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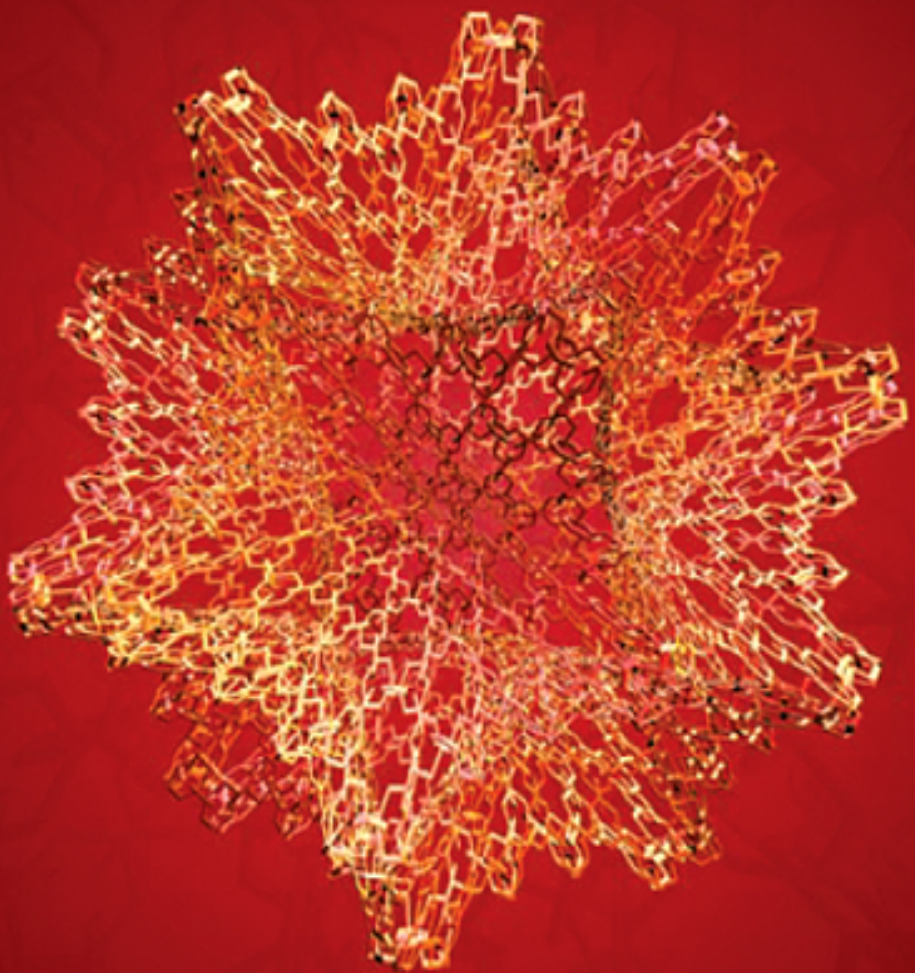

ROBERT G. MORTIMER

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Mathematics for Physical Chemistry

Third Edition

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Third Edition

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To my wife, Ann,
and to the memory of my parents,
William and Margaret Mortimer

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Preface

This book provides a survey of the mathematics needed for chemistry courses at the undergraduate level. In four decades of teaching general chemistry and physical chemistry, I have found that some students have not been introduced to all the mathematical topics needed in these courses and that most need some practice in applying their mathematical knowledge to chemical problems. The emphasis is on the mathematics that is useful in a physical chemistry course, but the first several chapters provide a survey of mathematics that is useful in a general chemistry course.

I have tried to write all parts of this book so that they can be used for self-study by someone not familiar with the material, although any book such as this cannot be a substitute for the traditional training offered in mathematics courses. Exercises and solved example are interspersed throughout the chapters, and these form an important part of the presentations. As you study any topic in the book, you should follow the solution to each example and work each exercise as you come to it.

The first ten chapters of the book are constructed around a sequence of mathematical topics, with a gradual progression into more advanced material. Chapter 11 is a discussion of mathematical topics needed in the analysis of experimental data. Most of the material in at least the first five chapters should be a review for nearly all readers of the book. I have tried to write all of the chapters so that they can be studied in any sequence, or piecemeal as the need arises.

This edition is a revision of a second edition published by Academic Press in 1999. I have reviewed every paragraph and have made those changes that were necessary to improve the clarity and correctness of the presentations. Chapter 9 of the second edition discussed the solution of algebraic equations. It has been divided into two chapters: a new Chapter 3, which contains the parts of the old chapter that apply to general chemistry, and a new Chapter 10, which deals with sets of three or more simultaneous equations. Chapter 5 of the second edition introduced functions of several independent variables, and Chapter 6 of the second edition discussed mathematical series and transforms. These two chapters have been interchanged, since the discussion of series and transforms involves only a single independent variable. Chapter 11 of the second edition involved computer usage. It contained material on word processors, spreadsheets, programming in the BASIC language, graphics packages, and the use of the Mathematica program. The material on word processors, graphics packages, and BASIC programming has been omitted, since most students are now familiar with word processors and tend to use spreadsheets and packaged programs instead of writing their own programs. The material on the use of spreadsheets and the use of Mathematica has been divided up and distributed among various chapters so that the topics are placed with

the discussion of the mathematics that is involved. I have continued the use of chapter summaries, chapter previews, lists of important facts and ideas at the beginning of each chapter, and chapter objectives.

This book serves three functions:

1. A review of topics already studied and an introduction to new topics for those preparing for a course in physical chemistry
2. A supplementary text to be used during a physical chemistry course
3. A reference book for graduate students and practicing chemists

I am pleased to acknowledge the cooperation and help of Jeremy Hayhurst and his collaborators at Academic Press. It is also a pleasure to acknowledge the assistance of all those who helped with the first and second editions of this book, and especially to thank my wife, Ann, for her patience, love, and forbearance.

1

Numbers, Measurements, and Numerical Mathematics

Preview

The first application of mathematics to chemistry deals with various physical quantities that have numerical values. In this chapter, we introduce the correct use of numerical values to represent measured physical quantities and the use of numerical mathematics to calculate values of other quantities. Such values generally consist of a number and a unit of measurement, and both parts of the value must be manipulated correctly. We introduce the use of significant digits to communicate the probable accuracy of the measured value. We also review the factor-label method, which is a routine method of expressing a measured quantity in terms of a different unit of measurement.

Principal Facts and Ideas

1. Specification of a measured quantity consists of a number and a unit.
2. A unit of measurement is an arbitrarily defined quantity that people have agreed to use.
3. The SI units have been officially adopted by international organizations of physicists and chemists.
4. Consistent units must be used in any calculation.
5. The factor-label method can be used to convert from one unit of measurement to another.
6. Reported values of all quantities should be rounded so that insignificant digits are not reported.

Objectives

After you have studied the chapter, you should be able to:

1. use numbers and units correctly to express measured quantities;
2. understand the relationship of uncertainties in measurements to the use of significant digits;
3. use consistent units, especially the SI units, in equations and formulas; and
4. use the factor-label method to convert from one unit of measurement to another.

1.1 Numbers and Measurements

The most common use that chemists make of numbers is to report values for measured quantities. Specification of a measured quantity generally includes a number and a unit of measurement. For example, a length might be given as 12.00 inches (12.00 in) or 30.48 centimeters (30.48 cm), or 0.3048 meters (0.3048 m), and so on. Specification of the quantity is not complete until the unit of measurement is specified. For example, 30.48 cm is definitely not the same as 30.48 in. We discuss numbers in this section of the chapter, and will use some common units of measurement. We discuss units in the next section.

Numbers

There are several sets into which we can classify numbers. The numbers that can represent physical quantities are called *real numbers*. These are the numbers with which we ordinarily deal, and they consist of a magnitude and a sign, which can be positive or negative. Real numbers can range from positive numbers of indefinitely large magnitude to negative numbers of indefinitely large magnitude. Among the real numbers are the *integers* $0, \pm 1, \pm 2, \pm 3$, and so on, which are part of the *rational numbers*. Other rational numbers are quotients of two integers, such as $\frac{2}{3}$, $\frac{7}{9}$, $\frac{37}{53}$. Fractions can be represented as decimal numbers. For example, $\frac{1}{16}$ is the same as 0.0625. Some fractions cannot be represented exactly by a decimal number with a finite number of nonzero digits. For example, $\frac{1}{3}$ is represented by $0.333333\cdots$. The three dots (an ellipsis) that follow the given digits indicate that more digits follow. In this case, infinitely many digits are required for an exact representation. However, the decimal representation of a rational number either has a finite number of nonzero digits or contains a repeating pattern of digits.

EXERCISE 1.1 ▶ Take a few simple fractions, such as $\frac{2}{3}$, $\frac{4}{9}$, or $\frac{3}{7}$ and express them as decimal numbers, finding either all of the nonzero digits or the repeating pattern of digits. ◀

The numbers that are not rational numbers are called *irrational numbers*. *Algebraic irrational number* include square roots of rational numbers, cube roots of rational numbers, and so on, which are not themselves rational numbers. All of the rest of the real numbers are called *transcendental irrational numbers*. Two commonly encountered transcendental irrational numbers are the ratio of the circumference of a circle to its diameter, called π and given by $3.141592653\cdots$, and

the *base of natural logarithms*, called e and given by $2.718281828\cdots$. Irrational numbers have the property that if you have some means of finding what the correct digits are, you will never reach a point beyond which all of the remaining digits are zero, or beyond which the digits form some other repeating pattern.[1]

In addition to real numbers, mathematicians have defined *imaginary numbers* into existence. The *imaginary unit*, i, is defined to equal $\sqrt{-1}$. An *imaginary number* is equal to a real number times i, and a *complex number* is equal to a real number plus an imaginary number. If x and y are real numbers, then the quantity $z = x + iy$ is a complex number. x is called the *real part* of z, and the real number y is called the *imaginary part* of z. Imaginary and complex numbers cannot represent physically measurable quantities, but turn out to have important applications in quantum mechanics. We will discuss complex numbers in the next chapter.

The numbers that we have been discussing are called *scalars*, to distinguish them from *vectors*. A scalar number has magnitude and sign, and a vector has both magnitude and direction. We will discuss vectors later, and will see that a vector can be represented by several scalars.

Measurements, Accuracy, and Significant Digits

A measured quantity can almost never be known with complete exactness. It is therefore a good idea to communicate the probable accuracy of a reported measurement. For example, assume that you measured the length of a piece of glass tubing with a meter stick and that your measured value was 387.8 millimeters (387.8 mm). You decide that your experimental error was probably no greater than 0.6 mm. The best way to specify the length of the glass tubing is

$$\textit{length} = 387.8\,\text{mm} \pm 0.6\,\text{mm}$$

If for some reason you cannot include a statement of the probable error, you should at least avoid including digits that are probably wrong. In this case, your estimated error is somewhat less than 1 mm, so the correct number is probably closer to 388 mm than to either 387 mm or 389 mm. If we do not want to report the expected experimental error, we report the length as 388 mm and assert that the three digits given are *significant digits*. This means that the given digits are correctly stated. If we had reported the length as 387.8 mm, the last digit is *insignificant*. That is, if we knew the exact length, the digit 8 after the decimal point is probably not the correct digit, since we believe that the correct length lies between 387.2 mm and 388.4 mm.

You should always avoid reporting digits that are not significant. When you carry out calculations involving measured quantities, you should always determine how many significant digits your answer can have and round off your result to that number of digits. When values of physical quantities are given in a physical chemistry textbook or in this book, you can assume that all digits specified are significant. If you are given a number that you believe to be correctly stated, you can count the number of significant digits. If there are no zeros in the number, the number of significant digits is just the number of digits. If the number contains one or more zeros, any zero that occurs between nonzero digits does count as a

[1] It has been said that early in the twentieth century the legislature of the state of Indiana, in an effort to simplify things, passed a resolution that henceforth in that state, π should be exactly equal to 3.

significant digit. Any zeros that are present only to specify the location of a decimal point do not represent significant digits. For example, the number 0.0000345 contains three significant digits, and the number 0.003045 contains four significant digits. The number 76,000 contains only two significant digits. However, the number 0.000034500 contains five significant digits. The zeros at the left are present only to locate the decimal point, but the final two zeros are not needed to locate a decimal point, and therefore must have been included because the number is known with sufficient accuracy that these digits are significant.

A problem arises when zeros that appear to occur only to locate the decimal point are actually significant. For example, if a mass is known to be closer to 3500 grams (3500 g) than to 3499 g or to 3501 g, there are four significant digits. If one simply wrote 3500 g, persons with training in significant digits would assume that the zeros are not significant and that there are two significant digits. Some people communicate the fact that there are four significant digits by writing 3500. grams. The explicit decimal point communicates the fact that the zeros are significant digits. Others put a bar over any zeros that are significant, writing $35\bar{0}\bar{0}$ to indicate that there are four significant digits.

Scientific Notation

The communication difficulty involving significant zeros can be avoided by the use of *scientific notation*, in which a number is expressed as the product of two factors, one of which is a number lying between 1 and 10 and the other is 10 raised to some integer power. The mass mentioned above would thus be written as 3.500×10^3 g. There are clearly four significant digits indicated, since the trailing zeros are not required to locate a decimal point. If the mass were known to only two significant digits, it would be written as 3.5×10^3 g.

Scientific notation is also convenient for extremely small or extremely large numbers. For example, *Avogadro's constant*, the number of molecules or other formula units per mole, is easier to write as 6.02214×10^{23} mol^{-1} than as 602,214,000,000,000,000,000,000 mol^{-1}, and the charge on an electron is easier to write and read as 1.60217×10^{-19} coulomb (1.60217×10^{-19} C) than as 0.000000000000000000160217 C.

EXERCISE 1.2 ► Convert the following numbers to scientific notation, using the correct number of significant digits:

(a) 0.000598 (b) 67, 342, 000

(c) 0.000002 (d) 6432.150

◄

Rounding

The process of rounding is straightforward in most cases. The calculated number is simply replaced by that number containing the proper number of digits that is closer to the calculated value than any other number containing this many digits. Thus, if there are three significant digits, 4.567 is rounded to 4.57, and 4.564 is rounded to 4.56. However, if your only insignificant digit is a 5, your calculated number is midway between two rounded numbers, and you must decide

whether to round up or to round down. It is best to have a rule that will round down half of the time and round up half of the time. One widely used rule is to round to the even digit, since there is a 50% chance that any digit will be even. For example, 2.5 would be rounded to 2, and 3.5 would be rounded to 4. An equally valid procedure that is apparently not generally used would be to toss a coin and round up if the coin comes up "heads" and to round down if it comes up "tails."

EXERCISE 1.3 ▶ Round the following numbers to four significant digits

(a) 0.2468985 (b) 78955

(c) 123456789 (d) 46.4535

◀

1.2 Numerical Mathematical Operations

We are frequently required to carry out numerical operations on numbers. The first such operations involve pairs of numbers.

Elementary Arithmetic Operations

The elementary mathematical operations are addition, subtraction, multiplication, and division. Some rules for operating on numbers with sign can be simply stated:

1. The product of two factors of the same sign is positive, and the product of two factors of different signs is negative.
2. The quotient of two factors of the same sign is positive, and the quotient of two factors of different signs is negative.
3. The difference of two numbers is the same as the sum of the first number and the negative of the second.
4. Multiplication is *commutative*, which means that[2] if a and b stand for numbers

$$\boxed{a \times b = b \times a.} \tag{1.1}$$

5. Multiplication is *associative*, which means that

$$\boxed{a \times (b \times c) = (a \times b) \times c.} \tag{1.2}$$

6. Multiplication and addition are *distributive*, which means that

$$\boxed{a \times (b + c) = a \times b + a \times c.} \tag{1.3}$$

[2] We enclose equations that you will likely use frequently in a box.

Additional Mathematical Operations

In addition to the four elementary arithmetic operations, there are some other important mathematical operations, many of which involve only one number. The *magnitude*, or *absolute value*, of a scalar quantity is a number that gives the size of the number irrespective of its sign. It is denoted by placing vertical bars before and after the symbol for the quantity. This operation means

$$|x| = \begin{cases} x & \text{if } x \geq 0 \\ -x & \text{if } x < 0 \end{cases} \tag{1.4}$$

For example,

$$\begin{aligned} |4.5| &= 4.5 \\ |-3| &= 3 \end{aligned}$$

The magnitude of a number is always nonnegative (positive or zero).

Another important set of numerical operations is the taking of *powers and roots*. If x represents some number that is multiplied by itself $n-1$ times so that there are n factors, we represent this by the symbol x^n, representing x to the nth power. For example,

$$x^2 = x \times x, \quad x^3 = x \times x \times x, \quad x^n = x \times x \times x \times \cdots \times x \quad (n \text{ factors}). \tag{1.5}$$

The number n in the expression x^n is called the *exponent* of x. If the exponent is not an integer, we can still define x^n. We will discuss this when we discuss logarithms. An exponent that is a negative number indicates the reciprocal of the quantity with a positive exponent:

$$\boxed{x^{-1} = \tfrac{1}{x}, \quad x^{-3} = \tfrac{1}{x^3}} \tag{1.6}$$

There are some important facts about exponents. The first is

$$\boxed{x^a x^b = x^{a+b}} \tag{1.7}$$

where x, a, and b represent numbers. We call such an equation an *identity*, which means that it is correct for all values of the variables in the equation. The next identity is

$$\boxed{(x^a)^b = x^{ab}} \tag{1.8}$$

Roots of real numbers are defined in an inverse way from powers. For example, the *square root* of x is denoted by $\sqrt{x}$ and is defined as the number that yields x when squared:

$$(\sqrt{x})^2 = x \tag{1.9}$$

The *cube root* of x is denoted by $\sqrt[3]{x}$, and is defined as the number that when cubed (raised to the third power) yields x:

$$\left(\sqrt[3]{x}\right)^3 = x \tag{1.10}$$

Fourth roots, fifth roots, and so on, are defined in similar ways. The operation of taking a root is the same as raising a number to a fractional exponent. For example,

$$\sqrt[3]{x} = x^{1/3} \tag{1.11}$$

This equation means that

$$\left(\sqrt[3]{x}\right)^3 = (x^{1/3})^3 = x = (x^3)^{1/3} = \sqrt[3]{x^3}.$$

This equation illustrates the fact that the order of taking a root and raising to a power can be reversed without changing the result. We say that these operations *commute* with each other.

There are two numbers that when squared will yield a given positive real number. For example, $2^2 = 4$ and $(-2)^2 = 4$. When the symbol $\sqrt{4}$ is used, only the positive square root, 2, is meant. To specify the negative square root of x, we write $-\sqrt{x}$. If we confine ourselves to real numbers, there is no square root, fourth root, sixth root, and so on, of a negative number. In Section 2.6, we define imaginary numbers, which are defined be square roots of negative quantities. Both positive and negative numbers can have real cube roots, fifth roots, and so on, since an odd number of negative factors yields a negative product.

The square roots, cube roots, and so forth, of integers and other rational numbers are either rational numbers or *algebraic irrational numbers*. The square root of 2 is an example of an *algebraic irrational number*. An algebraic irrational number produces a rational number when raised to the proper integral power. When written as a decimal number, an algebraic irrational number does not have a finite number of nonzero digits or exhibit any pattern of repeating digits. An irrational number that does not produce a rational number when raised to any integral power is a *transcendental irrational number*. Examples are e, the base of natural logarithms, and π, the ratio of a circle's circumference to its diameter.

Logarithms

We have discussed the operation of raising a number to an integral power. The expression a^2 means $a \times a$, a^{-2} means $1/a^2$, a^3 means $a \times a \times a$, and so on. In addition, you can have exponents that are not integers. If we write

$$y = a^x \tag{1.12}$$

the exponent x is called the *logarithm of y to the base a* and is denoted by

$$x = \log_a (y) \tag{1.13}$$

If a is positive, only positive numbers possess real logarithms.

Common Logarithms

If the base of logarithms equals 10, the logarithms are called *common logarithms:* If $10^x = y$, then x is the common logarithm of y, denoted by $\log_{10}(y)$. The subscript 10 is sometimes omitted, but this can cause confusion.

For integral values of x, it is easy to generate the following short table of common logarithms:

y	$x = \log_{10}(y)$	y	$x = \log_{10}(y)$
1	0	0.1	-1
10	1	0.01	-2
100	2	0.001	-3
1000	3	*etc.*	

In order to understand logarithms that are not integers, we need to understand exponents that are not integers.

EXAMPLE 1.1 Find the common logarithm of $\sqrt{10}$.

SOLUTION ► The square root of 10 is the number that yields 10 when multiplied by itself:

$$\left(\sqrt{10}\right)^2 = 10.$$

We use the fact about exponents

$$\left(a^x\right)^z = a^{xz}. \tag{1.14}$$

Since 10 is the same thing as 10^1,

$$\sqrt{10} = 10^{1/2}. \tag{1.15}$$

Therefore

$$\log_{10}\left(\sqrt{10}\right) = \log_{10}(3.162277...) = \frac{1}{2} = 0.5000$$

◄

Equation (1.14) and some other relations governing exponents can be used to generate other logarithms, as in the following problem.

EXERCISE 1.4 ► Use Eq. (1.14) and the fact that $10^{-n} = 1/(10^n)$ to generate the negative logarithms in the short table of logarithms. ◄

We will not discuss further how the logarithms of various numbers are computed. Extensive tables of logarithms with up to seven or eight significant digits were once in common use. Most electronic calculators provide values of logarithms with as many as 10 or 11 significant digits. Before the invention of electronic calculators, tables of logarithms were used when a calculation required more significant digits than a slide rule could provide. For example, to multiply two numbers together, one would look up the logarithms of the two numbers, add the logarithms and then look up the *antilogarithm* of the sum (the number possessing the sum as its logarithm).

Natural Logarithms

Besides 10, there is another commonly used base of logarithms. This is a transcendental irrational number called e and equal to 2.7182818 . . .

$$\boxed{\text{If } e^y = x \quad \text{then } y = \log_e(x) = \ln(x).} \tag{1.16}$$

Logarithms to this base are called *natural logarithms*. The definition of e is[3]

$$e = \lim_{n\to\infty} \left(1 + \frac{1}{n}\right)^n = 2.7182818\ldots \tag{1.17}$$

The "lim" notation means that larger and larger values of n are taken.

EXERCISE 1.5 ▶ Evaluate the quantity $(1 + \frac{1}{n})^n$ for several integral values of n ranging from 1 to 1, 000, 000. Notice how the value approaches the value of e as n increases. ◀

The notation $\ln(x)$ is more common than $log_e(x)$. Natural logarithms are also occasionally called *Napierian logarithms*.[4] Unfortunately, some mathematicians use the symbol $\log(y)$ without a subscript for natural logarithms. Chemists frequently use the symbol $\log(y)$ without a subscript for common logarithms and the symbol $\ln(y)$ for natural logarithms. Chemists use both common and natural logarithms, so the best practice is to use $\log_{10}(x)$ for the common logarithm of x and $\ln(x)$ for the natural logarithm of x.

