^{256}\mathrm{Lr}$ have half-lives of 3.9 and 28 seconds respectively

Source: Information from ref. [52.18]

Table 52.4 Properties of the transuranium actinides

Element	Atomic weight	Yearly production a)	Isotope range	Isotope examples			
				Nuclide	Half-life	Decay	
						Mode	Energy Q (MeV)
93 Np Neptunium	237	kilograms	225–244	^{237}Np	2.14×10^6 yr	α	4.959
94 Pu Plutonium	244	tonnes	228–247	^{238}Pu	87.7 yr	α	5.593
				^{239}Pu	24.1×10^3 yr	α	5.245
				^{242}Pu	3.73×10^5 yr	α	4.984
				^{244}Pu	8.08×10^7 yr	α	4.666
95 Am Americium	243	grams	232–247	^{241}Am	432 yr	α	5.638
				^{243}Am	7370 yr	α	5.438
96 Cm Curium	247	grams	238–252	^{242}Cm	163 day	α	6.216
				^{244}Cm	18.1 yr	α	5.902
				^{247}Cm	1.56×10^7 yr	α	5.353
				^{248}Cm	3.40×10^5 yr	α	5.162
97 Bk Berkelium	247	milligrams	238–251	^{247}Bk	1380 yr	α	5.889
				^{249}Bk	320 day	β^-	0.124
98 Cf Californium	251	grams	237–256	^{249}Cf	357 yr	α	6.295
				^{251}Cf	898 yr	α	6.176
				^{252}Cf	2.645 yr	α	6.217
99 Es Einsteinium	252	milligrams	241–256	^{252}Es	1.29 yr	α and	6.789
						EC	1.260
				^{253}Es	20.5 day	α	6.739
				^{254}Es	276 day	α	6.616
				^{255}Es	39.8 day	β^- and	0.290
						α	6.436
100 Fm Fermium	257	micrograms	242–259	^{255}Fm	20.1 h	α	7.240
				^{257}Fm	101 day	α	6.864
101 Md Mendelevium	258	zero	245–260	^{258}Md	51.5 day	α	7.271
102 No Nobelium	259	zero	250–262	^{259}No	58 min	α and	7.89
						EC	0.49
103 Lr Lawrencium	260	zero	253–262	^{260}Lr	180 s	α and	8.31
						EC	2.74

Source: Information mainly from ref. [52.15].
a) According to ref. [52.16].

52.16.3
Uses of the Transuranium Actinides

52.16.3.1 **Plutonium**

Plutonium is the most toxic substance known. It is a very dangerous radiological hazard and is specifically absorbed in bones and collected in the liver. For those reasons the element must be handled extremely carefully. Plutonium is produced in all uranium reactors according to the process in Figure 52.9.

$$
\begin{aligned}
&{}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U}\\
&{}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + \beta^{-}\ (t_{1/2} = 24\ \mathrm{min})\\
&{}^{239}_{93}\mathrm{Np} + {}^{239}_{94}\mathrm{Pu} + \beta^{-}\ (t_{1/2} = 2.36\ \mathrm{day})
\end{aligned}
$$

Figure 52.9 Formation of plutonium in a uranium reactor.

With more neutrons available than in an ordinary reactor, the production of ^{239}Pu would increase and become greater than the consumption of ^{235}U. This may be achieved by extra enrichment of the fuel and removal of the moderator. A *fast breeder reactor* is then obtained. The advantage of such a reactor is, as already mentioned in section 52.14.2, that both ^{235}U and ^{238}U are used to produce heat. Up to 60 times more energy can be obtained compared with a conventional reactor [52.17]. There are however many serious political objections to the use of the breeder technology, as plutonium may be used to produce nuclear weapons.

The originally discovered plutonium isotope ^{238}Pu is not fissile and has been used in quite other applications than nuclear power and weapons. It is an intensive α particle emitter and thus an energy producer. ^{238}Pu is used in kilogram quantities as the power source for satellites. In the Apollo lunar missions, it was used to power scientific equipment on the lunar surface.