If the common logarithm of a number is known, its natural logarithm can be computed as

$$e^{\ln(y)} = 10^{\log_{10}(y)} = \left(e^{\ln(10)}\right)^{\log_{10}(y)} = e^{\ln(10)\log_{10}(y)}. \tag{1.18}$$

The natural logarithm of 10 is equal to $2.302585\ldots$, so we can write

$$\boxed{\ln(y) = \ln(10)\log_{10}(y) = (2.302585\cdots)\log_{10}(y)}. \tag{1.19}$$

In order to remember Eq. (1.19) correctly, keep the fact in mind that since e is smaller than 10, the natural logarithm is larger than the common logarithm.

EXERCISE 1.6 ▶ Without using a calculator or a table of logarithms, find the following:

(a) $\ln(100.000)$ (b) $\ln(0.0010000)$

(c) $\log_{10}(e)$

◀

Logarithm Identities

There are a number of identities involving logarithms, some of which come from the exponent identities in Eqs. (1.6)–(1.8). Table 1.1 lists some identities involving exponents and logarithms. These identities hold for common logarithms and natural logarithms as well for logarithms to any other base.

[3]The base of natural logarithms, e, is named after Leonhard Euler, 1707–1783, a great Swiss mathematician.

[4]Naperian logarithms are named after John Napier, 1550–1617, a Scottish landowner, theologian, and mathematician, who was one of the inventors of logarithms.

TABLE 1.1 ► Properties of Exponents and Logarithms

Exponent fact	Logarithm fact
$a^0 = 1$	$\log_a(1) = 0$
$a^{1/2} = \sqrt{a}$	$\log_a\left(\sqrt{a}\right) = \frac{1}{2}$
$a^1 = a$	$\log_a(a) = 1$
$a^{x_1}a^{x_2} = a^{x_1+x_2}$	$\log_a(y_1y_2) = \log_a(y_1) + \log_a(y_2)$
$a^{-x} = \frac{1}{a^x}$	$\log_a\left(\frac{1}{y}\right) = -\log_a(y)$
$\frac{a^{x_1}}{a^{x_2}} = a^{x_1-x_2}$	$\log_a\left(\frac{y_1}{y_2}\right) = \log_a(y_1) - \log_a(y_2)$
$(a^x)^z = a^{xz}$	$\log_a(y^z) = z\log_a(y)$
$a^\infty = \infty$	$\log_a(\infty) = \infty$
$a^{-\infty} = 0$	$\log_a(0) = -\infty$

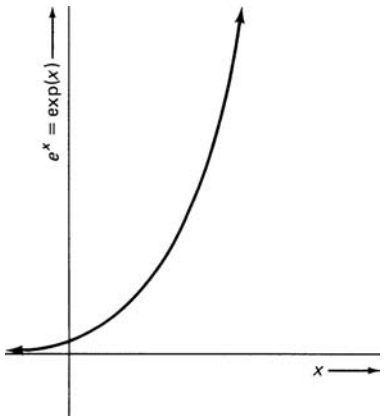

Figure 1.1 ► The exponential function.

The Exponential

The *exponential* is the same as raising e (the base of natural logarithms, equal to $2.7182818284\cdots$) to a given power and is denoted either by the usual notation for a power, or by the notation $\exp(\cdots)$.

$$y = ae^{bx} \equiv a\exp(bx)\,, \tag{1.20}$$

Figure 1.1 shows a graph of this function for $b > 0$.

The graph in Fig. 1.1 exhibits an important behavior of the exponential e^{bx}. For $b > 0$, it doubles each time the independent variable increases by a fixed amount whose value depends on the value of b. For large values of b the exponential function becomes large very rapidly. If $b < 0$, the function decreases to half its value each time the independent variable increases by a fixed amount. For large negative values of b the exponential function becomes small very rapidly.

EXERCISE 1.7 ► For a positive value of b find an expression for the change in x required for the function e^{bx} to double in size. ◄

An example of the exponential function is in the decay of radioactive isotopes. If N_0 is the number of atoms of the isotope at time $t = 0$, the number at any other time, t, is given by

$$N(t) = N_0 e^{-t/\tau}, \tag{1.21}$$

where τ is called the *relaxation time*. It is the time for the number of atoms of the isotope to drop to $1/e = 0.367879$ of its original value. The time that is required for the number of atoms to drop to half its original value is called the *half-time* or *half-life*, denoted by $t_{1/2}$.

EXAMPLE 1.2 Show that $t_{1/2}$ is equal to $\tau \ln(2)$.

SOLUTION ► If $t_{1/2}$ is the half-life, then

$$e^{-t_{1/2}/\tau} = \frac{1}{2}.$$

Thus

$$\frac{t_{1/2}}{\tau} = -\ln\left(\frac{1}{2}\right) = \ln(2)\,. \tag{1.22}$$

◄

EXERCISE 1.8 ► A certain population is growing exponentially and doubles in size each 30 years.
(a) If the population includes 4.00×10^6 individuals at $t = 0$, write the formula giving the population after a number of years equal to t.
(b) Find the size of the population at $t = 150$ years. ◄

EXERCISE 1.9 ► A reactant in a first-order chemical reaction without back reaction has a concentration governed by the same formula as radioactive decay,

$$[\mathrm{A}]_t = [\mathrm{A}]_0\, e^{-kt},$$

where $[\mathrm{A}]_0$ is the concentration at time $t = 0$, $[\mathrm{A}]_t$ is the concentration at time t, and k is a function of temperature called the rate constant. If $k = 0.123\,\mathrm{s}^{-1}$, find the time required for the concentration to drop to 21.0% of its initial value. ◄

1.3 Units of Measurement

The measurement of a length or other variable would be impossible without a standard definition of the unit of measurement. For many years science and commerce were hampered by the lack of accurately defined units of measurement. This problem has been largely overcome by precise measurements and international agreements. The internationally accepted system of units of measurements is called the *Systéme International d'Unités*, abbreviated *SI*. This is an *MKS system*, which means that length is measured in meters, mass in kilograms, and time in seconds. In 1960 the international chemical community agreed to use SI units,

TABLE 1.2 ► SI Units

SI base units (units with independent definitions)

Physical quantity	Name of unit	Symbol	Definition
Length	meter	m	Length such that the speed of light is exactly $299,792,458\,\mathrm{m\,s^{-1}}$.
Mass	kilogram	kg	The mass of a platinum-iridium cylinder kept at the International Bureau of Weights and Measures in France.
Time	second	s	The duration of $9,192,631,770$ cycles of the radiation of a certain emission of the cesium atom.
Electric current	ampere	A	The magnitude of current which, when flowing in each of two long parallel wires 1 m apart in free space, results in a force of 2×10^7 N per meter of length.
Temperature	kelvin	K	Absolute zero is 0 K; triple point of water is 273.16 K.
Luminous intensity	candela	cd	The luminous intensity, in the perpendicular intensity direction, of a surface of $1/600,000\,\mathrm{m^2}$ of a black body at temperature of freezing platinum at a pressure of $101,325\,\mathrm{N\,m^{-2}}$.
Amount of substance	mole.	mol	Amount of substance that contains as many elementary units as there are carbon atoms in exactly 0.012 kg of the carbon-12 (^{12}C) isotope.

Other SI units (derived units)

Physical quantity	Name of unit	Physical dimensions	Symbol	Definition
Force	newton	$\mathrm{kg\,m\,s^{-2}}$	N	$1\,\mathrm{N} = 1\,\mathrm{kg\,m\,s^{-2}}$
Energy	joule	$\mathrm{kg\,m^2\,s^{-2}}$	J	$1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}}$
Electrical charge	coulomb	A s	C	$1\,\mathrm{C} = 1\,\mathrm{A\,s}$
Pressure	pascal	$\mathrm{N\,m^{-2}}$	Pa	$1\,\mathrm{Pa} = 1\,\mathrm{N\,m^{-2}}$
Magnetic field	tesla	$\mathrm{kg\,s^{-2}\,A^{-1}}$	T	$1\,\mathrm{T} = 1\,\mathrm{kg\,s^{-2}\,A^{-1}} = 1\,\mathrm{Wb\,m^{-2}}$
Luminous flux	lumen	cd sr	lm	$1\,\mathrm{lm} = 1\,\mathrm{cd\,sr}$ (sr = steradian)

which had been in use by physicists for some time.[5] The seven base units given in Table 1.2 form the heart of the system. The table also includes some derived units, which owe their definitions to the definitions of the seven base units.

Multiples and submultiples of SI units are commonly used.[6] Examples are the millimeter and kilometer. These multiples and submultiples are denoted by standard prefixes attached to the name of the unit, as listed in Table 1.3. The abbreviation for a multiple or submultiple is obtained by attaching the prefix abbreviation

[5] See "Policy for NBS Usage of SI Units," *J. Chem. Educ.* **48**, 569 (1971).

[6] There is a possibly apocryphal story about Robert A. Millikan, a Nobel-prize-winning physicist who was not noted for false modesty. A rival is supposed to have told Millikan that he had defined a new unit for the quantitative measure of conceit and had named the new unit the kan. However, 1 kan was an exceedingly large amount of conceit so for most purposes the practical unit was to be the millikan.

TABLE 1.3 ► Prefixes for Multiple and Submultiple Units

Multiple	Prefix	Abbreviation	Multiple	Prefix	Abbreviation
10^{12}	tera-	T	10^{-3}	milli-	m
10^{9}	giga-	G	10^{-6}	micro-	μ
10^{6}	mega-	M	10^{-9}	nano-	n
10^{3}	kilo-	k	10^{-12}	pico-	p
1	—	—	10^{-15}	femto-	f
10^{-1}	deci-	d	10^{-18}	atto-	a
10^{-2}	centi-	c			

to the unit abbreviation, as in Gm (gigameter) or ns (nanosecond). Note that since the base unit of length is the kilogram, the table would imply the use of things such as the mega kilogram. Double prefixes are not used. We use gigagram instead of megakilogram. The use of the prefixes for 10^{-1} and 10^{-2} is discouraged, but centimeters will probably not be abandoned for many years to come. The Celsius temperature scale also remains in common use among chemists.

Some non-SI units continue to be used, such as the *atmosphere* (atm), which is a pressure defined to equal $101,325\,\mathrm{N\,m^{-2}}$ (101, 325 Pa), the *liter* (l), which is exactly $0.001\,\mathrm{m^3}$, and the *torr*, which is a pressure such that exactly 760 torr equals exactly 1 atm. The *Celsius temperature scale* is defined such that the degree Celsius (°C) is the same size as the kelvin, and 0 °C is equivalent to 273.15 K.

In the United States of America, English units of measurement are still in common use. The *inch* (in) has been redefined to equal exactly 0.0254 m. The *foot* (ft) is 12 inches and the mile (mi) is 5280 feet. The *pound* (lb) is equal to 0.4536 kg (not an exact definition; good to four significant digits).

Any measured quantity is not completely specified until its units are given. If a is a length equal to 10.345 m, one must write

$$a = 10.345\,\mathrm{m} \tag{1.23}$$

not just

$$a = 10.345 \quad \text{(not correct)}.$$

It is permissible to write

$$a/\,\mathrm{m} = 10.345$$

which means that the length a divided by 1 m is 10.345, a dimensionless number. When constructing a table of values, it is convenient to label the columns or rows with such dimensionless quantities.

When you make numerical calculations, you should make certain that you use consistent units for all quantities. Otherwise, you will likely get the wrong answer. This means that (1) you must convert all multiple and submultiple units to the base unit, and (2) you cannot mix different systems of units. For example, you cannot correctly substitute a length in inches into a formula in which the other quantities are in SI units without converting. It is a good idea to write the unit as well as the number, as in Eq. (1.23), even for scratch calculations. This will help you avoid some kinds of mistakes by inspecting any equation and making sure that both sides are measured in the same units. In 1999 a U.S. space vehicle optimistically named the *Mars Climate Orbiter* crashed into the surface of Mars instead of orbiting the planet. The problem turned out to be that engineers working on the project had

used English units such as feet and pounds, whereas physicists had used metric units such as meters and kilograms. A failure to convert units properly cost U.S. taxpayers several millions of dollars and the loss of a possibly useful mission. In another instance, when a Canadian airline switched from English units to metric units, a ground crew miscalculated the mass of fuel needed for a flight. The jet airplane ran out of fuel, but was able to glide to an unused military airfield and make a "deadstick" landing. Some people were having a picnic on the unused runway, but were able to get out of the way. There was even a movie made about the incident.

1.4 Numerical Calculations

The most common type of numerical calculation in a chemistry course is the calculation of one quantity from the numerical values of other quantities, guided by some formula. There can be familiar formulas that are used in everyday life and there can be formulas that are specific to chemistry. Some formulas require only the four basic arithmetic operations: addition, subtraction, multiplication, and division. Other formulas require the use of the exponential, logarithms, or trigonometric functions. The formula is a recipe for carrying out the specified numerical operations. Each quantity is represented by a symbol (a letter) and the operations are specified by symbols such as $\times$, $/$, $+$, $-$, ln, and so on. A simple example is the familiar formula for calculating the volume of a rectangular object as the product of its height (h), width (w), and length (l):

$$V = h \times w \times l$$

The symbol for multiplication is often omitted so that the formula would be written $v = hwl$. If two symbols are written side by side, it is understood that the quantities represented by the symbols are to be multiplied together. Another example is the *ideal gas equation*

$$P = \frac{nRT}{V} \tag{1.24}$$

where P represents the pressure of the gas, n is the amount of gas in moles, T is the absolute temperature, V is the volume, and R is a constant known as the *ideal gas constant*.

Significant Digits in a Calculated Quantity

When you calculate a numerical value that depends on a set of numerical values substituted into a formula, the accuracy of the result depends on the accuracy of the first set of values. The number of significant digits in the result depends on the numbers of significant digits in the first set of values. Any result containing insignificant digits must be rounded to the proper number of digits.

Multiplication and Division

There are several useful rules of thumb that allow you to determine the proper number of significant digits in the result of a calculation. For multiplication of

two or more factors, the rule is that the product will have the same number of significant digits as the factor with the fewest significant digits. The same rule holds for division. In the following example we use the fact that the volume of a rectangular object is the product of its length times its width times its height.

EXAMPLE 1.3 What is the volume of a rectangular object whose length is given as 7.78 m, whose width is given as 3.486 m, and whose height is 1.367 m?

SOLUTION ► We denote the volume by V and obtain the volume by multiplication, using a calculator.

$$V = (7.78\,\text{m})(3.486\,\text{m})(1.367\,\text{m}) = 37.07451636\,\text{m}^3 = 37.1\,\text{m}^3\,.$$

The calculator delivered 10 digits, but we round the volume to $37.1\,\text{m}^3$, since the factor with the fewest significant digits has three significant digits. ◄

EXAMPLE 1.4 Compute the smallest and largest values that the volume in Example 1.1 might have and determine whether the answer given in Example 1.1 is correctly stated.

SOLUTION ► The smallest value that the length might have, assuming the given value to have only significant digits, is 7.775 m, and the largest value that it might have is 7.785 m. The smallest possible value for the width is 3.4855 m, and the largest value is 3.4865 m. The smallest possible value for the height is 1.3665 m, and the largest value is 1.3675 m. The minimum value for the volume is

$$V_{\text{min}} = (7.775\,\text{m})(3.4855\,\text{m})(1.3665\,\text{m}) = 37.0318254562\,\text{m}^3\,.$$

The maximum value is

$$V_{\text{max}} = (7.785\,\text{m})(3.4865\,\text{m})(1.3675\,\text{m}) = 37.1172354188\,\text{m}^3\,.$$

Obviously, all of the digits beyond the first three are insignificant. The rounded result of $37.1\,\text{m}^3$ in Example 1.1 contains all of the digits that can justifiably be given. However, in this case there is some chance that $37.0\,\text{m}^3$ might be closer to the actual volume than is $37.1\,\text{m}^3$. We will still consider a digit to be significant if it might be incorrect by ± 1. ◄

Addition and Subtraction

The rule of thumb for significant digits in addition or subtraction is that for a digit to be significant, it must arise from a significant digit in every term of the sum or difference. You cannot simply count the number of significant digits in every term.

EXAMPLE 1.5 Determine the combined length of two objects, one of length 0.783 m and one of length 17.3184 m.

SOLUTION ► We make the addition:

$$\begin{array}{r} 0.783\,\text{m} \\ 17.3184\,\text{m} \\ \hline 18.1014\,\text{m} \end{array} \quad \approx 18.101\,\text{m}$$

The fourth digit after the decimal point in the sum could be significant only if that digit were significant in every term of the sum. The first number has only three significant digits after the decimal point. We must round the answer to 18.101 m. Even after this rounding, we have obtained a number with five significant digits, while one of our terms has only three significant digits. ◄

In a calculation with several steps, it is not a good idea to round off the insignificant digits at each step. This procedure can lead to accumulation of *round-off error*. A reasonable policy is to carry along at least one insignificant digit during the calculation, and then to round off the insignificant digits at the final answer. When using an electronic calculator, it is easy to use all of the digits carried by the calculator and then to round off at the end of the calculation.

Significant Digits in Trigonometric Functions, Logarithms, and Exponentials

If you are carrying out operations other than additions, subtractions, multiplications, and divisions, determining which digits are significant is not so easy. In many cases the number of significant digits in the result is roughly the same as the number of significant digits in the argument of the function, but more accurate rules of thumb can be found.[7] If you need an accurate determination of the number of significant digits when applying these functions, it might be necessary to do the operation with the smallest and the largest values that the number on which you must operate can have (incrementing and decrementing the number).

EXAMPLE 1.6 Calculate the following. Determine the correct number of significant digits by incrementing or decrementing.

(a) $\sin(372.15^\circ)$ (b) $\ln(567.812)$

(c) $e^{-9.813}$.

SOLUTION ► (a) Using a calculator, we obtain

$$\begin{aligned}\sin(372.155^\circ) &= 0.210557\\ \sin(372.145^\circ) &= 0.210386.\end{aligned}$$

Therefore,

$$\sin(372.15^\circ) = 0.2105.$$

The value could be as small as 0.2104, but we write 0.2105, since we routinely declare a digit to be significant if it might be wrong by just ± 1. Even though the argument of the sine had five significant digits, the sine has only four significant digits.

(b) By use of a calculator, we obtain

$$\begin{aligned}\ln(567.8125) &= 6.341791259\\ \ln(567.8115) &= 6.341789497.\end{aligned}$$

Therefore,

$$\ln(567.812) = 6.34179.$$

In this case, the logarithm has the same number of significant digits as its argument. If the argument of a logarithm is very large, the logarithm can have many more significant digits than its argument, since the logarithm of a large number is a slowly varying function of its argument.

[7] Donald E. Jones, "Significant Digits in Logarithm Antilogarithm Interconversions," *J. Chem. Educ.* **49**, 753 (1972).

(c) Using a calculator, we obtain

$$e^{-9.8135} = 0.00005470803$$
$$e^{-9.8125} = 0.00005476277.$$

Therefore, when we round off the insignificant digits,

$$e^{-9.8125} = 0.000547.$$

Although the argument of the exponential had four significant digits, the exponential has only three significant digits. The exponential function of fairly large arguments is a rapidly varying function, so fewer significant digits can be expected for large arguments. ◄

EXERCISE 1.10 ► Calculate the following to the proper numbers of significant digits.
(a) $(37.815 + 0.00435)(17.01 + 3.713)$
(b) $625[e^{12.1} + \sin(60.0\,^\circ)]$
(c) 65.718×12.3
(d) $17.13 + 14.6751 + 3.123 + 7.654 - 8.123$. ◄

The Factor-Label Method

This is an elementary method for the routine conversion of a quantity measured in one unit to the same quantity measured in another unit. The method consists of multiplying the quantity by a *conversion factor*, which is a fraction that is equal to unity in a physical sense, with the numerator and denominator equal to the same quantity expressed in different units. This does not change the quantity physically, but numerically expresses it in another unit, and so changes the number expressing the value of the quantity. For example, to express 3.00 km in terms of meters, one writes

$$(3.00\,\text{km})\left(\frac{1000\,\text{m}}{1\,\text{km}}\right) = 3000\,\text{m} = 3.00 \times 10^3\,\text{m}\,. \tag{1.25}$$

You can check the units by considering a given unit to "cancel" if it occurs in both the numerator and denominator. Thus, both sides of Eq. (1.25) have units of meters, because the km on the top cancels the km on the bottom of the left-hand side. In applying the method, you should write out the factors explicitly, including the units. You should carefully check that the unwanted units cancel. Only then should you proceed to the numerical calculation.

EXAMPLE 1.7 Express the speed of light, $2.9979 \times 10^8\ \text{m}\,\text{s}^{-1}$, in miles per hour. Use the definition of the inch, $1\,\text{in} = 0.0254\,\text{m}$ (exactly).

SOLUTION ►

$$\left(2.9979 \times 10^8\,\text{m}\,\text{s}^{-1}\right)\left(\frac{1\,\text{in}}{0.0254\,\text{m}}\right)\left(\frac{1\,\text{ft}}{12\,\text{in}}\right)\left(\frac{1\,\text{mi}}{5280\,\text{ft}}\right)\left(\frac{60\,\text{s}}{1\,\text{min}}\right)\left(\frac{60\,\text{min}}{1\,\text{h}}\right)$$
$$= 6.7061 \times 10^8\,\text{mi}\,\text{h}^{-1}\,.$$

The conversion factors that correspond to exact definitions do not limit the number of significant digits. In this example, all of the conversion factors are exact definitions, so our answer has five significant digits because the stated speed has five significant digits. ◄

EXERCISE 1.11 ► Express the following in terms of SI base units. The electron volt (eV), a unit of energy, equals 1.6022×10^{-19} J.

(a) 24.17 mi

(b) $75\,\text{mi}\,\text{h}^{-1}$

(c) $7.5\,\text{nm}\,\text{ps}^{-1}$

(d) 13.6 eV

◄

SUMMARY

In this chapter, we introduced the use of numerical values and operations in chemistry. In order to use such values correctly, one must handle the units of measurement in which they are expressed. Techniques for doing this, including the factor-label method, were introduced. One must also recognize the uncertainties in experimentally measured quantities. In order to avoid implying a greater accuracy than actually exists, one must express calculated quantities with the proper number of significant digits. Basic rules for significant digits were presented.

PROBLEMS

1. Find the number of inches in a meter. How many significant digits could be given?

2. Find the number of meters in 1 mile and the number of miles in 1 kilometer, using the definition of the inch. How many significant digits could be given?

3. A furlong is one-eighth of a mile and a fortnight is 2 weeks. Find the speed of light in furlongs per fortnight, using the correct number of significant digits.

4. The distance by road from Memphis, Tennessee, to Nashville, Tennessee, is 206 miles. Express this distance in meters and in kilometers.

5. A U.S. gallon is defined as 231.00 cubic inches.

a) Find the number of liters in one gallon.

b) The volume of a mole of an ideal gas at 0.00 °C (273.15 K) and 1.000 atm is 22.414 liters. Express this volume in gallons and in cubic feet.

6. In the USA, footraces were once measured in yards and at one time, a time of 10.00 seconds for this distance was thought to be unattainable. The best runners now run 100 m in 10 seconds. Express 100 m in yards, assuming three significant digits. If a runner runs 100 m in 10.00 s, find his time for 100 yards, assuming a constant speed.

7. Find the average length of a century in seconds and in minutes, finding all possible significant digits. Use the fact that a year ending in 00 is not a leap year unless the year is divisible by 400, in which case it is a leap year. Find the number of minutes in a microcentury.

8. A light year is the distance traveled by light in one year.

a) Express this distance in meters and in kilometers. Use the average length of a year as described in the previous problem. How many significant digits can be given?

b) Express a light year in miles.

9. The *Rankine temperature scale* is defined so that the Rankine degree is the same size as the Fahrenheit degree, and 0 °R is the same as 0 K.

a) Find the Rankine temperature at 0.00 °C.

b) Find the Rankine temperature at 0.00 °F.

10. Calculate the mass of AgCI that can be precipitated from 10.00 ml of a solution of NaCl containing 0.345 mol l^{-1}. Report your answer to the correct number of digits.

11. The volume of a sphere is given by

$$V = \frac{4}{3}\pi r^3 \tag{1.26}$$

where V is the volume and r is the radius. If a certain sphere has a radius given as 0.005250 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the sphere might have with the given information and check your first answer for the volume.

12. The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where V is the volume, r is the radius, and h is the height. If a certain right circular cylinder has a radius given as 0.134 m and a height given as 0.318 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the cylinder might have with the given information and check your first answer for the volume.

13. The value of a certain angle is given as 31 °. Find the measure of the angle in radians. Using a table of trigonometric functions or a calculator, find the smallest and largest values that its sine and cosine might have and specify the sine and cosine to the appropriate number of digits.

14.

a) Some elementary chemistry textbooks give the value of R, the ideal gas constant, as 0.0821 l atm K^{-1} mol^{-1}. Using the SI value, 8.3145 J K^{-1} mol^{-1}, obtain the value in l atm K^{-1} mol^{-1} to five significant digits.

b) Calculate the pressure in atmospheres and in N m^{-2} (Pa) of a sample of an ideal gas with $n = 0.13678$ mol, $V = 1.000$ l and $T = 298.15$ K, using the value of the ideal gas constant in SI units.

c) Calculate the pressure in part b in atmospheres and in N m^{-2} (Pa) using the value of the ideal gas constant in l atm K^{-1} mol^{-1}.

15. The van der Waals equation of state gives better accuracy than the ideal gas equation of state. It is

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

where a and b are parameters that have different values for different gases and where $V_m = V/n$, the molar volume. For carbon dioxide, $a = 0.3640\,\text{Pa}\,\text{m}^6\,\text{mol}^{-2}$, $b = 4.267 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$. Calculate the pressure of carbon dioxide in pascals, assuming that $n = 0.13678\,\text{mol}$, $V = 1.000\,\text{l}$, and $T = 298.15\,\text{K}$. Convert your answer to atmospheres and torr.

16. The *specific heat capacity* (specific heat) of a substance is crudely defined as the amount of heat required to raise the temperature of unit mass of the substance by 1 degree Celsius (1 °C). The specific heat capacity of water is $4.18\,\text{J}\,^\circ\text{C}^{-1}\,\text{g}^{-1}$. Find the rise in temperature if 100.0 J of heat is transferred to 1.000 kg of water.

2

Symbolic Mathematics and Mathematical Functions

Preview

In this chapter, we discuss symbolic mathematical operations, including algebraic operations on real scalar variables, algebraic operations on real vector variables, and algebraic operations on complex scalar variables. We introduce the concept of a mathematical function and discuss trigonometric functions, logarithms and the exponential function.

Principal Facts and Ideas

1. Algebra is a branch of mathematics in which operations are performed symbolically instead of numerically, according to a well-defined set of rules.
2. Trigonometric functions are examples of mathematical functions: To a given value of an angle there corresponds a value of the sine function, and so on.
3. There is a set of useful trigonometric identities.
4. A vector is a quantity with magnitude and direction.
5. Vector algebra is an extension of ordinary algebra with its own rules and defined operations.
6. A complex number has a real part and an imaginary part that is proportional to i, defined to equal $\sqrt{-1}$.
7. The algebra of complex numbers is an extension of ordinary algebra with its own rules and defined operations.
8. Problem solving in chemistry involves organizing the given information, understanding the objective, planning the approach, carrying out the procedures, and checking the answer.

Objectives

After you have studied the chapter, you should be able to:

1. manipulate variables algebraically to simplify complicated algebraic expressions;
2. manipulate trigonometric functions correctly;
3. work correctly with logarithms and exponentials;
4. calculate correctly the sum, difference, scalar product, and vector product of any two vectors, whether constant or variable;
5. perform elementary algebraic operations on complex numbers; form the complex conjugate of any complex number and separate the real and imaginary parts of any complex expression; and
6. plan and carry out the solution of typical chemistry problems.

2.1 Algebraic Operations on Real Scalar Variables

Algebra is a branch of mathematics that was invented by Greek mathematicians and developed by Hindu, Arab, and European mathematicians. It was apparently the first branch of *symbolic mathematics*. Its great utility comes from the fact that letters are used to represent constants and variables and that operations are indicated by symbols such as $+$, $-$, $\times$, $/$, $\sqrt{}$, and so on. Operations can be carried out symbolically instead of numerically so that formulas and equations can be modified and simplified before numerical calculations are carried out. This ability allows calculations to be carried out that arithmetic cannot handle.

The numbers and variables on which we operate in this section are called *real numbers* and *real variables*, They do not include imaginary numbers such as the square root of -1, which we discuss later. They are also called *scalars*, to distinguish them from *vectors*, which have direction as well as magnitude. Real scalar numbers have *magnitude*, a specification of the size of the number, and *sign*, which can be positive or negative.

Algebraic Manipulations

Algebra involves symbolic operations. You manipulate symbols instead of carrying out numerical operations. For example, you can symbolically divide an expression by some quantity by writing its symbol in a denominator. You can then cancel the symbol in the denominator against the same symbol in the numerator of the same fraction or carry out other operations. You can factor a polynomial expression and possibly cancel one or more of the factors against the same factors in a denominator. You can solve an equation by symbolically carrying out some set of operations on both sides of an equation, eventually isolating one of the symbols on one side of the equation. Remember that if one side of an equation is operated on by anything that changes its value, the same operation must be applied to the other side of the equation to keep a valid equation. Operations that do not change the value of an expression, such as factoring an expression, multiplying out factors, multiplying

the numerator and denominator of a fraction by the same factor, and so on, can be done to one side of an equation without destroying its validity.

EXAMPLE 2.1 Write the following expression in a simpler form:

$$A = \frac{(2x+5)(x+3) - 2x(x+5) - 14}{x^2 + 2x + 1}.$$

SOLUTION ► We multiply out the factors in the numerator and combine terms, factor the denominator, and cancel a common factor:

$$A = \frac{2x^2 + 11x + 15 - 2x^2 - 10x - 14}{(x+1)\,(x+1)} = \frac{x+1}{(x+1)\,(x+1)} = \frac{1}{x+1}$$

◄

EXERCISE 2.1 ► Write the following expression in a simpler form:

$$B = \frac{(x^2 + 2x)^2 - x^2(x-2)^2 + 12x^4}{6x^3 + 12x^4}.$$

◄

The van der Waals equation of state provides a more nearly exact description of real gases than does the ideal gas equation. It is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

where P is the pressure, V is the volume, n is the amount of gas in moles, T is the absolute temperature, and R is the ideal gas constant (the same constant as in the ideal gas equation, equal to $8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}$ or $0.08206\,\mathrm{l\,atm\,K^{-1}\,mol^{-1}}$). The symbols a and b represent *parameters*, which means that they are constants for a particular gas, but have different values for different gases.

EXERCISE 2.2 ► (a) Manipulate the van der Waals equation so that V_m, defined as V/n, occurs instead of V and n occurring separately.
(b) Manipulate the equation into an expression for P in terms of T and V_m.
(c) Manipulate the equation into a cubic equation in V_m. That is, make an expression with terms proportional to powers of V_m up to V_m^3. ◄

EXERCISE 2.3 ► Find the value of the expression

$$\frac{3\,(2+4)^2 - 6\,(7 + |-17|)^3 + \left(\sqrt{37 - |-1|}\right)^3}{\left(1 + 2^2\right)^4 - \left(|-7| + 6^3\right)^2 + \sqrt{12 + |-4|}}.$$

◄

2.2 Trigonometric Functions

The ordinary *trigonometric functions* include the sine, the cosine, the tangent, the cotangent, the secant, and the cosecant. These are sometimes called the *circular trigonometric functions* to distinguish them from the hyperbolic trigonometric functions discussed briefly in the next section of this chapter.

The trigonometric functions can be defined geometrically as in Fig. 2.1, which shows two angles, α_1 and α_2. Along the horizontal reference line drawn from the point E to the point D, the points C_1 and C_2 are chosen so that the triangles are right triangles (triangles with one right angle). In the right triangle AB_1C_1, the radius r is called the *hypotenuse*, the vertical side of length y_1 is called the *opposite side*, and the horizontal side of length x_1 is called the *adjacent side*. We define the trigonometric functions sine, cosine, and tangent of α_1 as follows:

$$\sin(\alpha_1) = \frac{y_1}{r} \quad \text{(opposite side over hypotenuse)} \tag{2.1}$$

$$\cos(\alpha_1) = \frac{x_1}{r} \quad \text{(adjacent side over hypotenuse)} \tag{2.2}$$

$$\tan(\alpha_1) = \frac{y_1}{x_1} \quad \text{(opposite side over adjacent side)} \tag{2.3}$$

$$\cot(\alpha_1) = \frac{x_1}{y_1} \quad \text{(adjacent side over opposite side)} \tag{2.4}$$

$$\sec(\alpha_1) = \frac{r}{x_1} \quad \text{(hypotenuse over adjacent side)} \tag{2.5}$$

$$\csc(\alpha_1) = \frac{r}{y_1} \quad \text{(hypotenuse over opposite side)} \tag{2.6}$$

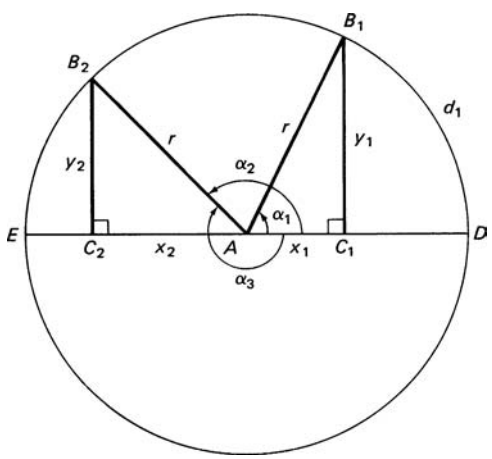

Figure 2.1 ► The figure used in defining trigonometric functions.

The trigonometric functions of the angle α_2 are defined in the same way, except that as drawn in Fig. 2.1, the distance x_2 must be counted as negative, because the point B_2 is to the left of A. If the point B_2 were below A, then y_2 would also be counted as negative.

There are three common ways to specify the size of an angle (*the "measure" of an angle*). *Degrees* are defined so that a right angle corresponds to $90\,^\circ$ (90 degrees), and a full circle contains $360\,^\circ$. The *grad* is defined so that 100 grad corresponds to a right angle and a full circle contains 400 grad. For most mathematical purposes, the best way to specify the size of an angle is with *radians*. The measure of an angle in radians is defined to be the length of the arc subtending the angle divided by the radius of the circle. In Fig. 2.1, the arc DB_1 subtends the angle α_1, so that in radians

$$\alpha_1 = \frac{d_1}{r}, \tag{2.7}$$

where d_1 is the length of the arc DB_1. The full circle contains 2π radians (2π rad), and 1 radian corresponds to $360^\circ/(2\pi) = 57.2957795\cdots^\circ$. The right angle, $90\,^\circ$, is $\pi/2$ radians = $1.5707963\cdots$ radians. We can express the angle α in terms of radians, degrees, or grad, but must understand which measure is being used. For example, we could write

$$\sin(90\,^\circ) = \sin(\pi/2) \tag{2.8}$$

This does not look like a correct equation until we understand that on the left-hand side the angle is measured in degrees and on the right-hand side the angle is measured in radians. If you use degrees, you should always include the degree sign ($^\circ$).

The trigonometric functions are examples of *mathematical functions*. A mathematical function is a rule that provides a unique connection between the value of one variable, called the *independent variable* or the *argument* of the function, and another variable, which we call the *dependent variable*. When we choose a value for the independent variable, the function provides a corresponding value for the dependent variable. For example, if we write

$$f(x) = \sin(x), \tag{2.9}$$

then f is the dependent variable and x the independent variable. The trigonometric functions illustrate a general property of the functions that we deal with. They are *single-valued*: for each value of the angle α, there is one and only one value of the sine, one and only one value of the cosine, and so on. Mathematicians usually use the name "function" to apply only to single-valued functions. We will discuss mathematical functions in more detail in Chapter 4.

Trigonometric Identities

There are a number of relations between trigonometric functions that are valid for all values of the given angles. Such relations are said to be *identically true*, or to be *identities*. We first present some identities involving an angle and its negative. A negative angle is measured in the clockwise direction while positive angles are measured in the counter-clockwise direction. A figure analogous to Fig. 2.1 with

a negative angle can be used to show that

$$\boxed{\sin(\alpha) = -\sin(-\alpha)} \tag{2.10}$$

$$\boxed{\cos(\alpha) = \cos(-\alpha)} \tag{2.11}$$

$$\boxed{\tan(\alpha) = -\tan(-\alpha)} \tag{2.12}$$

Equations (2.10) and (2.12) express the fact that the sine and the tangent are *odd functions*, and Eq. (2.11) expresses the fact that the cosine is an *even function*. If $f(x)$ is an odd function, then

$$f(-x) = -f(x) \quad \text{(odd function)} \tag{2.13}$$

If $f(x)$ is an even function, then

$$f(-x) = f(x) \quad \text{(even function)} \tag{2.14}$$

From Eqs. (2.1) through (2.6), we can deduce the additional identities:

$$\boxed{\cot(\alpha) = \frac{1}{\tan(\alpha)}} \tag{2.15}$$

$$\boxed{\sec(\alpha) = \frac{1}{\cos(\alpha)}} \tag{2.16}$$

$$\boxed{\csc(\alpha) = \frac{1}{\sin(\alpha)}} \tag{2.17}$$

Figure 2.1 also shows a third angle α_3, which is counted as negative. This angle has the same triangle, and therefore the same trigonometric functions as the positive angle α_2. Since α_3 is equal to $-(2\pi - \alpha_2)$ if the angles are measured in radians, we can write an identity

$$\sin(\alpha_3) = \sin[-(2\pi - \alpha_2)] = \sin(\alpha_2 - 2\pi) = \sin(\alpha_2) \tag{2.18}$$

with similar equations for the other trigonometric functions. This equation is related to the periodic behavior of trigonometric functions. If an angle is increased by 2π radians (360 °), the new angle corresponds to the same triangle as does the old angle, and we can write

$$\boxed{\sin(\alpha) = \sin(\alpha + 2\pi) = \sin(\alpha + 4\pi) = \cdots} \tag{2.19}$$

$$\boxed{\cos(\alpha) = \cos(\alpha + 2\pi) = \cos(\alpha + 4\pi) = \cdots} \tag{2.20}$$

with similar equations for the other trigonometric functions. The trigonometric functions are *periodic functions* with period 2π. That is, if any integral multiple of 2π is added to the argument, the value of the function is unchanged.

EXERCISE 2.4 ▶ Using a calculator, find the value of the cosine of 15.5° and the value of the cosine of 375.5°. Display as many digits as your calculator is able to display. Check to see if there is any round-off error in the last digit. Choose another pair of angles that differ by 360° and repeat the calculation. Set your calculator to use angles measured in radians. Find the value of $\sin(0.3000)$. Find the value of $\sin(0.3000 + 2\pi)$. See if there is any round-off error in the last digit. ◀

A useful trigonometric identity corresponds to the famous *theorem of Pythagoras*. Pythagoras drew a figure with three squares such that one side of each square formed a side of the same right triangle. He then proved by geometry that the area of the square on the hypotenuse was equal to the sum of the areas of the squares on the other two sides. In terms of the quantities in Fig. 2.1

$$\boxed{x^2 + y^2 = r^2} \tag{2.21}$$

We divide both sides of this equation by r^2 and use Eqs. (2.1) and (2.2) to obtain the identity:

$$\boxed{[\sin(\alpha)]^2 + [\cos(\alpha)]^2 = \sin^2(\alpha) + \cos^2(\alpha) = 1.} \tag{2.22}$$

Notice the common notation for a power of a trigonometric function: the exponent is written after the symbol for the trigonometric function and before the parentheses enclosing the argument.

EXERCISE 2.5 ▶ Using a calculator, find the values of the sine and cosine of 49.5°. Square the two values and add the results. See if there is any round-off error in your calculator. Choose another angle and repeat the calculation. ◀

Mathematical Limits and a Useful Approximation

Comparison of Eqs. (2.1) and (2.7) shows that for a fairly small angle, the sine of an angle and the measure of the angle in radians are approximately equal, since the sine differs from the measure of the angle only by having the opposite side in place of the arc length, which is approximately the same size. In fact,

$$\lim_{\alpha \to 0} \frac{\sin(\alpha)}{\alpha} = 1 \quad (\alpha \text{ must be measured in radians}). \tag{2.23}$$

The symbol on the left stands for a *mathematical limit*. In this case, the equation means that if we let the value of α become smaller and smaller until it becomes more and more nearly equal to zero, the ratio of $\sin(\alpha)$ to α becomes more and more nearly equal to unity. In some cases (but not in this case), there is a distinction between letting the variable draw closer in value to a constant value from the positive side or from the negative side. To indicate that α approaches zero from the positive side (takes on positive values closer and closer to zero), we would write

$$\lim_{\alpha \to 0^+} \frac{\sin(\alpha)}{\alpha} = 1 \tag{2.24}$$

To indicate that α approaches zero from the negative side, we would write

$$\lim_{\alpha \to 0^-} \frac{\sin(\alpha)}{\alpha} = 1 \tag{2.25}$$

In the present case, the limits in Eq. (2.24) and (2.25) are the same, and there is no need to specify which one is meant.

For fairly small angles, we write as an approximation

$$\alpha \approx \sin(\alpha) \quad (\alpha \text{ must be measured in radians}) \tag{2.26}$$

where the angle α must be measured in radians. Since the adjacent side of a right triangle is nearly equal to the hypotenuse for small angles, we can also write

$$\boxed{\alpha \approx \tan(\alpha) \approx \sin(\alpha) \quad (\alpha \text{ must be measured in radians})} \tag{2.27}$$

Equations (2.26) and (2.27) are valid for both positive and negative values of α. If you are satisfied with an accuracy of about 1%, you can use Eq. (2.27) for angles with magnitude up to about 0.2 radians (approximately 11 °).

EXERCISE 2.6 ► For an angle that is nearly as large as $\pi/2$, find an approximate equality similar to Eq. (2.27) involving $(\pi/2) - \alpha$, $\cos(\alpha)$, and $\cot(\alpha)$. ◄

General Properties of Trigonometric Functions

To use trigonometric functions easily, you must have a clear mental picture of the way in which the sine, cosine, and tangent depend on their arguments. Figures 2.2, 2.3, and 2.4 show these functions.

The tangent has a complicated behavior, becoming larger without bound as its argument approaches $\pi/2$ from the left, and becoming more negative without bound as its argument approaches the same value from the right. We can write

$$\lim_{\alpha \to \frac{\pi}{2}^+} [\tan(\alpha)] = -\infty$$
$$\lim_{\alpha \to \frac{\pi}{2}^-} [\tan(\alpha)] = \infty.$$

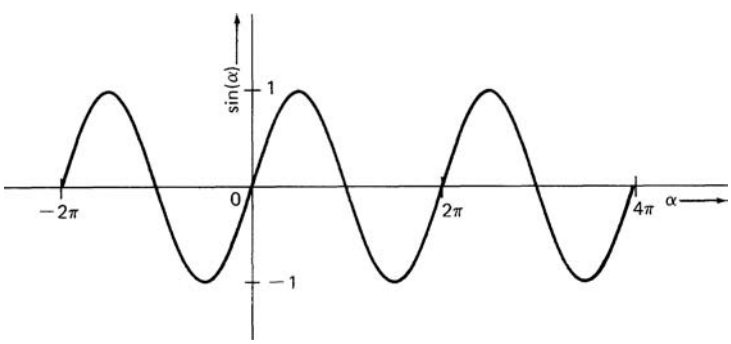

Figure 2.2 ► The sine of an angle α.

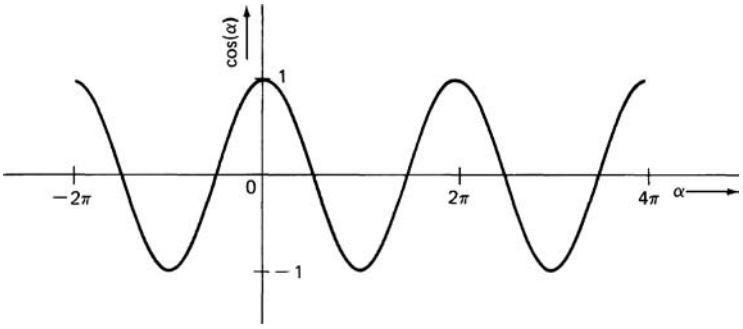

Figure 2.3 ► The cosine of an angle α.

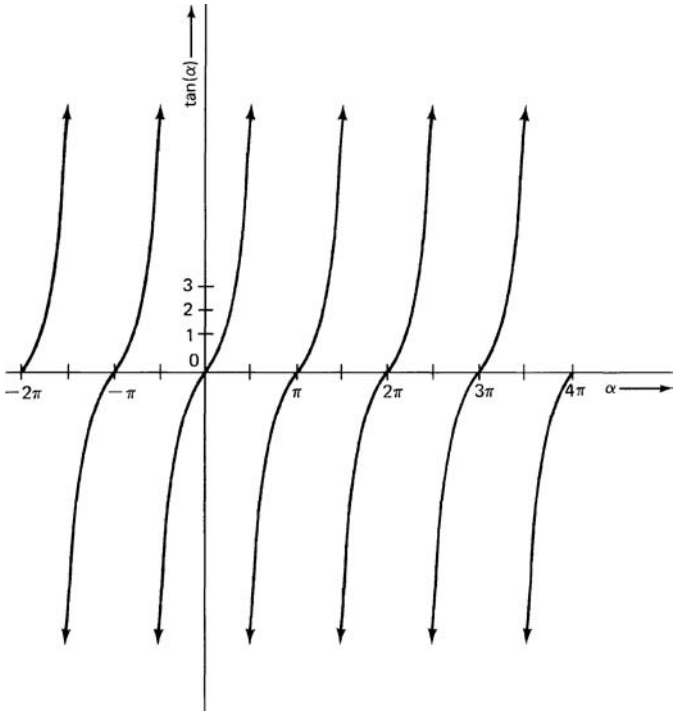

Figure 2.4 ► The tangent of an angle α.

In these equations, the superscript $+$ on the $\pi/2$ in the limit means that the value of α approaches $\pi/2$ from the right. That is, α is greater than $\pi/2$ as it becomes more and more nearly equal to $\pi/2$. The $-$ superscript in the limit means that α approaches $\pi/2$ from the left. The symbol ∞ stands for *infinity*, which is larger than any number that you or anyone else can name. This quantity is sometimes called "*undefined*."