Plutonium in irradiated fuel elements may be chemically separated from uranium. On treatment of a mixture of hexavalent uranium and tetravalent plutonium with divalent iron, plutonium is reduced to the trivalent stage. The stable uranyl nitrate is unaffected. In liquid–liquid extraction with tri-n-butyl phosphate (TBP) and kerosene, uranium goes into the organic phase, while plutonium stays in the water phase.

52.16.3.2 **Americium**

Americium (the isotope ^{241}Am) is the vital ingredient of household smoke detectors. The detector is a small chamber in which a low-level electrical voltage is applied between two electrodes. In an ordinary situation, without smoke in the room, alpha particles from the isotope collide with the oxygen and nitrogen molecules in the detector and ions are produced. As a consequence a steady small electric current flows between the electrodes. When smoke enters the space between the electrodes, the alpha radiation from the isotope is absorbed by smoke particles. This causes the rate of ionization of the air to fall, the current is changed and this change sets off an alarm. The alpha particles from the smoke detector do not themselves pose a health hazard, as they are absorbed in a few centimeters of air.

52.16.3.3 Curium

Curium may be used as a thermoelectric power source (a never-ending battery) for space flights. Curium was also the alpha particle source for the Alpha Proton X-Ray Spectrometer on Mars.

52.16.4
Physical Properties

For obvious reasons, the physical properties are fragmentarily known. Information about densities and melting points are given in Table 52.5.

Table 52.5 Density and melting points for the actinides[a)]

Element	Density g/cm³	Melting point		Element	Density g/cm³	Melting point	
		K	°C			K	°C
Actinium	10.07	1324	1051	Curium	13.51	1613	1340
Thorium	11.72	2023	1750	Berkelium	14.0	1259	986
Protactinium	15.37	1840	1567	Californium	15.1	1173	900
Uranium	19.0	1405.5	1132.3	Einsteinium	–	1133	860
Neptunium	20.45	913	640	Fermium	–	–	–
Plutonium	19.84	914	641	Mendelevium	–	–	–
Americium	13.67	1267	994	Nobelium	–	–	–
				Lawrencium	–	–	–

a) The values for neptunium and the subsequent elements are taken from ref. [52.19].

52.17
The Elements After the Actinides – The Transactinides

52.17.1
The Situation at the Beginning of the 1960s

When all the actinides had been synthesized and/or discovered, was the periodic table then complete? No! In Figure 52.10 the situation in 1965 is described for the two periods 6 and 7. After the actinides, a lot of empty squares were waiting for new discoveries or syntheses.

	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
6	55 Cs	56 Ba	57 La	58-71 Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	90-103 Actinides	**104**	**105**	**106**	**107**	**108**	**109**	**110**	**111**	**112**	**113**	**114**	**115**	**116**	**117**	**118**

Figure 52.10 The situation for the transuranium elements after 103, at the beginning of the 1960s.

52.17.2
New Discoveries

In fact all the discoveries of the transactinide elements have been made at three big institutes:

- The Lawrence Berkeley National Laboratory in California, active since 1940
- The Russian Joint Institute for Nuclear Research at Dubna near Moscow, active since the 1960s
- The Institute for Heavy Ion Research (Gesellschaft für Schwerionenforschung) GSI in Darmstadt, Germany, active since the 1970s

Two new techniques were gradually introduced:

- *Linear accelerators* as is shown in Figure 52.11, instead of cyclotrons

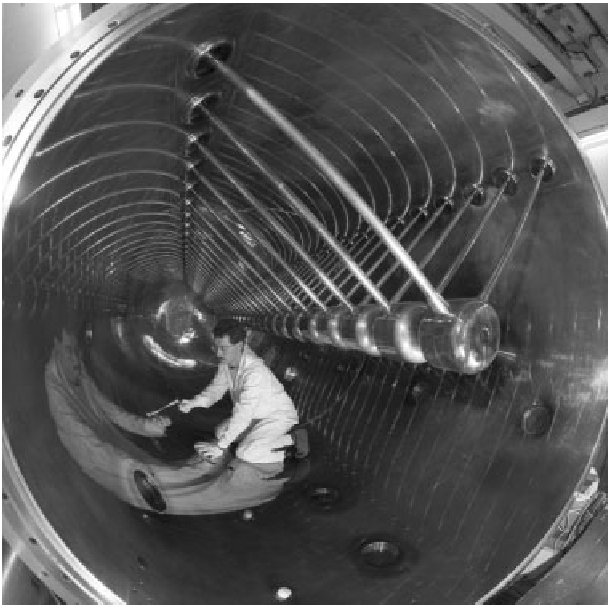


Figure 52.11 Heavy ion research at GSI in Darmstadt: a linear accelerator.