2.3 Inverse Trigonometric Functions

It is possible to think of trigonometric functions as defining a mathematical function in an inverse way. For example, if

$$y = \sin(x) \tag{2.28}$$

we can define a function to give a value for x as a function of y. We write

$$x = \arcsin(y). \tag{2.29}$$

This can be read as "x is the angle whose sine is y." The *arcsine* function is also called the *inverse sine* function, and another notation is also common:

$$x = \sin^{-1}(y). \tag{2.30}$$

The -1 superscript indicates an inverse function. It is not an exponent, even though exponents are written in the same position. If you need to write the reciprocal of $\sin(y)$, you should write $[\sin(y)]^{-1}$ to avoid confusion. It is probably better to use the notation of Eq. (2.29) rather than that of Eq. (2.30) to avoid confusion.

From Fig. 2.2, you can see that there are many angles that have the same value of the sine function. In order to make the arcsine in Eq. (2.29) or Eq. (2.30) into a single-valued function, we must restrict the values of x that we consider. With the arcsine function, these values are taken from $-\pi/2$ to $+\pi/2$ and are called the *principal values* of the arcsine function. The other inverse trigonometric functions such as the inverse cosine and inverse tangent are defined in the same way as the arcsine function, and must also have principal values defined. The principal values of the arctangent and arccosecant functions range from $-\pi/2$ to $+\pi/2$, the same as with the arcsine. The principal values of the arccosine, arccotangent, and arcsecant are taken from 0 to π.

EXERCISE 2.7 ▶ Sketch graphs of the arcsine function, the arccosine function, and the arctangent function. Include only the principal values. ◀

Hyperbolic Trigonometric Functions

These functions are closely related to the exponential function. The *hyperbolic sine* of x is denoted by $\sinh(x)$, and defined by

$$\sinh(x) = \frac{1}{2}(e^x - e^{-x}). \tag{2.31}$$

The *hyperbolic cosine* is denoted by $\cosh(x)$, and defined by

$$\cosh(x) = \frac{1}{2}\left(e^x + e^{-x}\right). \tag{2.32}$$

The other hyperbolic trigonometric functions are the *hyperbolic tangent*, denoted by $\tanh(x)$; the *hyperbolic cotangent*, denoted by $\coth(x)$; the *hyperbolic secant*, denoted by $\operatorname{sech}(x)$; and the hyperbolic cosecant, denoted by $\operatorname{csch}(x)$. These functions are given by the equations

$$\tanh(x) = \frac{\sinh(x)}{\cosh(x)} \tag{2.33}$$

$$\coth(x) = \frac{1}{\tanh(x)} \tag{2.34}$$

$$\operatorname{sech}(x) = \frac{1}{\cosh(x)} \tag{2.35}$$

$$\operatorname{csch}(x) = \frac{1}{\sinh(x)} \tag{2.36}$$

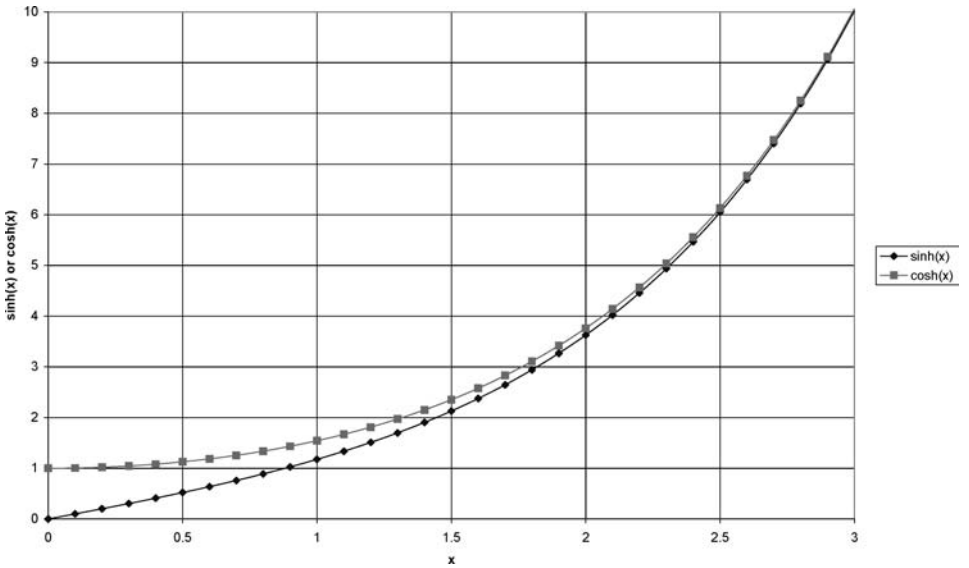

Figure 2.5 ► The hyperbolic sine and cosine.

Figure 2.5 shows the hyperbolic sine and hyperbolic cosine for values of x from 0 to 3. Note that the values of the hyperbolic sin and the hyperbolic cosine do not necessarily lie between -1 and 1 as do the values of the circular sine and cosine functions and that both functions approach $e^x/2$ for large values of x.

EXERCISE 2.8 ► Make a graph of $\tanh(x)$ and $\coth(x)$ on the same graph for values of x ranging from 0 to 3. ◄

EXERCISE 2.9 ► Find the value of each of the hyperbolic trigonometric functions for $x = 0$ and $x = \pi/2$. Compare these values with the values of the ordinary (circular) trigonometric functions for the same values of the independent variable. ◄

2.4 Vectors and Coordinate Systems

Quantities that have both magnitude and direction are called *vectors*. For example, the position of an object can be represented by a vector, since the position can be specified by giving the distance and the direction from a reference point (*an origin*). A force is also a vector, since it is not completely specified until its magnitude and direction are both given. Some other vectors that are important in physical chemistry are the dipole moments of molecules, magnetic and electric fields, angular momenta, and magnetic dipoles.

We will use a boldface letter to represent a vector. For example, the force on an object is denoted by **F**. When you are writing by hand, there is no easy way to write boldface letters, so you can use a letter with an arrow over it (e.g., $\vec{F}$) or you can use a wavy underscore (e.g., $\underset{\sim}{F}$), which is the typesetter's symbol for boldface type.

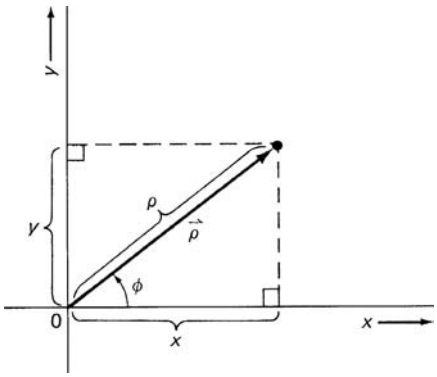

Figure 2.6 ► A position vector, ρ, in a plane, with plane polar coordinates and Cartesian coordinates.

Vectors in Two Dimensions

Two-dimensional vectors include position vectors of objects that remain on a flat surface. We represent this physical surface by a mathematical plane, which is a map of the surface so that each location in the physical surface corresponds to a point of the mathematical plane. We choose some point as an origin and pick some line passing through the origin as our x axis. One end of this axis is designated as the positive end. The line passing through the origin perpendicular to the x axis is our y axis, and the end that is counterclockwise 90 ° from the positive end of the y axis is its positive end. These axes are shown in Fig. 2.6. In this figure, the origin is labeled as point O, and the location of some object is labeled as point P.

The directed line segment beginning at O and ending at P is the *position vector* of the object. We denote the position vector in two dimensions by the boldface Greek letter $\boldsymbol{\rho}$. In the figure, we draw an arrowhead on the directed line segment to make its direction clear.

The negative of a given vector is a vector of the same length directed in the opposite direction. A vector and its negative have the same magnitude, as do all the vectors of the same length pointing in any other directions. The *magnitude* of $\boldsymbol{\rho}$ is denoted $|\boldsymbol{\rho}|$ or by ρ. It is a nonnegative quantity equal to the length of the vector ρ. One way to specify the location of the point P is to give the magnitude of $\boldsymbol{\rho}$ and the value of the angle ϕ between the positive end of the x axis and $\boldsymbol{\rho}$, measured counterclockwise from the axis. The variables ρ and ϕ are called the *plane polar coordinates* of the point P. If we allow ρ to range from zero to ∞ and allow ϕ to range from 0 to 2π radians, we can specify the location of any point in the plane.

There is another common way to specify the location of P. We draw two line segments from P perpendicular to the axes, as shown in Fig. 2.6. The distance from the origin to the intersection on the x axis is called x and is considered to be positive if the intersection is on the positive half of the axis, and negative if the intersection is on the negative half of the axis. The distance from the origin to the intersection on the y axis is called y, and its sign is assigned in a similar way. The variables x and y are the *Cartesian coordinates* of P.[1] The point P can be designated by its Cartesian coordinates within parentheses, as (x, y). The values of x and y are also called the*Cartesian components* of the position vector.

[1]Cartesian coordinates are named for Rene DuPerron Descarte, 1596–1650, French mathematician, philosopher, and natural scientist, who is famous (in part) for his statement, "I think, therefore I am."

Changing from plane polar coordinates to Cartesian coordinates is an example of *transformation of coordinates*, and can be done by using the equations

$$x = \rho \cos(\phi) \tag{2.37}$$
$$y = \rho \sin(\phi) \tag{2.38}$$

EXERCISE 2.10 ▶ Show that Eqs. (2.37) and (2.38) are correct. ◀

The coordinate transformation in the other direction is also possible. From the theorem of Pythagorus, Eq. (2.21),

$$\rho = \sqrt{x^2 + y^2}. \tag{2.39}$$

From the definition of the tangent function, Eq. (2.3),

$$\phi = \arctan\left(\frac{y}{x}\right). \tag{2.40}$$

However, since we want ϕ to range from 0 to 2π radians, we must specify this range for the inverse tangent function, instead of using the principal value. If we are using a calculator that is programmed to deliver the principal value, we must decide in advance which quadrant ϕ lies in and be prepared to add π or 2π to the calculator result if it lies in the wrong quadrant.

EXERCISE 2.11 ▶ (a) Find x and y if $\rho = 6$ and $\phi = \pi/6$ radians. (b) Find ρ and ϕ if $x = 5$ and $y = 10$. ◀

A position vector is only one example of a vector. Anything, such as a force, a velocity, or an acceleration, which has magnitude and direction, is a vector. Figure 2.6 is a map of physical space, and a distance in such a diagram is measured in units of length, such as meters. Other kinds of vectors can also be represented on vector diagrams by directed line segments. However, such a diagram is not a map of physical space, and the length of a line segment representing a vector will represent the magnitude of a force, or the magnitude of a velocity, or something else. Position vectors ordinarily remain with their tails at the origin, but since other vector diagrams do not necessarily represent a physical (geographical) space, we will consider a vector to be unchanged if it is moved from one place in a vector diagram to another, as long as its length and its direction do not change.

Vector Algebra in Two Dimensions

Figure 2.7 is a vector diagram in which two vectors, **A** and **B,** are shown. The sum of the two vectors is obtained as follows: (1) Move the second vector so that its tail coincides with the head of the first. (2) Draw the sum vector from the tail of the first vector to the head of the second. The addition of vectors is commutative: $\mathbf{A} + \mathbf{B}$ is the same as $\mathbf{B} + \mathbf{A}$.

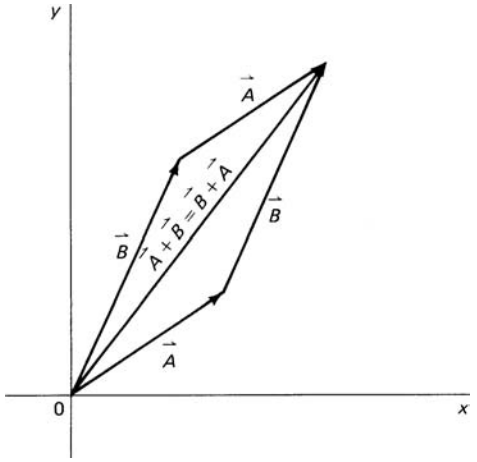

Figure 2.7 ► Two vectors and their sum.

The components of **A** and **B** are defined in the same way as the components of the position vector in Fig. 2.6. The x components are called A_x and B_x, and the y components are called A_y and B_y. We can denote the vector **A** by its component in x, y order inside parentheses, as (A_x, A_y) Vector addition can be performed using the components of the vectors. If the sum of **A** and **B** is called **C**,

$$\mathbf{C} = \mathbf{A} + \mathbf{B} \tag{2.41}$$
$$C_x = A_x + B_x \tag{2.42}$$
$$C_y = A_y + B_y. \tag{2.43}$$

EXAMPLE 2.2 Find the sum of the two vectors (2.5, 3) and (3.1, 4).

SOLUTION ► $\mathbf{A} + \mathbf{B} = (5, 6, 7)$ ◄

The difference of two vectors is the sum of the first vector and the negative of the second. The negative of **B** is denoted by $-\mathbf{B}$ and is the vector with components $-B_x$ and $-B_y$. If the vector $\mathbf{A} - \mathbf{B}$ is called **D**,

$$\mathbf{D} = \mathbf{A} - \mathbf{B} \tag{2.44}$$
$$D_x = A_x - B_x \tag{2.45}$$
$$D_y = A_y - B_y. \tag{2.46}$$

If the tail of the vector $-\mathbf{B}$ is placed at the head of the vector **A**, the vector $\mathbf{D} = \mathbf{A} - \mathbf{B}$ has its tail at the tail of **A** and its head at the head of $-\mathbf{B}$. The difference $\mathbf{D} = \mathbf{A} - \mathbf{B}$ can also be represented by placing the tails of both **A** and **B** at the same place and drawing the vector **D** with its tail at the head of **B** and its head at the head of **A**.

EXERCISE 2.12 ► Draw vector diagrams and convince yourself that the two schemes presented for the construction of $\mathbf{D} = \mathbf{A} - \mathbf{B}$ give the same result. ◄

If **A** is a vector and a is a scalar, the *product of the scalar and the vector* $a\mathbf{A}$ has the components

$$(aA)_x = aA_x \tag{2.47}$$
$$(aA)_y = aA_y \tag{2.48}$$

If a is a positive scalar, the vector $a\mathbf{A}$ points in the same direction as **A**, and if a is a negative scalar, the vector $a\mathbf{A}$ points in the opposite direction. The magnitude of $a\mathbf{A}$ is equal to $|a|\,|\mathbf{A}| = |a|A$.

The magnitude of a vector **A** in two dimensions is denoted by A or by $|\mathbf{A}|$. It is obtained in the same manner as the magnitude of a position vector:

$$A = |\mathbf{A}| = \sqrt{A_x^2 + A_y^2} \tag{2.49}$$

EXERCISE 2.13 ▶ The vector **A** has the components $A_x = 2$, $A_y = 3$. The vector **B** has the components $B_x = 3$, $B_y = 4$. (a) Find $|\mathbf{A}|$ and $|\mathbf{B}|$. (b) Find the components and the magnitude of $\mathbf{A} + \mathbf{B}$. (c) Find the components and the magnitude of $\mathbf{A} - \mathbf{B}$. (d) Find the components and the magnitude of $2\mathbf{A} - \mathbf{B}$. ◀

We next define the *scalar product* of two vectors, which is also called the *dot product* because of the use of a dot to represent the operation. If **A** and **B** are two vectors, and α is the angle between them, their scalar product is denoted by $\mathbf{A} \cdot \mathbf{B}$ and given by

$$\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}|\,|\mathbf{B}| \cos(\alpha)\,. \tag{2.50}$$

The result is a scalar, as the name implies.

EXERCISE 2.14 ▶
(a) Let $|\mathbf{A}| = 4.5$, $|\mathbf{B}| = 6.0$, and let the angle between them equal 30.0°. Find $\mathbf{A} \cdot \mathbf{B}$.
(b) Let $|\mathbf{A}| = 4.0$, $|\mathbf{B}| = 2.0$, and let the angle between them equal 45.0°. Find $\mathbf{A} \cdot \mathbf{B}$. ◀

The following are properties of the scalar product:

1. If **A** and **B** are parallel, $\mathbf{A} \cdot \mathbf{B}$ is the product of the magnitudes of **A** and **B**.
2. The scalar product of **A** with itself is the square of the magnitude of **A**:
$$\mathbf{A} \cdot \mathbf{A} = \left|\mathbf{A}^2\right| = \left|A^2\right| = A^2 = A_x^2 + A_y^2.$$
3. If **A** and **B** are perpendicular to each other, $\mathbf{A} \cdot \mathbf{B} = 0$. Such vectors are said to be *orthogonal* to each other.
4. If **A** and **B** point in opposite directions (are antiparallel), $\mathbf{A} \cdot \mathbf{B}$ is the negative of the product of the magnitudes of **A** and **B**.

A convenient way to represent vectors is by using *unit vectors*. We define **i** to be a vector of unit length pointing in the direction of the positive end of the x axis, and **j** to be a vector of unit length pointing in the direction of the positive end of the y axis. These are shown in Fig. 2.8.

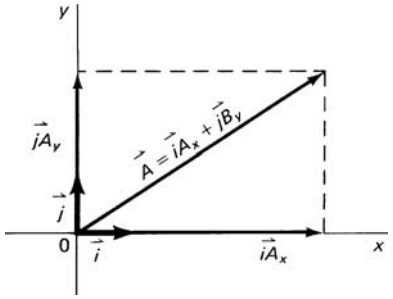

Figure 2.8 ► A vector in terms of the unit vectors **i** and **j**.

A vector **A** is represented as

$$\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y. \tag{2.51}$$

The first term on the right-hand side of this equation is a product of the component A_x and a vector **i**, so it is a vector of length A_x pointing along the x axis, as shown in Fig. 2.8. The other term is similarly a vector of length A_y pointing along the y axis. The vector **A** is the vector sum shown in Fig. 2.8. A similar equation can be written for another vector, **B**:

$$\mathbf{B} = \mathbf{i}B_x + \mathbf{j}B_y. \tag{2.52}$$

The scalar product $\mathbf{A} \cdot \mathbf{B}$ can be written

$$\begin{aligned} \mathbf{A} \cdot \mathbf{B} &= \left(\mathbf{i}A_x + \mathbf{j}A_y\right) \cdot \left(\mathbf{i}B_x + \mathbf{j}B_y\right) \\ &= \mathbf{i} \cdot \mathbf{i}A_xB_x + \mathbf{i} \cdot \mathbf{j}A_xB_y + \mathbf{j} \cdot \mathbf{i}A_yB_x + \mathbf{j} \cdot \mathbf{j}A_yB_y. \end{aligned}$$

From the definitions of **i** and **j** and the definition of the scalar product,

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = 1 \tag{2.53}$$

$$\mathbf{i} \cdot \mathbf{j} = \mathbf{j} \cdot \mathbf{i} = 0 \tag{2.54}$$

so that

$$\boxed{\mathbf{A} \cdot \mathbf{B} = A_xB_x + A_yB_y} \tag{2.55}$$

EXAMPLE 2.3 Consider the following vectors: $\mathbf{A} = 2.5\mathbf{i} + 4\mathbf{j}$ and $\mathbf{B} = 3\mathbf{i} - 5\mathbf{j}$.

(a) Find $\mathbf{A} \cdot \mathbf{B}$.

(b) Find $|\mathbf{A}|$ and $|\mathbf{B}|$ and use them to find the angle between **A** and **B**.

SOLUTION ► $\mathbf{A} \cdot \mathbf{B} = (2.5)(3) + (4)(-5) = 7.5 - 20 = -12.5.$

$$\begin{aligned} |\mathbf{A}| &= (6.25 + 16)^{1/2} = (22.25)^{1/2} = 4.717\ldots \\ |\mathbf{B}| &= (9 + 25)^{1/2} = (34)^{1/2} = 5.8309\ldots \\ \cos(\alpha) &= \frac{\mathbf{A} \cdot \mathbf{B}}{|\mathbf{A}|\,|\mathbf{B}|} = \frac{-12.5}{(4.717)(5.831)} = -0.4545 \\ \alpha &= \arccos(-0.4545) = 2.043\,\text{rad} = 117.0\,^\circ \end{aligned}$$

◄

EXERCISE 2.15 ► Consider two vectors $\mathbf{A} = (3.00)\mathbf{i} - (4.00)\mathbf{j}$ and $\mathbf{B} = (1.00)\mathbf{i} + (2.00)\mathbf{j}$.
(a) Draw a vector diagram of the two vectors.
(b) Find $\mathbf{A} \cdot \mathbf{B}$ and $(2\mathbf{A}) \cdot (3\mathbf{B})$.
(c) Find the magnitude of $\mathbf{A} \cdot \mathbf{B}$.
(d) Find the angle between $\mathbf{A}$ and $\mathbf{B}$. Use the principal value of the arccosine, so that an angle of less than π radians (180°) results. ◄

Vectors and Coordinate Systems in Three Dimensions

Figure 2.9 depicts the three-dimensional version of *Cartesian coordinates*. We define the x and y axes as before, and erect the z axis through the origin and perpendicular to the x and y axes.

The axes are viewed from the *first octant*, lying between the positive ends of the x, y, and z axes. The octants are numbered from 1 to 8, beginning with the first octant in the upper front right part of the coordinate system and moving counterclockwise around the upper part, and then moving to the lower front right part (octant 5) and moving counterclockwise around the bottom part. A coordinate system such as that shown is called a *right-handed coordinate system*. For such a system, the thumb, index finger, and middle finger of the right hand can be aligned with the positive ends of the x, y, and z axes, respectively. If the left hand must be used for such an alignment, the coordinate system is called a *left-handed coordinate system.*

The location of the point P is specified by x, y, and z, which are the *Cartesian coordinates* of the point. These are the distances from the origin to the points on the axes reached by moving perpendicularly from P to each axis. These coordinates can be positive or negative. In the first octant, x, y,and z are all positive. In the second octant, x is negative, but y and z are positive. The point P can be denoted by its coordinates, as (x, y, z). The directed line segment from the origin to P is

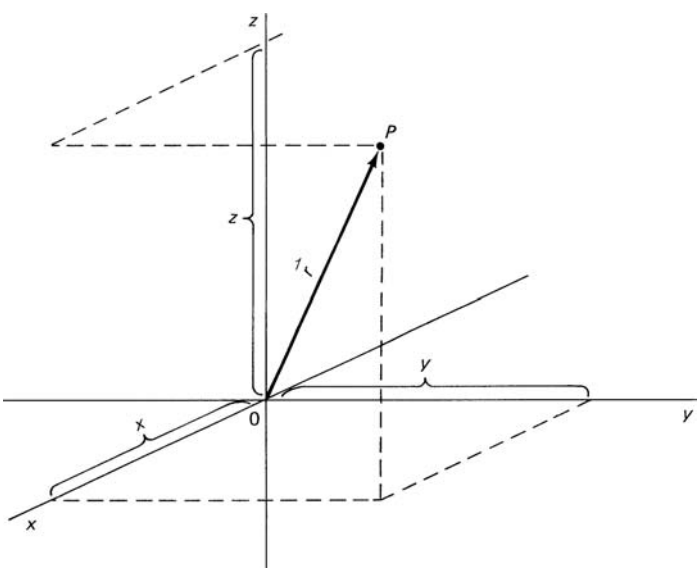

Figure 2.9 ► Cartesian coordinates in three dimensions.

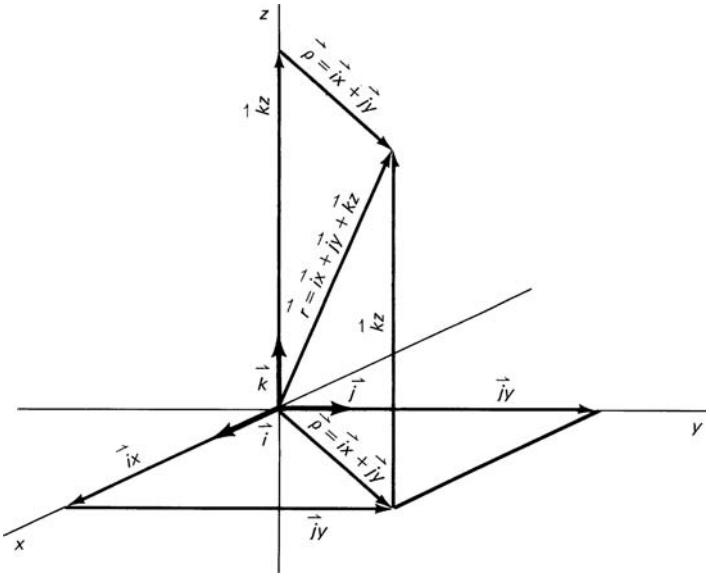

Figure 2.10 ► A position vector in terms of the unit vectors **i**, **j**, and **k**.

the *position vector* of P, and is denoted by **r**. The Cartesian coordinates x, y, and z are also called the *Cartesian components* of **r**. A vector can be represented by the list of its components inside parentheses so that the position vector is denoted by (x, y, z) and the vector **A** can be denoted by (A_x, A_y, A_z).

We can represent a three-dimensional vector by the use of unit vectors as we did in two dimensions. In addition to the unit vectors **i** and **j** in the x and y directions, we define **k**, a vector of unit length pointing in the direction of the positive end of the z axis. Figure 2.10 shows these unit vectors and the position vector written as

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z. \tag{2.56}$$

The magnitude of r of the vector **r** can be obtained from the theorem of Pythagoras. In Fig. 2.10 you can see that r is the hypotenuse of a right triangle with sides ρ and z, where $\rho = \sqrt{x^2 + y^2}$ so that the square of the magnitude of **r** is given by a three-dimensional version of the theorem of Pythagoras:

$$\boxed{r^2 = \rho^2 + z^2 = x^2 + y^2 + z^2} \tag{2.57}$$

or

$$\boxed{r = |\mathbf{r}| = \sqrt{x^2 + y^2 + z^2}}. \tag{2.58}$$

The magnitude of any vector is analogous to the magnitude of the position vector. If **A** is a vector with Cartesian components A_x, A_y, and A_z, the magnitude of **A** is given by

$$\boxed{|\mathbf{A}| = A = \left(A_x^2 + A_y^2 + A_z^2\right)^{1/2} = \sqrt{A_x^2 + A_y^2 + A_z^2}}. \tag{2.59}$$

EXAMPLE 2.4 Find the magnitude of the vector $\mathbf{A} = (3.00, 4.00, 5.00)$.

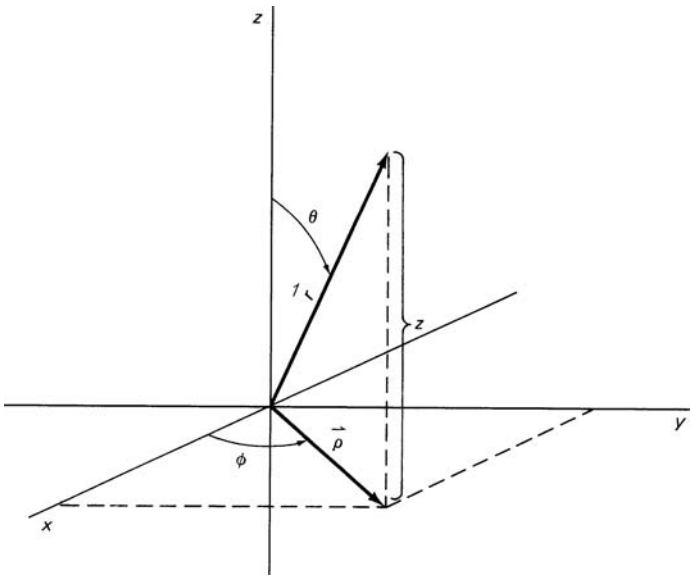

Figure 2.11 ► Spherical polar coordinates.

SOLUTION ► $A = \sqrt{3.00^2 + 4.00^2 + 5.00^2} = \sqrt{50.00} = 7.07$ ◄

Figure 2.11 shows the way in which *spherical polar coordinates* are used to specify the location of the point P and the vector $\mathbf{r}$ from the origin to P. The vector $\boldsymbol{\rho}$ in the x-y plane is also shown. The vector ρ is called the *projection* of $\mathbf{r}$ into the x-y plane. Its head is reached from the head of $\mathbf{r}$ by moving to the x-y plane in a direction perpendicular to the plane. The three spherical polar coordinates are r, θ, and ϕ. The coordinate r is the magnitude of the vector $\mathbf{r}$ as in Eq. (2.58), θ is the angle between the positive z axis and the position vector $\mathbf{r}$, and ϕ is the angle between the positive x axis and the vector $\boldsymbol{\rho}$, as in two-dimensional polar coordinates. The angle θ is allowed to range from 0 to π and the angle ϕ is allowed to range from 0 to 2π. The distance r is allowed to range from 0 to ∞, and these ranges allow the location of every point in the three-dimensional space to be given.

The following equations and Eq. (2.58) can be used to transform from Cartesian coordinates to spherical polar coordinates:

$$\boxed{\theta = \arccos\left(\frac{z}{r}\right)} \tag{2.60}$$

and

$$\boxed{\phi = \arctan\left(\frac{y}{x}\right)}. \tag{2.61}$$

Equation (2.61) is the same as Eq. (2.40).

The following equations can be used to transform from spherical polar coordinates to Cartesian coordinates:

$$\boxed{x = r\sin(\theta)\cos(\phi)} \tag{2.62}$$

$$\boxed{y = r\sin(\theta)\sin(\phi)} \tag{2.63}$$

$$\boxed{z = r\cos(\theta)} \tag{2.64}$$

EXAMPLE 2.5 Find the spherical polar coordinates of the point whose Cartesian coordinates are (1.000, 1.000, 1.000).

SOLUTION ►

$$\begin{aligned} r &= \sqrt{(1.000)^2 - (1.000)^2 - (1.000)^2} = \sqrt{3.000} = 1.732 \\ \phi &= \arctan\left(\frac{1.000}{1.000}\right) = \frac{\pi}{4}\,\text{rad} = 45^\circ \\ \theta &= \arccos\left(\frac{1.000}{1.732}\right) = 0.955\ \text{rad} = 54.7^\circ \end{aligned}$$

◄

EXERCISE 2.16 ► Find the spherical polar coordinates of the point whose Cartesian coordinates are (2, 3, 4). ◄

The *cylindrical polar coordinate system* is another three-dimensional coordinate system. It uses the variables ρ, ϕ, and z, already defined and shown in Fig. 2.11. The equations needed to transform from Cartesian coordinates to cylindrical polar coordinates are Eqs. (2.39) and (2.40). The third coordinate, z, is the same in both Cartesian and cylindrical polar coordinates. Equations (2.37) and (2.38) are used for the reverse transformation.

EXAMPLE 2.6 Find the cylindrical polar coordinates of the point whose Cartesian coordinates are (1.000, −4.000, −2.000).

SOLUTION ►

$$\begin{aligned} \rho &= \sqrt{(1.000)^2 + (4.000)^2} = \sqrt{17.000} = 4.123 \\ \phi &= \arctan\left(\frac{-4.000}{1.000}\right) = 4.957\ \text{radians} = 284^\circ \\ z &= -2.000. \end{aligned}$$

◄

EXERCISE 2.17 ► (a) Find the Cartesian coordinates of the point whose cylindrical polar coordinates are $\rho = 25.00$, $\phi = 60.0^\circ$, $z = 17.50$
(b) Find the cylindrical polar coordinates of the point whose Cartesian coordinates are (−2.000, −2.000, 3.000). ◄

The magnitude of the position vector in cylindrical polar coordinates is given by

$$r = \left(\rho^2 + z^2\right)^{1/2} \tag{2.65}$$

EXAMPLE 2.7 Find the spherical polar coordinates of the points whose cylindrical polar coordinates are ($\rho = 10.00, \phi = 45.00\,^\circ, z = 15.00$)

SOLUTION ► $r = \sqrt{10.00^2 + 15.00^2} = \sqrt{325.00} = 18.03$, $\theta = \arccos(\frac{15.00}{18.03}) = \arccos(0.83205) = 33.69\,^\circ$, $\phi = 45.00\,^\circ$ ◄

Vector Algebra in Three Dimensions

The sum of two vectors are similar to the sum in two dimensions. Let **A** and **B** be two vectors, represented in terms of their components and the unit vectors **i**, **j**, and **k** by

$$\boxed{\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z} \tag{2.66a}$$

$$\boxed{\mathbf{B} = \mathbf{i}B_x + \mathbf{j}B_y + \mathbf{k}B_z.} \tag{2.66b}$$

The sum is still obtained by placing the tail of the second vector at the head of the first and drawing the sum vector from the tail of the first to the head of the second. If **C** is the sum of **A** and **B**, then

$$\boxed{\begin{array}{c}\mathbf{C} = \mathbf{A} + \mathbf{B} \\ C_x = A_x + B_x \\ C_y = A_y + B_y \\ C_z = A_z + B_z\end{array}}. \tag{2.67}$$

There are three kinds of products involving vectors. The product of a vector **A** and a scalar a is

$$\boxed{\mathbf{C} = a\mathbf{A} = \mathbf{i}aA_x + \mathbf{j}aA_y + \mathbf{k}aA_z.} \tag{2.68}$$

The scalar product of two vectors is still given by

$$\boxed{\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}|\,|\mathbf{B}| \cos(\alpha)}. \tag{2.69}$$

where α is the angle between the vectors.

Analogous to Eq. (2.55), we have

$$\boxed{\mathbf{A} \cdot \mathbf{B} = A_x B_x + A_y B_y + A_z B_z}. \tag{2.70}$$

EXAMPLE 2.8 Let $A = 2\mathbf{i} + 3\mathbf{j} + 7\mathbf{k}$ and $B = 7\mathbf{i} + 2\mathbf{j} + 3\mathbf{k}$. Find $\mathbf{A} \cdot \mathbf{B}$ and the angle between **A** and **B**. Find $(3\mathbf{A}) \cdot \mathbf{B}$.

SOLUTION ►

$$\mathbf{A}\cdot\mathbf{B} = 14 + 6 + 21 = 41$$

The magnitude of **A** is

$$|\mathbf{A}| = A = (2^2 + 3^2 + 7^2)^{1/2} = \sqrt{62} \tag{2.71}$$

The magnitude of **B** happens to be the same. Let α be the angle between the vectors **A** and **B**.

$$\begin{aligned}\alpha &= \arccos\left(\frac{\mathbf{A}\cdot\mathbf{B}}{|\mathbf{A}|\,|\mathbf{B}|}\right)\\ &= \arccos\left(\frac{41}{\sqrt{62}\sqrt{62}}\right) = \arccos(0.6613) = 0.848\,\text{rad} = 48.6^\circ\\ (3\mathbf{A})\cdot\mathbf{B} &= 3\times 14 + 3\times 6 + 3\times 21 = \mathbf{A}\cdot\mathbf{B} = 4\times 41 = 123.\end{aligned}$$

Notice that $(3\mathbf{A})\cdot\mathbf{B} = 3(\mathbf{A}\cdot\mathbf{B})$. ◄

EXERCISE 2.18 ► Find the cartesian components of the position vector of the point whose spherical polar coordinates are $r = 2, \theta = 90^\circ, \phi = 0^\circ$. Call this vector **A**.
(a) Find the scalar product of the vector **A** from part a and the vector **B** whose cartesian components are (1, 2, 3).
(b) Find the angle between these two vectors. ◄

We now introduce another kind of a product between two vectors, called the *vector product* or *cross product*, and denoted by $\mathbf{A}\times\mathbf{B}$. If

$$\mathbf{C} = \mathbf{A}\times\mathbf{B}$$

then **C** is defined to be perpendicular to the plane containing **A** and **B** and to have the magnitude

$$C = |\mathbf{C}| = |\mathbf{A}|\,|\mathbf{B}|\sin(\alpha)\,, \tag{2.72}$$

where α is the angle between **A** and **B**, measured so that it lies between 0 and 180°. The direction of the cross product $\mathbf{A}\times\mathbf{B}$ is defined as follows: If the first vector listed is rotated through the angle α so that its direction coincides with that of **B**, then **C** points in the direction that an ordinary (right-handed) screw thread would move with this rotation. Another rule to obtain the direction is a *right-hand rule*. If the thumb of the right hand points in the direction of the first vector and the index finger points in the direction of the second vector, the middle finger can point in the direction of their cross product.

EXERCISE 2.19 ► From the geometrical definition just given, show that

$$\boxed{\mathbf{A}\times\mathbf{B} = -\mathbf{B}\times\mathbf{A}}. \tag{2.73}$$

◄

In this exercise you have shown that the vector product of two vectors is not *commutative*, which means that you get a different result if you switch the order of the two factors.

From Eq. (2.72),

$$\boxed{\mathbf{A}\times\mathbf{A} = \mathbf{0}}. \tag{2.74}$$

where **0** is the *null vector*. The null vector has zero magnitude and no particular direction. To express the cross product in terms of components, we can use the

definition of the vector product to write

$$\mathbf{i} \times \mathbf{i} = \mathbf{j} \times \mathbf{j} = \mathbf{k} \times \mathbf{k} = 0 \tag{2.75a}$$

and

$$\mathbf{i} \times \mathbf{j} = \mathbf{k} \tag{2.75b}$$
$$\mathbf{j} \times \mathbf{i} = -\mathbf{k} \tag{2.75c}$$
$$\mathbf{i} \times \mathbf{k} = -\mathbf{j} \tag{2.75d}$$
$$\mathbf{k} \times \mathbf{i} = \mathbf{j} \tag{2.75e}$$
$$\mathbf{j} \times \mathbf{k} = \mathbf{i} \tag{2.75f}$$
$$\mathbf{k} \times \mathbf{j} = -\mathbf{i}. \tag{2.75g}$$

By use of these relations, we obtain

$$\mathbf{C} = \mathbf{A} \times \mathbf{B}$$

$$\boxed{\begin{aligned} \mathbf{C} &= \mathbf{i}C_x + \mathbf{j}C_y + \mathbf{k}C_z \\ &= \mathbf{i}(A_yB_z - A_zB_y) + \mathbf{j}(A_zB_x - A_xB_z) + \mathbf{k}(A_xB_y - A_yB_x) \end{aligned}}. \tag{2.76}$$

EXERCISE 2.20 ► Show that Eq. (2.76) follows from Eq. (2.75). ◄

EXAMPLE 2.9 Find the cross product $\mathbf{A} \times \mathbf{B}$, where $\mathbf{A} = (1, 2, 3)$ and $\mathbf{B} = (1, 1, 1)$.

SOLUTION ► Let $\mathbf{C} = \mathbf{A} \times \mathbf{B}$.

$$\mathbf{C} = \mathbf{i}(2 - 3) + \mathbf{j}(3 - 1) + \mathbf{k}(1 - 2) = -\mathbf{i} + 2\mathbf{j} - \mathbf{k}.$$

◄

EXAMPLE 2.10 Show that the vector $\mathbf{C}$ obtained in the previous example is perpendicular to $\mathbf{A}$.

SOLUTION ► We do this by showing that $\mathbf{A} \cdot \mathbf{C} = 0$.

$$\begin{aligned} \mathbf{A} \cdot \mathbf{C} &= A_xC_x + A_yC_y + A_zC_z \\ &= -1 + 4 + 3 = 0. \end{aligned}$$

◄

EXERCISE 2.21 ► Show that the vector $\mathbf{C}$ is perpendicular to $\mathbf{B}$, and that Eq. (2.72) is satisfied. Do this by finding the angle between $\mathbf{A}$ and $\mathbf{B}$ through calculation of $\mathbf{A} \cdot \mathbf{B}$. ◄

An example of a vector product is the force on a moving charged particle due to a magnetic field. If q is the charge on the particle measured in coulombs (C), $\mathbf{v}$ is the velocity of the particle in meters per second, and $\mathbf{B}$ is the *magnetic induction* (often called the "magnetic field") measured in *tesla* (T),[2] the force in newtons is given by

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}. \tag{2.77}$$

Since this force is perpendicular to the velocity, it causes the trajectory of the particle to curve, rather than changing the speed of the particle.

EXAMPLE 2.11 Find the force on an electron in a magnetic field if $\mathbf{v} = \mathbf{i}(1.000 \times 10^5\,\mathrm{m\,s^{-1}})$ and $\mathbf{B} = \mathbf{j}(1.000 \times 10^{-4}\,\mathrm{T})$.

SOLUTION ► The value of q is -1.602×10^{-19} C (note the negative sign).

$$\begin{aligned}\mathbf{F} &= (\mathbf{i} \times \mathbf{j})\left(-1.602 \times 10^{-19}\,\mathrm{C}\right)\left(1.000 \times 10^{5}\,\mathrm{m\,s^{-1}}\right)(1.000 \times 10^{-4}\,\mathrm{T}) \\ &= -\mathbf{k}\left(1.602 \times 10^{-18}\,\mathrm{A\,s\,m\,s^{-1}\,kg\,s^{-2}\,A^{-1}}\right) \\ &= -\mathbf{k}\left(1.602 \times 10^{-18}\ \mathrm{kg\,m\,s^{-2}}\right) = -\mathbf{k}(1.602 \times 10^{-18}\,\mathrm{N}).\end{aligned}$$

◄

The force on a charged particle due to an *electric field* is

$$\mathbf{F} = q\mathbf{E}, \tag{2.78}$$

where $\mathbf{E}$ is the electric field and q is the charge on the particle. If the charge is measured in coulombs and the field in volts per meter, the force is in newtons.

EXERCISE 2.22 ► Find the direction and the magnitude of the electric field necessary to provide a force on the electron in the previous example that is equal in magnitude to the force due to the magnetic field but opposite in direction. If both these forces act on the particle, what will be their effect? ◄

2.5 Imaginary and Complex Numbers

Imaginary numbers have been defined into existence by mathematicians. They cannot be used to represent any physically measured quantity, but turn out to be useful in quantum mechanics. The *imaginary unit* is called i (not to be confused with the unit vector **i**) and is defined to be the square root of -1:

$$\boxed{i = \sqrt{-1}} \tag{2.79}$$

If b is a real number, the quantity ib is said to be *pure imaginary*, and if a is also real, the quantity

$$c = a + ib \tag{2.80}$$

[2] The tesla is named for Nikola Tesla, 1856–1943, the electrical engineer who invented the rotating-field electric motor and other electrical devices.

is said to be a *complex number*. The real number a is called the *real part* of c and is denoted by

$$a = R(c). \tag{2.81}$$

The real number b is called the *imaginary part* of c and is denoted by

$$b = I(c). \tag{2.82}$$

All of the rules of ordinary arithmetic apply with complex numbers. The sum of two complex numbers is obtained by adding the two real parts together and adding the two imaginary parts together. If $c_1 = a_1 + ib_1$and $c_2 = a_2 + ib_2$, then

$$c_1 + c_2 = a_1 + a_2 + i\,(b_1 + b_2)$$

The product of two complex numbers is obtained by the same procedure as multiplying two real binomials.

$$\begin{aligned} c_1c_2 &= a_1a_2 + i\,(a_1b_2 + b_1a_2) + \left(i^2\right) b_1b_2 \\ &= a_1a_2 + i\,(a_1b_2 + b_1a_2) - b_1b_2 \end{aligned}$$

Addition and multiplication are *associative*. That is, if A, B, and C are complex numbers,

$$A + (B + C) = (A + B) + C \tag{2.83}$$

$$A(BC) = (AB)C. \tag{2.84}$$

Addition and multiplication are *distributive*. That is,

$$A(B + C) = AB + AC. \tag{2.85}$$

Addition and multiplication are *commutative*. That is, addition or multiplication of two complex numbers yields the same result in either order:

$$A + B = B + A \tag{2.86}$$

$$AB = BA. \tag{2.87}$$

Subtraction is the addition of a number whose real and imaginary parts are the negatives of the number to be subtracted, and division is multiplication by the reciprocal of a number. If

$$z = x + iy \tag{2.88}$$

then the *reciprocal* of z, called z^{-1}, is given by

$$\boxed{z^{-1} = \frac{x}{x^2 + y^2} - i\frac{y}{x^2 + y^2}} \tag{2.89}$$

EXAMPLE 2.12 Show that $z(z^{-1}) = 1$.

SOLUTION ►

$$\begin{aligned} z(z^{-1}) &= (x+iy)\left(\frac{x}{x^2+y^2} - i\frac{y}{x^2+y^2}\right) \\ &= \frac{1}{x^2+y^2}\left(x^2 + ixy - ixy - i^2y^2\right) \\ &= \frac{1}{x^2+y^2}\left(x^2 - i^2y^2\right) = 1. \end{aligned}$$

◄

EXERCISE 2.23 ► Show that

$$(a+ib)(c+id) = ac - bd + i(bc+ad). \tag{2.90}$$

◄

EXERCISE 2.24 ► Show that

$$\frac{a+ib}{c+id} = \frac{(ac+bd-iad+ibc)}{c^2+d^2}. \tag{2.91}$$

◄

EXERCISE 2.25 ► Find the value of

$$(4+6i)(3+2i) + 4i - \frac{1+i}{3-2i}. \tag{2.92}$$

◄

Specifying a complex number is equivalent to specifying two real numbers, one for the real part and one for the imaginary part. A complex number is therefore similar to a vector in two dimensions. We can therefore represent a complex number by the location of a point in a plane, as shown in Fig. 2.12.

This kind of a figure is called an *Argand diagram*, and the plane of the figure is called the *Argand plane* or the *complex plane*. The horizontal coordinate represents the real part of the number and the vertical coordinate represents the imaginary part. The horizontal axis, labeled R, is called the *real axis*, and the vertical axis, labeled I, is called the *imaginary axis*.

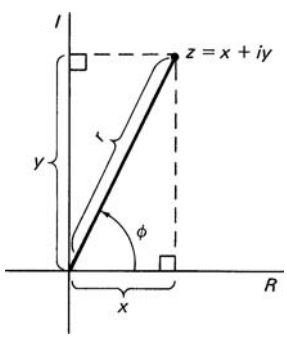

Figure 2.12 ► Representation of the complex number $z = x + iy$ in the Argand diagram.

The location of the point in the Argand plane can be given by polar coordinates. We use the symbol r for the distance from the origin to the point, and the symbol ϕ for the angle in radians between the positive real axis and the line segment joining the origin and the point. The quantity r is the *magnitude* of the complex number. It is also called the *absolute value* or the *modulus* of the complex number. The angle ϕ is called the *argument* or *phase* of the complex number. From Eq. (2.37) and (2.38),

$$z = x + iy = r\cos(\phi) + ir\sin(\phi).$$

There is a theorem, known as *Euler's formula*, that allows a complex number to be written as an exponential with an imaginary exponent,

$$\boxed{z = re^{i\phi} = r\cos(\phi) + ir\sin(\phi) = x + iy}, \tag{2.93}$$

where e is the base of natural logarithms, $e = 2.7182818\ldots$, and where r and ϕ are the magnitude and phase of the complex number. This form is called the *polar representation* of the complex number. In this formula, ϕ must be measured in radians.