- *"Cold fusion"* between two heavy isotopes instead of the early conventional practice with high speed collisions between light ions and heavy transuranic isotopes. With this new technique the heating of the formed nuclei was considerably lower and far more nuclei could survive the fusion process. The synthesis of darmstadtium (Table 52.6) is a typical example of cold fusion.

Table 52.6 The syntheses of transactinide elements 104–112 and some of their properties

Element				**Discovery year**	**Production method**[b)]	
Atomic number Z	**Mass number**[a)] **A**	**Half-life**[a)]	**Name or designation**		**Bombard-ment of**	**With**
104	257	4.7 s	Rutherfordium Rf	1969	Californium	Carbon
	261	1.1 min				
105	260	1.5 s	Dubnium Db	1968–1970	Californium	Nitrogen
	262	34 s				
106	263	0.8 s	Seaborgium Sg	1974	Californium	Oxygen
	266	21 s				
107	262	0.1 s	Bohrium Bh	1981	Bismuth	Chromium
	264	0.44 s				
108	265	1.55 ms	Hassium Hs	1984	Lead	Iron
	269	9.3 s				
109	266	3.8 ms	Meitnerium Mt	1982	Bismuth	Iron
	268	70 ms				
110	271	1.1 ms	Darmstadtium Ds	1994	Lead	Nickel
	273	120 ms				
111	272	1.5 ms	Unununium Uuu	1994	Bismuth	Nickel
	–	–				
112	277	0.24 ms	Ununbium Uub	1996	Lead	Zinc
	–	–				

a) Values found in connection with the discoveries are reported in the first rows. In the second rows some examples are given of half-lifes for heavier isotopes.
b) Alternatives to mentioned methods are available and used.
Sources: Information mainly from ref. [52.15] and [52.18]

52.17.3
Notes About the Elements

52.17.3.1 Number 104, Rutherfordium

In 1964 a Soviet team led by G. N. Flerov at the Joint Institute for Nuclear Research at Dubna announced the discovery of element 104 after bombarding plutonium-242 atoms with neon-22 ions. They proposed that the element name should be *kurchatovium* Ku to honor Igor Kurchatov, a Soviet pioneer in nuclear physics. At Berkeley a group led by A. Ghiorso announced in 1969 that they had been unable to confirm the result of the Dubna group. Instead, they had themselves identified at least two isotopes of element 104 when they bombarded californium-249 atoms with carbon-12 and carbon-13 ions. The Americans suggested the name *rutherfordium* to honor the British physicist Lord Ernest Rutherford. An international committee, set up to resolve such disputes, decided in 1992 that the Berkeley and Dubna laboratories should share credit for the discovery. In 1997 the name *rutherfordium* Rf for element 104 was however recognized internationally.

52.17.3.2 **Number 105, Dubnium**

In 1968 a Soviet team led by G. N. Flerov at the Joint Institute for Nuclear Research at Dubna announced the discovery of element 105. They claimed that they had isolated isotopes with mass numbers 260 and 261 by bombarding americium-243 atoms with neon-22 ions. In 1970, a Berkeley group led by A. Ghiorso announced that they had been unable to confirm the Dubna group's results, but synthesized an isotope of element 105 by bombarding californium-249 atoms with nitrogen-15 ions. The international committee set up to resolve this type of dispute decided in 1992 that the Berkeley and Dubna laboratories should share credit for the discovery. In 1997 the name *dubnium* Db was accepted internationally for element 105, in recognition of the pioneering work done at the Dubna laboratory.