In the polar representation, the product of two complex numbers, say $z_1 = r_1e^{i\phi_1}$ and $z_2 = r_2e^{i\phi_2}$, is given in a convenient form:

$$\boxed{z_1z_2 = r_1r_2e^{i(\phi_1+\phi_2)}}. \tag{2.94}$$

The quotient z_1z_2 is given by

$$\boxed{\frac{z_1}{z_2} = \left(\frac{r_1}{r_2}\right)e^{i(\phi_1-\phi_2)}}. \tag{2.95}$$

DeMoivre's formula gives the result of raising a complex number to a given power:

$$\boxed{\left(re^{i\phi}\right)^n = r^ne^{in\phi} = r^n[\cos(n\phi) + i\sin(n\phi)]}.$$

EXAMPLE 2.13 Evaluate the following.

(a) $\left(4e^{i\pi}\right)\left(3e^{2i\pi}\right)$ (b) $\left(8e^{2i\pi}\right)\left(2e^{i\pi/2}\right)$

(c) $\left(8e^{4i}\right)^2$

SOLUTION ►

(a) $\left(4e^{i\pi}\right)\left(3e^{2i\pi}\right) = 12e^{3i\pi} = 12e^{i\pi}$

(b) $\left(8e^{2i\pi}\right)\left(2e^{i\pi/2}\right) = 4e^{5i\pi/2}$

(c) $\left(8e^{4i}\right)^2 = 64e^{8i}$.

◄

In part (a) of the preceding example we have used the fact that an angle of 2π radians gives the same point in the complex plane as an angle of 0, so that

$$\boxed{e^{2\pi i} = 1} \tag{2.96}$$

Similarly,

$$\boxed{e^{\pi i} = -1} \tag{2.97}$$

Since an angle is unchanged if any multiple of 2π is added or subtracted from it, we can write

$$e^{i(\phi+2n\pi)} = e^{i\phi} \tag{2.98}$$

where n is an integer. If a number is given in the form $z = x + iy$, we can find the magnitude and the phase as

$$r = \sqrt{x^2 + y^2} \tag{2.99}$$

$$\phi = \arctan\left(\frac{y}{x}\right) \tag{2.100}$$

Just as with a transformation from cartesian coordinates to polar coordinates, we do not necessarily use the principal value of the arctangent function, but must obtain an angle in the proper quadrant, with ϕ ranging from 0 to 2π.

EXERCISE 2.26 ▶ Express the following complex numbers in the form $re^{i\phi}$:

(a) $4 + 4i$ (b) -1

(c) 1 (d) $1 - i$.

◀

EXERCISE 2.27 ▶ Express the following complex numbers in the form $x + iy$:

(a) $e^{i\pi}$ (b) $3e^{\pi i/2}$

(c) $e^{3\pi i/2}$

◀

The *complex conjugate* of a number is defined as the number that has the same real part and an imaginary part that is the negative of that of the original number. We will denote the complex conjugate by an asterisk (*). It is also denoted by a bar over the letter for the number.

If $z = x + iy$, then

$$\boxed{\bar{z} = z^* = (x + iy)^* = x - iy}. \tag{2.101}$$

Figure 2.13 shows the location of a complex number and of its complex conjugate in the Argand plane.

The phase of the complex conjugate is $-\phi$ if the phase of the original number is ϕ. The magnitude is the same, so

$$\boxed{\left(re^{i\phi}\right)^* = re^{-i\phi}}. \tag{2.102}$$

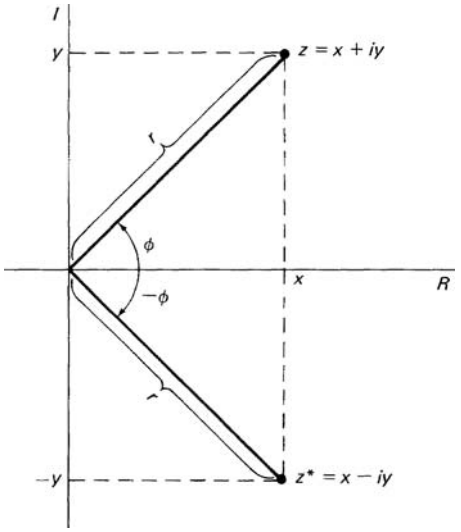

Figure 2.13 ► A complex number, $z = x + iy$, and its complex conjugate, $z^* = x - iy$, in the Argand plane.

Although we do not prove it, the following fact is useful in obtaining the complex conjugate of a complex quantity: *The complex conjugate of any expression is obtained by changing the sign in front of every i that occurs in the expression.*

EXAMPLE 2.14 Find the complex conjugates of the following, where a, b, c, and d are real quantities:
(a) $A = (1 + 2i)^{3/2} - \exp(3 + 4i)$
(b) $B = a(b + ci)^2 + 4(c - id)^{-1}$.

SOLUTION ► (a) $A^* = (1 - 2i)^{3/2} - \exp(3 - 4i)$ (b) $B^* = a(b - ci)^2 + 4(c + id)^{-1}$. ◄

EXERCISE 2.28 ► Find the complex conjugates of
(a) $A = (x + iy)^2 - 4e^{ixy}$ (b) $B = (3 + 7i)^3 - (7i)^2$.
◄

Once we have an expression for the complex conjugate of a quantity, we can use it to express the real and imaginary parts separately:

$$R(z) = \frac{z + z^*}{2} \tag{2.103}$$

$$I(z) = \frac{z - z^*}{2i} \tag{2.104}$$

EXERCISE 2.29 ► Use Eq. (2.101) to show that Eqs. (2.103) and (2.104) are correct.
◄

EXERCISE 2.30 ► Obtain the famous formulas

$$\boxed{\cos(\phi) = \frac{e^{i\phi} + e^{-i\phi}}{2} = R\left(e^{i\phi}\right)} \tag{2.105}$$

◄

$$\boxed{\sin(\phi) = \frac{e^{i\phi} - e^{-i\phi}}{2i} = I\left(e^{i\phi}\right)} \tag{2.106}$$

The magnitude of an expression can also be obtained by using the complex conjugate. We find that

$$\boxed{zz^* = \left(re^{i\phi}\right)\left(re^{-i\phi}\right) = r^2} \tag{2.107}$$

so that

$$\boxed{r = \sqrt{zz^*}}, \tag{2.108}$$

where the positive square root is to be taken. The product of any complex number and its complex conjugate is always real and nonnegative.

EXERCISE 2.31 ► Write a complex number in the form $x + iy$ and show that the product of the number with its complex conjugate is real and nonnegative. ◄

EXAMPLE 2.15 If $z = 4e^{3i} + 6i$, find $R(z)$, $I(z)$, r, and ϕ.

SOLUTION ►

$$\begin{aligned}
R(z) &= \frac{z + z^*}{2} = \frac{4e^{3i} + 6i + 4e^{-3i} - 6i}{2} \\
&= 2(e^{3i} + e^{-3i}) = 4\cos(3) = -3.960 \\
I(z) &= \frac{z - z^*}{2i} = \frac{4e^{3i} + 6i - 4e^{-3i} + 6i}{2i} \\
&= \frac{4(e^{3i} - e^{-3i})}{2i} + 6 = 4\sin(3) + 6 \\
&= 4\sin\left(171.89^\circ\right) + 6 = 6.5645 \\
r &= (zz^*)^{1/2} = (x^2 + y^2)^{1/2} \\
&= [(-3.960)^2 + (6.5645)^2]^{1/2} = 7.666 \\
\phi &= \arctan\left(\frac{I}{R}\right) = \arctan\left(\frac{-6.5645}{3.960}\right) \\
&= \arctan(-1.6577)
\end{aligned}$$

The principal value of this arctangent is -58.90°. However, since $R(z)$ is negative and $I(z)$ is positive, we require an angle in the second quadrant.

$$\phi = 180^\circ - 58.90^\circ = 121.10^\circ = 2.114 \text{ rad.}$$

◄

EXERCISE 2.32 ► If $z = \left(\dfrac{3 + 2i}{4 + 5i}\right)^2$, find $R(z)$, $I(z)$, r, and ϕ. ◄

The *square root of a complex number* is a number that will yield the first number when multiplied by itself. Just as with real numbers, there are two square roots of a complex number. If $z = re^{i\phi}$, one of the square roots is given by

$$\sqrt{re^{i\phi}} = \sqrt{r}e^{i\phi/2}. \tag{2.109}$$

The other square root is obtained by realizing that if ϕ is increased by 2π, the same point in the Argand plane is represented. Therefore, the square root of $re^{i(2\pi+\phi)}$ is the same as the other square root of $re^{i\phi}$.

$$\sqrt{re^{i\phi}} = \sqrt{re^{i(2\pi+\phi)}} = \sqrt{r}e^{i(\pi+\phi/2)}. \tag{2.110}$$

EXAMPLE 2.16 Find the square roots of $3e^{i\pi/2}$.

SOLUTION ► One square root is, from Eq. (2.109),

$$\sqrt{3e^{i\pi/2}} = \sqrt{3}e^{i\pi/4}.$$

The other square root is, from Eq. (2.110),

$$\sqrt{3}e^{i(\pi+\pi/4)} = \sqrt{3}e^{i5\pi/4}.$$

If a complex number is represented as $x + iy$, it is usually best to transform to polar coordinates before taking the square root of the number. ◄

EXERCISE 2.33 ► Find the square roots of $4 + 4i$. Sketch an Argand diagram and locate the roots on it. ◄

There are three *cube roots of a complex number*. These can be found by looking for the numbers that when cubed yield $re^{i\phi}$, $re^{i(2\pi+\phi)}$, and $re^{i(4\pi+\phi)}$. These numbers are

$$\sqrt[3]{re^{i\phi}} = \sqrt[3]{r}e^{i\phi/3},\ \sqrt[3]{r}e^{i(2\pi+\phi)/3},\ \sqrt[3]{r}e^{i(4\pi+\phi)/3}.$$

Higher roots are obtained similarly.

EXAMPLE 2.17 Find the three cube roots of -1.

SOLUTION ► In the polar representation, $-1 = e^{i\pi}$. The three cube roots are

$$\sqrt[3]{e^{i\pi}} = e^{i\pi/3},\ e^{i\pi},\ e^{5i\pi/3} \tag{2.111}$$

◄

Higher roots are defined similarly.

EXERCISE 2.34 ► Find the four fourth roots of -1. ◄

2.6 Problem Solving and Symbolic Mathematics

We have already seen a number of relatively simple exercises, examples, and problems in this and the previous chapter. In most cases, these involved carrying out operations that we either specified or that were fairly obvious. We now make some general comments on solving chemistry problems, which are usually a little more complicated. A typical chemistry problem is similar to what was once called a *story problem* or a *word problem* in elementary school. You are given some factual information (or asked to find some), together with a verbal statement of what answer is required, but you must find your own method of obtaining the answer from the given information. In a simple problem, this may consist only of substituting numerical values into a formula, but in a more complicated problem you might have to derive your own mathematical formula or carry out other procedures. The method, or *algorithm*, must be developed for each problem. Sometimes the algorithm is the use of a single formula. The principal tool for obtaining a useful formula from another formula is *algebra*, In algebra we manipulate the symbols standing for variables without actually carrying out numerical operations. An algebraic equation has a set of symbols for variables and operations on each side of the equation, with the assertion that if we replace the variable symbols by their numerical values and carry out the indicated operations, we obtain the same numerical value for each side of the equation. If we have a valid algebraic equation, we can symbolically carry out the same operation on both sides of the equation and obtain a valid new equation. For example, we can symbolically divide both sides of the equation by some variable by writing the symbol for the variable as a denominator in a fraction and canceling symbols on both the top and bottom of the fraction.

EXAMPLE 2.18 Under ordinary conditions, ordinary gases nearly obey the *ideal gas equation* is

$$PV = nRT \tag{2.112}$$

where V is the volume, n is the amount of gas in moles, T is the temperature, P is the pressure, and R is the *ideal gas constant*, equal to $8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} = 0.08206\,\mathrm{l\,atm\,K^{-1}\,mol^{-1}}$. Calculate the volume occupied by 1.278 mol of an ideal gas if the pressure is 2.341 atm and the temperature is 298.15 K.

SOLUTION ► Since there are four variables, we can calculate the value of one of them if the values of the other three are given. We solve the ideal gas equation for V by symbolically dividing both sides of the equation by P, obtaining

$$V = \frac{nRT}{P}. \tag{2.113}$$

We substitute the numerical values into Eq. (2.113), convert the pressure from atmospheres to pascals by use of the factor label method, and carry out the numerical operations:

$$\begin{aligned} V &= \frac{(1.278\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}{2.314\,\mathrm{atm}} \left(\frac{1\,\mathrm{atm}}{101325\,\mathrm{Pa}}\right) \\ &= 1.351 \times 10^{-2}\ \mathrm{J\,Pa^{-1}} \\ &= 1.351 \times 10^{-2}\ \mathrm{J\,Pa^{-1}} \left(\frac{1\,\mathrm{Pa}}{1\,\mathrm{N\,m^{-2}}}\right)\left(\frac{1\,\mathrm{N\,m}}{1\,\mathrm{J}}\right) \\ &= 1.351 \times 10^{-2}\,\mathrm{m^3}. \end{aligned}$$

We give the answer to four significant digits, because both the pressure and the amount of gas are specified to four significant digits. We can now make an additional conversion to express the volume in liters:

$$\left(1.351 \times 10^{-2}\,\mathrm{m}^3\right)\left(\frac{1\,\mathrm{l}}{10^{-3}\,\mathrm{m}^3}\right) = 13.51\,\mathrm{l}$$

We know that this solution is in the correct range of values, since a mole of gas at room temperature and one atmosphere pressure occupies about 25 liters. ◀

The preceding example was a simple one, but it illustrates some of the principles of problem solving. Let's summarize the procedure that was used. We first determined that the ideal gas equation of state was sufficient to work the problem and that enough information was given. This equation was solved algebraically for the volume to give a working formula. The given values of quantities were substituted into the formula, and the necessary unit conversion was made. After all factors were written out and the units checked, the multiplications and divisions were carried out and it was determined that the answer was about the right size.

The general problem-solving procedure can be summarized as follows:

1. Analyze the given information and the desired answer.
2. Decide what kind of a procedure is needed to process the given information and obtain the desired answer. Determine whether enough information is contained in the given information. If one or more formulas are needed, find the formulas. In working a complicated problem, it might be useful to map out on a piece of paper how you are going to get from the given information to the desired answer.[3]
3. Find any addition information that is needed.
4. Carry our any necessary symbolic manipulations to obtain a working formula from the formula or formulas that you found. In some problems you might be asked to obtain a formula, and if so this is the end of the procedure.
5. Carry out any numerical operations to obtain the desired answer.
6. Look at your answer to see it if is reasonable. Simple numerical mistakes will usually cause your answer to be much too large or too small, and you can usually see if this is the case. For example, if your answer is a molecular diameter and you obtain a value of roughly 1000 m, you know that there is a mistake somewhere. You should also check your answer by substituting it into the original formula.

In order to judge whether an answer is reasonable, it is useful to be able to estimate approximate sizes of things. You need to start with reasonable estimates and work out an estimate of the desired quantity. For example, a professor asked a class to estimate the number of piano tuners in New York City. One would start with an estimate of the population—say, 10 million people—which might amount to 5 million households. Perhaps one household in 10 might have a piano, for 500,000 pianos. A professional pianist might have a piano tuned every month, but most people might let it go for several years. We assume that on the average, each piano is tuned once in two years, for 250,000 tunings per year. A professional

[3]Some unkind soul has defined a mathematician as a person capable of designing a mathematically precise path from an unwarranted assumption to a foregone conclusion.

piano tuner might be able to tune 6 pianos in a day, or about 1200 pianos in a year. The result is that there might be about 200 full-time piano tuners in New York City. This number is surely wrong, but must be in the right order of magnitude.

EXERCISE 2.35 ► Estimate the number of house painters in Chicago. ◄

In the remaining chapters of this book, you will see a number of examples worked out, and you will see a number of exercises and problems that you can solve. In most of these, a method must be found and applied that will lead from the given information to the desired answer. In some problems there will be a choice of methods. Perhaps you must choose between a graphical procedure and a numerical procedure, or between an approximate formula and an exact formula. In some of these cases, it would be foolish to carry out a more difficult solution, because an approximate solution will give you an answer that will be sufficient for the purpose at hand. In other cases, you will need to carry out a more nearly exact solution. You will need to learn how to distinguish between these two cases.

SUMMARY

In this chapter we have introduced symbolic mathematics, which involves the manipulation of symbols instead of performing numerical operations. We have presented the algebraic tools needed to manipulate expressions containing real scalar variables, real vector variables, and complex scalar variables. We have also introduced ordinary and hyperbolic trigonometric functions, exponentials, and logarithms. A brief introduction to the techniques of problem solving was included.

PROBLEMS

1. A Boy Scout finds a tall tree while hiking and wants to estimate its height. He walks away from the tree and finds that when he is 98 m from the tree, he must look upward at an angle of 35 ° to look at the top of the tree. His eye is 1.50 m from the ground, which is perfectly level. How tall is the tree?

2. The equation $x^2 + y^2 + z^2 = c^2$, where c is a constant, represents a surface in three dimensions. Express the equation in spherical polar coordinates. What is the shape of the surface?

3. Express the equation $y = b$, where b is a constant, in plane polar coordinates.

4. Express the equation $y = mx + b$, where m and b are constants, in plane polar coordinates.

5. Find the values of the plane polar coordinates that correspond to $x = 2$, $y = 4$.

6. Find the values of the cartesian coordinates that correspond to $r = 10, \theta = 45\,^\circ, \phi = 135\,^\circ$.

7. Find the values of the spherical polar coordinates that correspond to $x = 2,\ y = 2,\ z = 4$.

8. A surface is represented in cylindrical polar coordinates by the equation $z = \rho^2$. Describe the shape of the surface.

9. Find $\mathbf{A} - \mathbf{B}$ if $\mathbf{A} = 2\mathbf{i} + 3\mathbf{j}$ and $\mathbf{B} = \mathbf{i} + 3\mathbf{j} - \mathbf{k}$.

10. Find $\mathbf{A} \cdot \mathbf{B}$ if $\mathbf{A} = (0, 2)$ and $\mathbf{B} = (2, 0)$.

11. Find $|\mathbf{A}|$ if $\mathbf{A} = 3\mathbf{i} + 4\mathbf{j} - \mathbf{k}$.

12. Find $\mathbf{A} \cdot \mathbf{B}$ if $\mathbf{A} = \mathbf{i} + \mathbf{j} + \mathbf{k}$ and $\mathbf{B} = \mathbf{i} + 3\mathbf{j} - 2\mathbf{k}$.

13. Find $\mathbf{A} \cdot \mathbf{B}$ if $\mathbf{A} = (1, 1, 1)$ and $\mathbf{B} = (2, 2, 2)$.

14. Find $\mathbf{A} \times \mathbf{B}$ if $\mathbf{A} = (0, 1, 2)$ and $\mathbf{B} = (2, 1, 0)$.

15. Find $\mathbf{A} \times \mathbf{B}$ if $\mathbf{A} = (1, 1, 1)$ and $\mathbf{B} = (2, 2, 2)$.

16. Find the angle between $\mathbf{A}$ and $\mathbf{B}$ if $\mathbf{A} = \mathbf{i} + 2\mathbf{j} + \mathbf{k}$ and $\mathbf{B} = \mathbf{i} + \mathbf{j} + \mathbf{k}$.

17. Find the angle between $\mathbf{A}$ and $\mathbf{B}$ if $\mathbf{A} = 3\mathbf{i} + 2\mathbf{j} + \mathbf{k}$ and $\mathbf{B} = \mathbf{i} + 2\mathbf{j} + 3\mathbf{k}$.

18. A spherical object falling in a fluid has three forces acting upon it: (1) The gravitational force, whose magnitude is $F_g = mg$, where m is the mass of the object and g is the acceleration due to gravity, equal to $9.8\,\mathrm{m\,s^{-2}}$; (2) The buoyant force, whose magnitude is $F_b = m_f g$, where m_f is the mass of the displaced fluid, and whose direction is upward; (3) The frictional force, which is given by $\mathbf{F}_f = -6\pi\eta r\mathbf{v}$, where r is the radius of the object, $\mathbf{v}$ its velocity, and η the coefficient of viscosity of the fluid. This formula for the frictional forces applies only if the flow around the object is laminar (flow in layers). The object is falling at a constant speed in glycerol, which has a viscosity of $1490\,\mathrm{kg\,m^{-1}\,s^{-1}}$. The object has a mass of 0.00381 kg, has a radius of 0.00432 m, a mass of 0.00381 kg, and displaces a mass of fluid equal to 0.000337 kg. Find the speed of the object.

19. The solutions to the Schrödinger equation for the electron in a hydrogen atom have three quantum numbers associated with them, called n, l, and m, and these solutions are often denoted by ψ_{nlm}. One of the solutions is

$$\psi_{211} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{-r/2a_0}\sin(\theta)\,e^{i\phi},$$

where a_0 is a distance equal to 0.529×10^{-10} m, called the *Bohr radius*.

a) Write this function in terms of cartesian coordinates.

b) Write an expression for the magnitude of this complex function.

c) This function is sometimes called ψ_{2p1}. Write expressions for the real and imaginary parts of the function, which are proportional to the related functions called ψ_{2px} and ψ_{2py}.

20. Find the sum of $4e^{3i}$ and $5e^{2i}$.

21. Find the difference $3e^{\pi i} - 2e^{2i}$.

22. Find the three cube roots of $3 - 2i$.

23. Find the four fourth roots of $3i$.

24.

a) Find the real and imaginary parts of

$$\sqrt{3+i} + (6+5i)^2$$

Obtain a separate answer for each of the two square roots of the first term.

b) Write the complex conjugate of each answer.

25. An object has a force on it given by $(4.75\,\mathrm{N})\mathbf{i} + (7.00\,\mathrm{N})\mathbf{j} + (3.50\,\mathrm{N})\mathbf{k}$.

a) Find the magnitude of the force.

b) Find the projection of the force in the x-y plane. That is, find the vector in the x-y plane whose head is reached from the head of the force vector by moving in a direction perpendicular to the x-y plane.

26. An object of mass 12.000 kg is moving in the x direction. It has a gravitational force acting on it equal to $-mg\mathbf{k}$, where m is the mass of the object and g is the acceleration due to gravity, equal to $9.80\,\mathrm{m\,s^{-1}}$.There is a frictional force equal to $(0.240\,\mathrm{N})\mathbf{i}$. What is the magnitude and direction of the resultant force (the vector sum of the forces on the object)?

27. The potential energy of a magnetic dipole in a magnetic field is given by the scalar product

$$\mathcal{V} = -\mu \cdot \mathbf{B},$$

where $\mathbf{B}$ is the magnetic induction (magnetic field) and μ is the magnetic dipole. Make a graph of $\mathcal{V}/\left(|\mu|\,|\mathbf{B}|\right)$ as a function of the angle between μ and $\mathbf{B}$.

28. Estimate the number of grains of sand on the beaches of the major continents of the earth. Exclude islands and inland bodies of water. You should come up with a number somewhere near Avogadro's number.

29. Assume that a gas has a molar volume of 20 liters. Estimate the average distance between nearest-neighbor molecules.

30. Estimate the number of blades of grass in a lawn with an area of 1000 square meters.

3

The Solution of Algebraic Equations

Preview

If an equation is written in the form $f(x) = 0$, where f is some function and x is a variable, solving the equation means to find those constant values of x such that the equation is satisfied. These values are called solutions or roots of the equation. We discuss both algebraic and numerical methods for finding roots to algebraic equations. If there are two variables in the equation, such as $F(x, y) = 0$, then the equation can be solved for y as a function of x or x as a function of y, but in order to solve for constant values of both variables, a second equation, such as $G(x, y) = 0$, is required, and the two equations must be solved simultaneously. In general, if there are n variables, n independent and consistent equations are required.

Principal Facts and Ideas

1. The solution to an algebraic equation is generally a value or a set of values of the independent variable such that substitution of such a value into the equation produces an numerically correct equation such as $0 = 0$.
2. For a single independent variable, one equation is required.
3. An algebraic equation in one variable can be solved algebraically, graphically, or numerically.
4. Polynomial equations through the fourth degree can be solved algebraically, but some equations of fifth and higher degree cannot be solved algebraically.
5. For n variables, n equations are required, but these equations must be independent and consistent.
6. Linear homogeneous simultaneous equations have a nontrivial solution only when a certain dependence condition is met.

Objectives

After studying this chapter, you should be able to:

1. solve any quadratic equation and determine which root is physically meaningful;
2. obtain an accurate numerical approximation to the roots of any single equation in one unknown, using graphical and numerical techniques;
3. solve any fairly simple set of two simultaneous linear equations.

3.1 Algebraic Methods for Solving One Equation with One Unknown

If you have one algebraic equation containing one variable, there will generally be a set of one or more constant values of that variable which make the equation valid. They are said to satisfy the equation, and the values in the set are called the *roots* or *solutions* of the equation. Other values of the variable do not produce a valid equation and are said not to satisfy the equation.

Polynomial Equations

A *polynomial equation* in the variable x is written in the form

$$f(x) = a_0 + a_1x + a_2x^2 + \cdots + a_nx^n = 0, \tag{3.1}$$

where n, the largest exponent in the equation, is some positive integer. The integer n is called the *degree* of the equation. If $n = 1$, the equation is a *linear equation*. If $n = 2$, the equation is a *quadratic equation*. If $n = 3$, the equation is a *cubic equation*. If $n = 4$, it is a *quartic equation*, and so on.

Generally, there are n roots to an nth-degree polynomial equation, but two or more of the roots can be equal to each other. It is also possible for some of the roots to be imaginary or complex numbers. If complex roots occur, there is always an even number of them. For most equations arising from physical and chemical problems, there will be only one root that is physically reasonable, and the others must be disregarded. For example, a concentration cannot be negative, and if a quadratic equation for a concentration produces a positive root and a negative root, the negative root disregarded. Complex roots cannot represent physically measurable quantities and must be disregarded if we are solving for a physically meaningful quantity.

Linear Equations

If an equation is of the form

$$a_0 + a_1x = 0 \tag{3.2}$$

then the single root of the equation is

$$x = -\frac{a_0}{a_1}. \tag{3.3}$$

Quadratic Equations

A quadratic equation is written in a standard form as

$$ax^2 + bx + c = 0. \tag{3.4}$$

Some quadratic expressions can be factored, which means that the equation can be written

$$a(x - x_1)(x - x_2) = 0, \tag{3.5}$$

where x_1 and x_2 are constants. In this case, x_1 and x_2 are the two roots of the equation. If a quadratic equation cannot easily be factored, you can apply the *quadratic formula*

$$\boxed{x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}. \tag{3.6}$$

This equation provides two roots, one when the positive sign in front of the square root is chosen and one when the negative sign is chosen. There are three cases: (1) if the *discriminant* $b^2 - 4ac$ is positive, the roots will be real and unequal; (2) if the discriminant is equal to zero, the two roots will be real and equal to each other; (3) if the discriminant is negative, the roots will be unequal and complex, since the square root of a negative quantity is imaginary. Each imaginary root will be the complex conjugate of the other root.

EXERCISE 3.1 ▶ Show by substituting Eq. (3.6) into Eq. (3.4) that the quadratic formula provides the roots to a quadratic equation. ◀

A common application of a quadratic equation in elementary chemistry is the calculation of the hydrogen ion concentration in a solution of a weak acid. If activity coefficients are assumed to equal unity, the equilibrium expression in terms of *molar concentrations* is

$$K_a = \frac{([\mathrm{H}^+]/\mathrm{c}^\circ)([\mathrm{A}^-]/\mathrm{c}^\circ)}{([\mathrm{HA}]/\mathrm{c}^\circ)}, \tag{3.7}$$

where $[\mathrm{H}^+]$ is the hydrogen-ion concentration expressed in moles per liter, $[\mathrm{A}^-]$ the acid-anion concentration, [HA] is the concentration of the undissociated acid, c° is defined to equal 1 mol l^{-1}, and K_a is the acid ionization constant. The expression in terms of molalities can also be used and has the same appearance. It is true that the hydrogen ions are nearly all attached to water molecules or water molecule dimers, and so forth, so that we could write $[\mathrm{H_3O}^+]$ instead of $[\mathrm{H}^+]$, but this makes no difference in the calculation.

EXAMPLE 3.1 For acetic acid, $K_a = 1.754 \times 10^{-5}$ at 25 °C. Find $\left[\mathrm{H}^+\right]$ if 0.1000 mol of acetic acid is dissolved in enough water to make 1.000 l. We say that the *stoichiometric concentration* (the concentration that would occur if no ionization occurred) is equal to 0.100 mol l^{-1}.

SOLUTION ► Assuming that no other sources of hydrogen ions or acetate ions are present, $[H^+]/c^\circ = [\mathbf{A}^-]/c^\circ$, which we denote by x,

$$K_a = \frac{x^2}{0.1000 - x}$$

or

$$x^2 + K_a x - 0.1000 K_a = 0.$$

From Eq. (3.6), our solution is

$$\begin{aligned} x &= \frac{-K_a \pm \sqrt{K_a^2 - 0.4000 K_a}}{2} \\ &= 1.316 \times 10^{-3} \quad \text{or} \quad -1.333 \times 10^{-3} \\ [H^+] &= [A^-] = 1.316 \times 10^{-3} \text{ mol l}^{-1}. \end{aligned}$$

We have disregarded the negative root because a concentration cannot be negative. ◄

EXERCISE 3.2 ► Express the answer to the previous example in terms of pH, defined for our present purposes as

$$pH = -\log_{10}([H^+]/c^\circ) \tag{3.8}$$

◄

EXERCISE 3.3 ► Find the pH of a solution formed from 0.075mol of NH_3 and enough water to make 1.00 l of solution. The ionization that occurs is

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

The equilibrium expression in terms of molar concentrations is

$$K_b = \frac{([NH_4^+]/c^\circ)([OH^-]/c^\circ)}{([NH_3]/c^\circ)}$$

where the water concentration is replaced by its mole fraction, which is very nearly equal to unity. K_b equals 1.80×10^{-5} for NH_3. ◄

Approximate Solutions to Equations

It is usually necessary to seek approximate roots to equations other than linear or quadratic equations, especially with equations containing sines, cosines, logarithms, exponentials, and so on. These equations are called *transcendental equations*. Cubic and quartic polynomial equations can be solved algebraically, but it is probably best to apply approximation techniques rather than attempting an algebraic solution.[1] There are two approaches: one is to modify the equation by making simplifying assumptions, and the other is to seek a numerical approximation that can be made to approximate the correct solution to any desired degree of accuracy.

[1] Older editions of *The Handbook of Chemistry and Physics* give methods for cubic equations. See, for example, the 33rd edition, pp. 272–273, Chem. Rubber Co., Cleveland, 1951–1952.

Approximation by Use of Simplifying Assumptions

The first method for finding approximate roots to an equation is to modify the equation by making simplifying assumptions. As an example, let us consider an equation for the hydrogen-ion concentration in a solution of a weak acid in which the hydrogen ions from the ionization of water cannot be ignored. We must solve simultaneous equations for the ionization of the weak acid and ionization of water. Later in this chapter, we will derive the equation

$$K_a = \frac{x(x - K_w/x)}{c/c^\circ - x + K_w/x}, \tag{3.9}$$

where c is the stoichiometric concentration of the acid, where c° is defined to equal 1 mol l^{-1}, where K_w is the ionization constant of water, equal to 1.00×10^{-14} near 25 °C, and where $x = [H^+]/c^\circ$. If we multiply this equation out, we obtain the cubic equation

$$x^3 + K_a x^2 - \left(\frac{cK_a}{c^\circ} + K_w\right) x - K_a K_w = 0. \tag{3.10}$$

This equation can be solved numerically for any specific case, but in some cases, it is possible to simplify this equation by making approximations.

EXERCISE 3.4 ▶ Carry out the algebraic manipulations to obtain the cubic equation version of Eq. (3.9). ◀

EXAMPLE 3.2 For the case of acetic acid with a stoichiometric concentration of 0.100 mol l^{-1}, convert Eq. (3.9) to a simpler approximate equation by discarding any negligibly small terms.

SOLUTION ▶ Equation (3.9) contains two terms in the numerator and three in the denominator. If one term in a polynomial is much smaller than the other terms, it might be possible to neglect this term. In the numerator, we know that $x = [H^+]/c^\circ$ will lie somewhere between 0.1 and 10^{-7}, the value for pure water. In fact, we know from our approximate solution in the previous example that $[H^+]$ is near 10^{-3} mol l^{-1}. Since K_w equals 1.00×10^{-14}, the second term must be near 10^{-11} mol l^{-1}, which is smaller than the first term by a factor of 10^8. We therefore drop the term K_w/x. We also drop the same term in the denominator, and obtain the equation

$$K_a = \frac{x^2}{c/c^\circ - x} \tag{3.11}$$

which is the same as Eq. (3.7), which was obtained with the assumption that $[H^+] = [A^-]$. ◀

It is possible in some cases to make a further approximation on Eq. (3.11). If only a small fraction of the weak acid ionizes, $[H^+]$ will be small compared with c, so that x can be neglected in the denominator. In the case of acetic acid and a gross acid concentration of 0.100 mol l^{-1}, $[H^+]$ is approximately equal to 10^{-3} mol l^{-1}, only about 1% as large as c. If we can tolerate an error of about 1%, we can neglect x compared with c/c°. We obtain

$$K_a = \frac{x^2}{c/c^\circ} \tag{3.12}$$

TABLE 3.1 ► Results for the Hydrogen-Ion Concentration in Acetic Acid Solutions at 25 °C from Different Equations at Different Concentrations

c (mol liter^{-1})	$[H^+]$ (mol liter^{-1}) by Eq. (3.10)	by Eq. (3.11)	by Eq. (3.13)
0.1000	1.31565×10^{-3}	$1.31565 \times 10^{-}3$	1.324×10^{-3}
1.000×10^{-3}	1.23959×10^{-4}	1.23959×10^{-4}	1.324×10^{-4}
1.000×10^{-5}	0.711545×10^{-5}	0.711436×10^{-5}	1.324×10^{-5}
1.000×10^{-7}	0.161145×10^{-6}	0.099435×10^{-6}	1.324×10^{-6}

which has the solution

$$x = \sqrt{(c/c^\circ)\, K_a}. \tag{3.13}$$

However, as c is made smaller, Eq. (3.13) quickly becomes a poor approximation, and for very small acid concentrations, Eq. (3.11) also becomes inaccurate. Table 3.1 shows the results from the three equations at different acid concentrations. Equation (3.11), the quadratic equation, remains fairly accurate down to $c = 10^{-5}$ mol l^{-1}, but Eq. (3.13) is wrong by about 7% at 10^{-3} mol l^{-1}, and much worse than that at lower concentrations.

In the case that approximations such as that of Eq. (3.13) are inaccurate, we can apply the method of *successive approximations*. In this method, one begins by solving an equation such as Eq. (3.13). The result of this approximation is used to approximate the term which was neglected in the first approximation and the solution is repeated. If needed, the result of this second approximation is used to replace the term that was originally neglected and the solution is repeated. This procedure is repeated (iterated) as many times as is necessary.

EXAMPLE 3.3 Solve the problem of Example 3.1 by successive approximation.

SOLUTION ► We write the equilibrium expression in the form

$$x^2 = K_a(0.1000 - x)$$

Since x is presumably much smaller than 0.1000, we neglect it compared with 0.1000. We obtain

$$x^2 \approx (1.754 \times 10^{-5})\,(0.1000) = (1.754 \times 10^{-6})$$
$$x \approx 0.00132$$

This is the result that would be obtained from Eq. (3.13). The next approximation is obtained by replacing the x in the right-hand side of the first equation by this value,

$$x^2 \approx (1.754 \times 10^{-5})(0.1000 - 0.00132) = 1.731 \times 10^{-6}$$
$$x \approx \sqrt{1.731 \times 10^{-6}} = 0.001316 \approx 0.00132.$$

This result shows that the first approximation is acceptable. Further iterations would make even smaller changes, so we stop at this point. ◄

EXERCISE 3.5 ► Solve for the hydrogen ion concentration in solutions of acetic acid with gross molarities equal to

(a) 0.00100 mol l^{-1}

(b) 0.0000100 mol l^{-1}.
Use the method of successive approximations on Eq. (3.9) and on Eq. (3.11).

◄

Approximation by linearization

In the next example, we see another way in which an equation can be made into a tractable approximate equation, by linearizing a function. We illustrate this technique in the following example:

EXAMPLE 3.4 The Dieterici equation of state is

$$P e^{a/V_m RT}(V_m - b) = RT, \tag{3.14}$$

where P is the pressure, T is the temperature, V_m is the molar volume, and R is the ideal gas constant. The constant parameters a and b have different values for different gases. For carbon dioxide, $a = 0.468$ Pa m^6 mol^{-2}, $b = 4.63 \times 10^{-5}$m^3 mol^{-1}. Find the molar volume of carbon dioxide if $T = 298.15$ K and $P = 10.000$ atm $= 1.01325 \times 10^6$ Pa.

SOLUTION ► The exponential function can be represented by the power series

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots$$

where $n!$ stands for *n factorial*, defined as $n(n-1)(n-2)(n-3)\cdots(3)(2)(1)$. We write

$$e^{a/V_m RT} = 1 + a/V_m RT + \frac{1}{2!}(a/V_m RT)^2 + \cdots. \tag{3.15}$$

Rough calculation shows that $a/V_m RT \approx 0.09$ so that $(a/V_m RT)^2 \approx 0.008$. We therefore discard all of the terms past the $a/V_m RT$ term and write to a fairly good approximation:

$$e^{a/V_m RT} \approx 1 + a/V_m RT.$$

We say that we have linearized the exponential function. We substitute this approximation into the original equation of state, obtaining

$$P(1 + a/V_m RT)(V_m - b) = RT$$

which can be written in the standard form for a quadratic equation:

$$PV_m^2 + \left(\frac{Pa}{RT} - Pb - RT\right)V_m - \frac{Pab}{RT} = 0.$$

We divide by P and substitute the numerical values. We temporarily let $x = V_m/(1\text{ m}^3\text{ mol}^{-1})$ and obtain after some manipulation

$$x^2 - (2.304 \times 10^{-3})x + 8.741 \times 10^{-9} = 0.$$

Applying the quadratic formula,

$$x = \frac{2.304 \times 10^{-3} \pm \sqrt{(0.002304)^2 - 4(8.741 \times 10^{-9})}}{2} = \begin{cases} 2.3 \times 10^{-3} \\ 4.000 \times 10^{-6}. \end{cases}$$

We disregard the second value as too small to correspond to the physical situation, and obtain

$$V_m = 2.30 \times 10^{-3}\text{m}^3\text{ mol}^{-1}.$$

The ideal gas equation of state gives $V_m = 2.447 \times 10^{-3}$ m^3 mol^{-1}, for a difference of about 6%. ◄

EXERCISE 3.6 ► (a) Verify the prediction of the ideal gas equation of state given in the previous example.
(b) Substitute the value of the molar volume obtained in the previous example and the given temperature into the Dieterici equation of state to calculate the pressure. Compare the calculated pressure with 10.00 atm, to check the validity of the linearization approximation used in the example. ◄

3.2 Graphical Solution of Equations

Instead of approximating an equation and then solving the approximate equation algebraically, we can apply the *graphical method* to obtain a numerical approximation to the correct root. This method is sometimes very useful because you can see what you are doing and you can usually be sure that you do not obtain a different root than the one you want to find. The equation to be solved is written in the form

$$f(x) = 0$$

where we denote the independent variable by x. If a graph of the function f is drawn, any real roots to the equation correspond to the places where the curve crosses the x axis.

EXAMPLE 3.5 By graphing, find a root of the equation

$$2\sin(x) - x = 0.$$

in the interval $1.8 < x < 2.0$.

SOLUTION ► A graph of the function for the interval $1.8 < x < 2.0$ is shown in Fig. 3.1. From the graph, it appears that the root is near $x = 1.895$. ◄

EXERCISE 3.7 ► Find approximately the smallest positive root of the equation

$$\tan(x) - x = 0.$$

◄

Graphing with a Spreadsheet

Drawing a graph by hand is tedious, and almost no one actually makes graphs by hand, since it is possible to make graphs more easily with a spreadsheet program

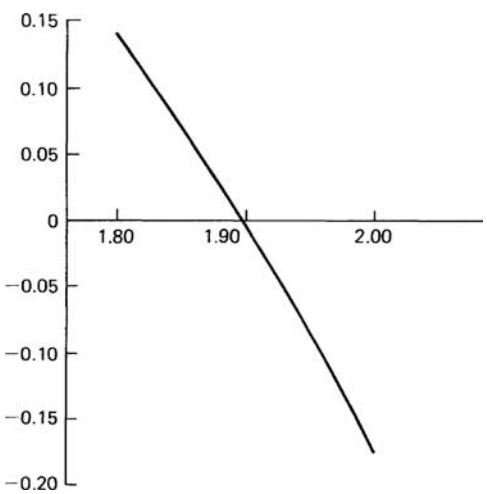

Figure 3.1 ► Graph of Example 3.5.

on a computer. A *spreadsheet* can perform various mathematical and other operations on sets of items that are entered by the user and displayed in the form of a table. A common spreadsheet is Microsoft Excel®. Another spreadsheet is Lotus 1-2-3®. Microsoft Works® contains a spreadsheet that is a simplified version of Excel, and Claris Works® contains a similar spreadsheet program. At the time of this writing, the latest version of Excel is called Excel 2003. Previous versions were called Excel 2000, 1998, 4.0, 3.0, and so on. We describe briefly how to make a graph on the Excel spreadsheet. The instructions are written for a computer using the Windows operating system, but the procedure is similar on a Macintosh computer.

Creating and Editing a Worksheet in Excel

When one first opens Excel a window is displayed on the screen with a number of rectangular areas called cells arranged in rows and columns. This window is called a worksheet. The rows are labeled by numbers and the columns are labeled by letters. Any cell can be specified by giving its column and its row (its address). For example, the address of the cell in the third row of the second column is B3. A list of menu headings appears across the top of the screen and a double strip of small icons called a "toolbar" appears under the menu headings.

Any cell can be selected by using the arrow buttons on the keyboard or by moving the mouse until its cursor is in the desired cell and clicking the left mouse button. One can then type one of three kinds of information into the cell: a number, some text, or a formula. For example, one might want to use the top cell in each column for a label for that column. One would first select the cell and then type the label. As the label is typed, it appears in a line above the cells. It is then entered into the cell by moving the cursor away from that cell or by pressing the "Return" key. A number is entered into another cell in the same way. To enter a number but treat it as text, precede the number with a single quotation mark (').

The use of formulas in cells is a useful features of Excel. A formula is entered by typing an equal sign followed by the formula, using the symbol * (asterisk) for multiplication, / (slash) for division, + (plus) for addition, and – (minus) for subtraction. The caret symbol ^ is used for powers. For example, $3.26^{3/2}$ would be represented by 3.26^1.5. Don't use 3.26^3/2 to represent $3.26^{3/2}$, since the computer carries out operations in a predetermined sequence. Powers are carried out before multiplications and divisions, so the computer would interpret this entry as $3.26^3/2$. Since the formula must be typed on a single line, parentheses are used as necessary to make sure that the operations are carried out correctly, using the rule that all operations inside a pair of parentheses are carried out before being combined with anything else. Other operations are carried out from left to right, with multiplications and divisions carried out before additions and subtractions. If there is any doubt about which operations are carried out first, use parentheses to make the formula unambiguous. If a number or a variable stored in another cell is needed in a formula, one types the address of that cell into the formula in place of the number. A number of common functions can be included in formulas. The following abbreviations must be used. The argument of a function is enclosed in parentheses in place of the ellipsis ($\cdots$), as indicated:

Abbreviation	Function
SIN(· · ·)	sine
COS(· · ·)	cosine
EXP(· · ·)	exponential (e raised to the argument)
LOG(· · ·)	common logarithm (base 10)
LN(· · ·)	natural logarithm (base e)

For example, if you want the cell to contain the natural logarithm of the number presently contained in cell B2, you would type =LN(B2) in the cell. Lowercase letters can also be used and LOG10(· · ·) can also be used for the common logarithm. The argument of the sine and cosine must be expressed in radians. An arithmetic expression can be used as the argument and will automatically be evaluated when the function is evaluated. These rules are similar to those used in the BASIC and FORTRAN programming languages and in Mathematica, a comprehensive mathematical computer package. After the formula is typed one enters it into a cell by pressing the "return" key. When a formula is entered into a cell, the computer will automatically calculate the appropriate number from whatever constants and cell contents are specified and will display the numerical result in the cell. If the value of the number in a cell is changed, any formulas in other cells containing the first cell's address will automatically recalculate the numbers in those cells.

EXAMPLE 3.6 Enter a formula into cell C1 to compute the sum of the number in cell A1 and the number in cell B2, divide by 2, and take the common logarithm of the result.

SOLUTION ► With the cursor in cell C1 we type the following:

$$= LOG((A1 + B2)/2)$$

We then press the "return" key to enter the formula into that cell. If numbers are stored in cells A1 and B2, the numerical answer will appear in cell C1. ◄

EXERCISE 3.8 ► Enter a formula into cell D2 that will compute the mean of the numbers in cells A2, B2, and C2. ◄

If you move a formula from one cell to another, any addresses entered as in the above example will change. Such addresses are called *relative addresses* or *relative references*. For example, say that the address A1 and the address B2 were typed into a formula placed in cell C1. If this formula is copied and placed into another cell, the address A1 is replaced by the address of whatever cell is two columns to the left of the new location of the formula. The address B2 is replaced by the address of whatever cell is one column to the left and one row below the new location of the formula. This feature is very useful, but you must get used to it. If you want to move a formula to a new cell but still want to refer to the contents of a particular cell, put a dollar sign ($) in front of the column letter and another dollar sign in front of the row number. For example, $A$1 would refer to cell A1 no matter what cell the formula is placed in. Such an address is called a *absolute address* or an *absolute reference*.