52.17.3.3 **Number 106, Seaborgium**

The discovery of element 106 took place almost simultaneously at the Joint Institute for Nuclear Research, Dubna, Russia, and the Lawrence Berkeley National Laboratory, Berkeley, California, USA. In June 1974 a Soviet team led by G. N. Flerov bombarded lead-207 and lead-208 atoms with chromium-54 ions to produce an isotope with mass number 259. In September the same year A. Ghiorso and his colleagues bombarded californium-249 atoms with oxygen-18 ions and created an isotope with mass number 263. Because their work was independently confirmed first, the Americans suggested the name *seaborgium* to honor the American chemist Glenn T. Seaborg. In 1992 it was decided that the Berkeley and Dubna laboratories should share credit for the discovery. In 1997 the name *seaborgium* Sg for element 106 was recognized internationally.

52.17.3.4 **Number 107, Bohrium**

In 1976 a Soviet team led by Y. Oganessian at the Joint Institute for Nuclear Research at Dubna bombarded bismuth-209 atoms with chromium-54 ions to produce an isotope with mass number 261. In 1981 a German research team led by P. Armbruster and G. Münzenberg at the Institute for Heavy Ion Research at Darmstadt also bombarded bismuth-209 atoms with chromium-54 ions. By reducing the temperature of the target atoms, the Germans were able to produce and without doubt identify an isotope of element 107 having mass number 262. In 1994 a committee of the International Union of Pure and Applied Chemistry (IUPAC) recommended that element 107 should have the name *bohrium* Bh. It was recognized internationally in 1997.

52.17.3.5 Number 108, Hassium

In 1984 P. Armbruster's group at the Institute for Heavy Ion Research at Darmstadt bombarded lead-208 atoms with ions of iron-58. In 10 days of bombardment, they successfully produced three atoms of an isotope of element 108 with mass number 265. They suggested that the new element should be named *hassium*, which is derived from the Latin name *Hassias* for the German state of Hessen, in which the institute is situated. The name *hassium* Hs was adopted internationally in 1997.

52.17.3.6 Number 109, Meitnerium

The element 109 was made and identified in August 1982 by physicists at the Heavy Ion Research Laboratory, Darmstadt, Germany. They bombarded bismuth-209 with accelerated ions of Fe-58. The existence of element 109 was confirmed by four independent measurements.

52.17.3.7 Number 110, Darmstadtium

The element 110 was created in November 1994 at the Heavy Ion Research Laboratory, Darmstadt, by a team led by Sigurd Hofmann [52.20]. They used a ^{62}Ni beam for bombardment of a ^{208}Pb target, by nuclear fusion of lead and nickel in a heavy ion accelerator. In accordance with IUPAC procedures, the discoverers at the Heavy Ion Research Laboratory were invited to propose a name and symbol for the element. Hofmann's team proposed the name *darmstadtium* Ds. This continued the long-established tradition of naming an element after the place of its discovery.

52.17.3.8 Number 111, Unununium

In 1994 an international research team led by Peter Armbruster and Sigurd Hofmann at the Institute for Heavy Ion Research, Darmstadt, Germany, bombarded bismuth-209 atoms with nickel-64 ions. In an 18-day experiment, three atoms were unambiguously identified as an isotope of element 111 with mass number 272. No name has yet been suggested for the element, which is therefore called *unununium*, meaning element 111.

52.17.3.9 Number 112, Ununbium

In 1996 an international research team led by Peter Armbruster and Sigurd Hofmann at the Institute for Heavy Ion Research, Darmstadt, Germany, bombarded lead-208 atoms with high-energy zinc-70 ions. In a two-week experiment, one of the resultant atoms was unambiguously identified as an isotope of element 112 with mass number 277. The element's name is *ununbium*, meaning element 112.

52.17.4
An island of stability

Synthetic elements heavier than uranium are generally unstable and especially the transactinide elements have very short half-lives (Table 52.6). On the basis of theories of nuclear structure it has however been predicted that certain transactinide elements may have relatively stable isotopes [52.21]. It is supposed that in a nucleus the protons and neutrons are arranged in concentric shells with some similarity to the electron shells, surrounding a nucleus. An element with the atomic number Z = 114 and the mass number of 298, thus containing 184 neutrons in the nucleus, is expected to be a super-heavy element with good stability and a long half-life. Element 114 might be the first element in an "island of stability" among super-heavy nuclei.

In December 1998 Russian scientists utilized a cyclotron at the Joint Institute for Nuclear Research in Dubna to produce some few atoms of element 114. They bombarded ^{244}Pu with the neutron-rich ^{48}Ca isotopes provided by the Lawrence Berkeley National Laboratory in California. In the target they could identify an isotope of the element 114 with a mass number of 289. Although the goal, mass number 298, was not attained, a surprisingly long half-life of 30 seconds was obtained [52.22].

Leaving the 114-position evidently decreases the stability. In February 2004 scientists in the Dubna Institute could identify two isotopes ^{287}Uup and ^{288}Uup of the element ununpentium after a long bombardment of 243-americium with the same neutron-rich calcium isotope 48. The few atoms of Uup quickly decayed to ununtrium, ^{283}Uut and ^{284}Uut. The half-lifes of these 113 and 115 nuclides are less than one second.

52.17.5
The Properties of the Transactinides

Element 104 rutherfordium and the following ones have been synthesized in such small quantities that it is impossible to determine their chemical and physical properties. To get some idea it is necessary to utilize the original method of Mendeleev to make conclusions from the element's position in the periodic table. According to Figure 52.12, the following similarities should be expected:

- ^{104}Rf similar to zirconium and hafnium;
- ^{105}Db similar to niobium and tantalum;
- ^{106}Sg similar to molybdenum and tungsten;
- ^{107}Bh similar to rhenium;
- ^{108}Hs similar to ruthenium and osmium;
- ^{109}Mt similar to rhodium and iridium;
- ^{110}Ds similar to palladium and platinum;
- ^{111}Uuu similar to silver and gold;
- ^{112}Uub similar to cadmium and mercury;
- ^{114}Uuq similar to tin and lead.

Group → Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	113	114 Uuq	115	116	117	118

Figure 52.12 Periods 4, 5 and 6 of the periodic table, with the known transactinides in their places.

52.17.6
Naming of the elements – a continuous cause of dispute and controversy

As had always been the rule in element discovery the discoverer proposed a name for the new element. As one element often was synthesized in two or even three of the big research institutes an inflamed debate arose regarding some of the elements. The Commission of Nomenclature of Inorganic Chemistry (CNIC) proposed a name list in 1994 but the controversies remained. The International Union of Pure and Applied Chemistry (IUPAC) interviewed chemists round the world regarding the naming and has, since 1997, decided about official names for the transuranium elements.

For No. 104 Dubna proposed the name *kurchatorium,* Berkeley the name *rutherfordium* and CNIC the name *dubnium.* IUPAC decided *rutherfordium Rf.*

For No. 105 Dubna proposed *nielsbohrium,* Berkeley *hahnium* and CNIC *joliotium.* IUPAC decided *dubnium Db.*

For No. 106 CNIC proposed *rutherfordium,* Berkeley *Seaborgium Sg* that also became the official name.

For No. 107 GSI proposed *nielsbohrium,* CNIC *bohrium Bh* that also became the decision of IUPAC.

For No. 108 GSI proposed *hassium* after an old name for the German state Hessen, where Darmstadt is situated. CNIC proposed *hahnium* but IUPAC decided *hassium Hs.*

For No. 109 both GSI and CNIC proposed *meitnerium Mt.* It became, without dispute, the official name.

For No. 110 GSI proposed *darmstadtium Ds* and IUPAC officially approved that name.

For No. 111 GSI proposed *roentgenium Rg* in May 2004.

In 2002 IUPAC published a recommendation for naming of new elements [52.23]. The elements from 111 and upward have not yet got official specific names. They are simply designated with their atomic numbers, expressed in a Latin/Greek based code: nil(0), un(1), bi(2), tri(3), quad(4), pent(5), hex(6), sept(7), oct(8), en or enn(9).

The element names have the general suffix -ium. This is exemplified in Table 52.6 and in section 52.17.4.

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Index