There is a convenient way to put the same formula or the same number in an entire column or an entire row of a table. Type a formula with the cursor in the

topmost cell of a given portion of a column, and then press the "return" key to enter the formula in the first cell. Then select a portion of the column by dragging the cursor down the column (while holding down the mouse button) from the cell containing the formula as far as desired. Then choose the "Fill" command in the "Edit" menu and choose "Down" from a small window that appears. You can also hold down the "Ctrl" key and then type a "d." When you do this, the cells are all "filled" with the formula. The formulas in different cells will refer to different cells according to the relative addressing explained above. Selecting a given cell will show the formula for that cell, with the addresses that will actually be used. A similar procedure is used to fill a portion of a row by entering the formula in the leftmost cell of a portion of a row, selecting the portion of the row, and using the "Fill" command in the "Edit" menu and choosing "Right" in the next window. The same procedures can be used to fill a column or a row with the same number in every cell.

A block of cells can be selected by moving the cursor to the upper left cell of the block and then moving it to the opposite corner of the block while holding down the mouse button ("dragging" the cursor). You can also drag the cursor in the opposite direction. The contents of the cell or block of cells can then be cut or copied into the clipboard, using the "Cut" command or the "Copy" command in the "Edit" menu. The contents of the clipboard can be pasted into a new location. One selects the upper left cell of the new block of cells and then uses the "Paste" command in the "Edit" menu to paste the clipboard contents into the workbook. If you put something into a set of cells and want to change it, you can select the cells and then choose "Clear" in the "Edit" menu. To clear the cells completely, choose "All" in the window that appears.

Excel has the capability of using routines called "Macros" that can be called inside the spreadsheet. These routines can be programs written in a version of the BASIC programming language called "Visual Basic for Applications." Macros can be obtained from other sources, such as internet websites, and placed in any spreadsheet.

Creating Graphs with Excel

Excel can be used to produce graphs of various kinds (Excel refers to graphs as "charts"). We present a procedure to construct a two-dimensional graph using the "Chart Wizard." The graph is constructed from values of an independent variable in one column values of a dependent variable in another column. These values must first be loaded into the columns. After the values have been loaded into the spreadsheet, you follow the procedure:

1. Save the spreadsheet, and if you want a printed copy of it without the graph, print it now by using the "Print" command in the "File" menu.

2. Select the two columns by dragging the mouse cursor over them. If the two columns are not adjacent, drag the cursor over the first column, and then hold down the "Ctrl" key while dragging the cursor over the second column. The values of the independent variable must be in the column to the left of the other column. Copy and paste a column of values if necessary.

3. Click on the icon for the Chart Wizard in the toolbar at the top of the spreadsheet. It looks like a small bar graph with three bars.

4. A window labeled "Step 1" appears showing different types of graphs to choose from. Most of the graph types plot categories, not values of a variable, on the horizontal axis. That is, the row number is used as the variable on this axis. To put values of a variable on the horizontal axis, choose the type of graph called "XY(Scatter)" by putting the cursor on this icon and clicking. Several types of graphs can now be chosen by clicking on one of five areas on the screen. The topmost area produces a graph with only the data points showing. The one below that produces a graph with the data points and a smooth curve passing nearly through the data points. The one to its right produces a graph with the smooth curve but no data points. The bottom two produce graphs with line segments connecting the data points. Make your choice and click on the "Next" button.

5. Another window labeled "step 2" appears. The range of data is exhibited. You can verify or change the range of cells from which the graph will be made. Click on the "Next" button.

6. A window labeled "step 3" appears. There are several areas on which you can click. These are self-explanatory. For example, you can click on the "Titles" area and then type in a title for the graph and labels for the axes. You can click on the "Axes" area and choose whether you want numeric labels on the axes. You can click on the "Grid lines" area and choose whether you want horizontal and vertical grid lines. You can click on the "Legend" area and decide whether you want a labeled symbol to the right of the graph (the "legend"). For a graph with a single curve, this is superfluous. Click on the "Next" button.

7. A window labeled "Step 4" appears that allows you to choose whether to place the graph in your worksheet or on a separate sheet. If you want to print the graph, choose a separate sheet. After you do this, click on the "Finish" button and the finished graph appears.

Printing a graph in Excel is done by using the "Print" command in the "File" menu in the usual way. You can use the "Print Preview" command in the "File" menu to see on the screen how the printed version will be arranged. You can change this by choosing "Page Setup."

We illustrate this procedure in the following example

EXAMPLE 3.7 Find the positive root of the cubic equation

$$x^3 - 0.6000x = 0$$

This cubic equation has three real roots, one of which is obviously at $x = 0$.

SOLUTION ► We open a blank spreadsheet in Excel. We start by making a table of values of the function

$$f(x) = x^3 - 0.6000x$$

in the range $-2 < x < 2$. We first type the value -2 in the cell A1. In cell A2 we type $= A1 + 0.2$ and press "enter." or "return." We then select 20 cells in the first column by dragging the cursor

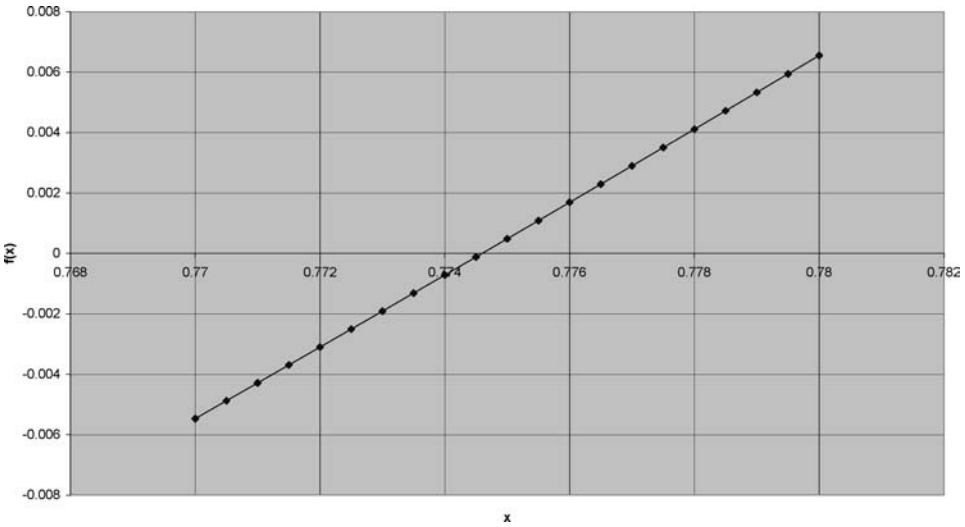

Figure 3.2 ► Graph of Example 3.7.

over the cells, starting with the A2 cell and ending with the A21 cell. We press the "d" key while holding down the "Ctrl" key. This fills the first column with 21 values of x ranging from -2 to 2 in increments of 0.2. We then type the formula in cell B1 that will evaluate the polynomial. We type $= A1\text{\^{}}3 - 0.6 * A1$ and press the "enter" key or the "return" key. This inserts the formula into cell B1 and the places the value of the function (-6.8) in that cell. We then drag the cursor down the B column to B21, and then fill the cells with the formula by pressing the "d" key while holding down the "Ctrl" key. The values of the function appear in column B. Inspection of the values shows that the function changes sign three times in the interval, so all three of the roots lie in this region. We now construct a graph of the function, following the above procedure. Inspection of the graph indicates that there are roots near $x = -0.77$, at $x = 0$, and near $x = 0.77$. To locate the positive root more accurately, we construct a graph with a smaller range of x. We enter 0.77 in cell C1 and enter the formula $= C1 + 0.0005$ in cell C2. We then fill the formula down to cell C11. We then copy the formula in cell B1 and paste it into cell D1 and then fill the formula down to cell D21. We select columns C and D and make a second graph. This graph is shown in Figure 3.2. The root appears to lie near $x = 0.7745$.

EXERCISE 3.9 ► Using a graphical procedure, find the most positive real root of the quartic equation:

$$x^4 - 4.500x^3 - 3.800x^2 - 17.100x + 20.000 = 0$$

You will note that the curve in the graph crosses the x axis in only two places. This indicates that two of the four roots are imaginary or complex numbers. Chemists are not usually interested in complex roots to equations. ◄

◄

A spreadsheet such as Excel is a large and powerful program, and can perform many different tasks, most of which are not needed by a physical chemistry student. You can consult the manual provided by the software manufacturer to learn more about Excel. There are also several textbooks listed at the end of the book that are more easily used than the manufacturer's manual.

EXERCISE 3.10 ► Using a graphical method, find the two positive roots of the following equation.

$$e^x - 3x = 0.$$

◄

3.3 Numerical Solution of Algebraic Equations

Strictly speaking, one does not solve an equation numerically. One obtains an approximation to a root. However, with a computer or with a hand calculator, it is easy to obtain enough significant digits for almost any purpose.

Trial and Error

If the equation is written in the form

$$f(x) = 0$$

one repeatedly evaluates the function f, choosing different values of x, until f nearly vanishes. When using this method with a hand calculator or a spreadsheet, it is usually possible to adopt a strategy of finding two values of x such that f has different signs for the two values of x, and then to choose values of x within this interval until $f \approx 0$. If the equation has more than one root, you must either find all of the roots, or must make sure that you have found the one that you want. If the equation has complex roots and if you care about them, you must vary both the real and imaginary parts of x, which can be done by using a computer program that will carry out arithmetic with complex quantities.

EXAMPLE 3.8 Use the method of trial and error to find the positive root of the equation

$$2\sin(x) - x = 0$$

SOLUTION ► We let $f(x) = 2\sin(x) - x$, which vanishes at the root. It is convenient to use a spreadsheet to carry out the evaluation of the function $f(x)$. We put the formula in the B column, filling it down to enough rows for the number of times we think we will have to evaluate the function. We then put trial values into column A and inspect the value of the function in column B. We find quickly that $f(1) = 0.68294$, and that $f(2) = -0.1814$, so that there must be a root between $x = 1$ and $x = 2$. We find that $f(1.5) = 0.49499$, so the root lies between 1.5 and 2. We find that $f(1.75) = 0.21798$, so the root is larger than 1.75. However, $f(1.9) = -0.00740$, so the root is smaller than 1.9. We find that $f(1.89) = 0.00897$, so the root is between 1.89 and 1.90. We find that $f(1.895) = 0.000809$ and that $f(1.896) = -0.000829$. To five significant digits, the root is $x = 1.8955$. ◄

EXERCISE 3.11 ► Use the method of trial and error to find the two positive roots of the equation

$$e^x - 3x = 0$$

to five significant digits. Make a graph of the function to find the approximate locations of the roots. ◄

The Method of Bisection

This is a systematic variation of the method of trial and error. You start with two values of x for which the function $f(x)$ has opposite signs, and then evaluate the function for the midpoint of the interval and determine which half of the interval

contains the root. If the function has the same sign at the midpoint as at the left end of the interval, the root is in the right half of the interval. The midpoint of the half of the original interval containing the root is taken, and it is determined which half of this new interval contains the root. The method is continued, repeating the process until the interval known to contain the root is as small as twice the error you are willing to tolerate. The middle of the last interval is then taken as the approximation to the root.

Solution of Equations Using Mathematica

Mathematica is a complete mathematics package that can carry out both numerical and symbolic mathematics. Before we discuss the solution of equations using Mathematica, we provide an elementary introduction to the program. When you open Mathematica, a blank "untitled" window appears on the video screen. This window is called a *notebook*. Mathematica is now ready to accept instructions.

Numerical Calculations with Mathematica

You can use Mathematica to make numerical calculations much as you would a calculator. In an open notebook, you can type in numbers and symbols for arithmetic operations:

addition: +
subtraction: –
negation: –
division: /
multiplication: blank space or asterisk (∗)
exponentiation: ^
factorial: !
Parentheses are used in the same way as in writing ordinary formulas.

Numbers in scientific notation are entered in a fairly obvious way. To enter 1.234×10^4, you would type 1.234 10^4 with the space standing for multiplication, or 1.234*10^4. In the output lines, Mathematica always uses the space for multiplication.

Most of the Mathematica symbols are the same as those used in Excel or various computer programming languages such as BASIC except for the use of a blank space for multiplication. Excel and BASIC use only the asterisk for multiplication. In ordinary formulas, placing two symbols together without a space between them can stand for multiplication. In Mathematica, if you write xy, the software will think you mean a variable called xy, and not the product of x and y. However, you can write either $2x$ or $2\ x$ for 2 times x, but not $x2$. It is probably best to use the asterisk (∗) for multiplication rather than a space in input statements. Watch for the use of the blank space in output statements. Complex arithmetic is done automatically, using the capital letter I for $\sqrt{-1}$. Several constants are available by using symbols: Pi, E, I, Infinity, and Degree stand for π, e, $i = \sqrt{-1}$, ∞, and $\pi/180$ (conversion from degrees to radians). The first letter of each symbol must be capitalized.

For example, to obtain $(4.67841 + 3.58731)^{56.3}$, you type in an open notebook the following expression:

$$(4.67841 + 3.58731)\text{\^{}}56.3$$

using the caret (^) to stand for exponentiation. Parentheses are used to determine the sequence of operations. The rule is that all operations inside a pair of parentheses will be carried out before the result is combined with anything else. After finishing your input statement you then press the "Enter" key (the "Enter" key at the far right of the keyboard in the number keypad, not the "Return" key in the main part of the keyboard, which is also labeled "Enter" on some keyboards). Instead of pressing the "Enter" key, you can press the "Return" key in the main part of the keyboard while holding down the "Shift" key (a "Shift-Return"). If you press the "Return" key without the "Shift" key, you are signaling Mathematica that you are continuing one statement onto a second line. When you press the "Enter" key, you are ending a unit called a "cell."

Mathematica labels each input cell by a number. If you are at the beginning of a notebook, after you press the "Enter" key you will see

In[1]: =**(4.67841+3.58731)^56.3**

Mathematica prints input in boldface type. When you press the "Enter" key, it will immediately print out the result, labeling it as output number 1:

Out[1]=4.39443 10^{51}

In this expression, the space before the 10 stands for multiplication, which is standard notation in Mathematica.

On the screen there is now a square bracket at the right of your input and another at the right of the output, as well as a larger square bracket to the right of both of these brackets and encompassing them. The smaller brackets identify the cells. Mathematica assumes that any new cell is an input cell. When you press the "Enter" key, you notify Mathematica that you are ending the input cell, and that you want any expression in the input cell to be evaluated. When Mathematica prints your output, it creates an output cell for the output, and also prints a larger bracket linking the input cell with its output cell. Any Mathematica notebook consists of a sequence of cells, which are numbered sequentially.

Pressing the "Return" key on the main part of a keyboard does not end a cell. If a piece of input requires more than one line, you can press the "Return" key at the end of each line, and then press the "Enter" key or the "Shift-Return" at the end of the cell. You can put several executable statements in the same cell. It is best to separate them by pressing the "Return" key after each statement.

Many functions are available in Mathematica. The names of the functions must be entered with the first letter capitalized and sometimes a letter in the middle capitalized. The other letters must be in lower case and the argument of the function must be enclosed in square brackets, not parentheses. You will have to get used to this. No deviation from the capitalization rule is allowed, and Mathematica will not recognize parentheses instead of brackets. Some common functions are given in Table 3.2. Other functions are described in the book by Wolfram listed at the end of the chapter.

EXERCISE 3.12 ► Write Mathematica expressions for the following:

(a) The complex conjugate of $(10)e^{2.657i}$

(b) $\ln(100!) - (100\ln(100) - 100)$

(c) The complex conjugate of $(1 + 2i)^{2.5}$ ◄

Mathematica will print out numerical values with any specified number of digits. You enter the letter N followed by the expression, then a comma, and then

TABLE 3.2 ► Mathematical Functions in Mathematica

Symbol	Function	Result
Abs[x]	absolute value (magnitude) of x	nonzero constant
Arg[z]	argument ϕ of complex expression $\lvert z\rvert e^{i\phi}$	nonzero constant
ArcCos[x]	inverse cosine in radians	constant, $0 < c < \pi$
ArcSin[x]	inverse sine in radians	constant, $-\frac{\pi}{2} < c < \frac{\pi}{2}$
ArcTan[x]	inverse tangent in radians	constant, $-\frac{\pi}{2} < c < \frac{\pi}{2}$
Conjugate[z]	complex conjugate of $z = x + iy$	$x - iy$
Cos[x]	cosine of an angle in radians	constant, $-1 < c < 1$
Exp[x]	exponential function, e^x	positive constant
Im[z]	imaginary part of complex expression z	constant
Log[x]	natural logarithm (base e)	constant
Log[b,x]	logarithm to the base b	constant
n!	n factorial	constant
Random[ ]	random number generator	constant, $0 < c < 1$
Re[z]	real part of complex expression z	constant
Round[x]	closest integer to x	constant
Sin[x]	sine of an angle in radians	constant, $-1 < c < 1$
Sqrt[x]	square root of x	constant
Tan[x]	tangent of an angle in radians	constant

the number of digits desired. For example, if you want to have the value of $(3.58731)^{56.3}$ to 15 digits, you use the input statement

N[3.58731^56.3, 15]

and press the "Enter" key. Mathematica will print

In[1]:=**N[3.58731^56.3,15]**

Out[1] = 1.71194390461979 10^{31}

The entire expression and the number of digits are enclosed in the square brackets following the N. If you do not specify the number of digits, Mathematica will give you a standard number of digits (usually six) for an expression that contains a decimal point. It will give all of the digits if possible for an expression that does not contain a decimal point. If you enter 30!, it will give you the entire value, with 33 digits. If you enter 30.!, it will give you a value with six digits. However, if you enter Sqrt[3], it will not give you a value, since an exact value of 3 cannot be written with a finite number of digits. It will print Sqrt[3] as output. If you enter

Sqrt[3.], it will give you a value with six digits, and you can also get a six-digit answer by entering N[Sqrt[3]] or Sqrt[3]//N. If you want 20 digits, you can enter N[Sqrt[3],20].

You can refer to the last output cell with a percent sign (%) or to any other output cell by its number following a percent sign. If you want to refer to output cell number 3, you would type %3. If you had entered Sqrt[3] and had obtained Sqrt[3] as your output, you could type N[%] and press the enter key to obtain a numerical value with six digits, or could type N[%,15] to obtain a numerical value with 15 digits.

Mathematica statements can contain symbols for stored *variables* as well as constants. A variable stands for a location in the computer memory in which a numerical value can be stored. Variable names can contain any number of letters and/or digits. However, they cannot begin with a digit. Begin your variable names with a lowercase letter to avoid confusion with Mathematica functions and other Mathematica objects, which always begin with a capital letter. Also remember that xy would represent a variable called xy while x y (with a space between the letters) stands for the product of the two variables x and y.

Values are assigned to variables by using an ordinary equal sign, which stands for an *assignment operator*. For example, a value of 75.68 would be assigned to the variable x by entering the statement:

```
x = 75.68
```

and pressing the "Enter" key. The variable x will be replaced by the value 75.68 whenever it occurs in a Mathematica expression until a new value is assigned. To remove a value from the variable x, type the statement

```
Clear[x].
```

If you are not sure whether a given variable already has a value, use the *Clear statement* before using the variable.

You can also define one variable in terms of other variables. Assuming that x already has a value, the statement

```
y = x^3
```

will assign the cube of the value of x to the variable y. The variable y will keep that numerical value until it is explicitly assigned a new value, even if the value of x is changed. You can also define y as a function of x such that the value of y will change if a new value of x is assigned. To do this, you use the second type of equal sign that is used in Mathematica, denoted by the symbol := (a colon followed by an equal sign). The statement

```
y:= x^3
```

will cause y to be evaluated as the cube of whatever value x has at the time of execution. You can see what the value of any variable is at the moment by typing the name of the variable and pressing the Enter key. If you type a question mark followed by the name of the variable and press the Enter key, you can see whether it is defined as a function of other variables.

You can also define a function. For example, if you want to define the function

$$f = abce^{-x/y} \tag{3.16}$$

you can type

```
Clear[a,b,c,f,x,y]
f[x_]:=a b c Exp[-x/y]
```

where we have used the space to stand for multiplication. You can also type

```
Clear[a,b,c,f,x,y]
f[x_]:=a*b*c*Exp[-x/y]
```

The underscore following the symbol for the independent variable in the function expression on the left-hand side of the statement is part of the function definition and must be typed in. Mathematica's second type of equal sign, := (a colon followed by an equal sign), must be used. After defining a function, you can use it in a Mathematica expression, as in the statement

```
g=x*f[x]*Cos[x/y]
```

The underline is used only in the definition of the function. It is not used after the symbol for the function's argument in an expression. Note that Mathematica uses square brackets for the argument of a function, not parentheses. The rules of Mathematica must be followed exactly. There is no provision for alternative symbols.

A cell can also be designated as a text cell, allowing Mathematica to be used like a word processor. You can convert any cell to a text cell as follows: first "select" the cell by placing the mouse cursor on the bracket to the right of the cell and pressing on the mouse button (clicking on the bracket). Then type the numeral 7 while depressing the "Alt" key. Mathematica will store text in a text cell, but will not perform any mathematical operations on anything in a text cell. You can delete the contents of any cell by selecting the cell and then choosing "Clear" from the "Edit" menu or typing the letter x while depressing the "Ctrl" key.

Symbolic Algebra with Mathematica

Mathematica has a powerful capability to carry out symbolic mathematics on algebraic expressions and can solve equations symbolically. In addition to the arithmetic operations, the principal Mathematica statements for manipulating algebraic expressions are Expand[ ], Factor[ ], Simplify[ ], Together[ ], and Apart[ ]. The *Expand statement* multiplies factors and powers out to give an expanded form of the expression. The following input and output illustrate this action:

```
In[1]:=Clear[a,x]
      Expand[(a+x)^3]
Out[1] =a^3+3 a^2 x+3 a x^2+x^3
```

The Clear statement is included in case a and x had been previously defined as variables with specific values, which would cause Mathematica to return a numerical result instead of a symbolic result.

The *Factor statement* manipulates the expression into a product of factors. The following input and output illustrate this action:

```
In[2]:=Clear[y]
      Factor[1+5 y+6 y^2]
Out[2] =(1+2 y) (1+3 y)
```

Note the use of the blank space for multiplication. Note also that the Factor statement does not have its own input line number, because the "Return" key was pressed after the Clear statement, not the "Enter" key. The *Simplify statement*

manipulates an expression into the form that is considered by the rules built into Mathematica to be the simplest form (with the fewest parts). This form might be the factored form or the expanded form, depending on the expression.

The *Together* statement collects all terms of an expression together over a common denominator, while the *Apart* statement breaks the expression apart into terms with simple denominators, as in the method of *partial fractions*. The theorem of partial fractions states that if $Q(x)$ can be factored in the form

$$Q(x) = (a_1x + b_1)(a_2x + b_2)(a_3x + b_3)\cdots(a_nx + b_n), \tag{3.17}$$

where all the a's and b's are constants and if $P(x)$ is of lower degree than $Q(x)$, then

$$\boxed{\frac{P(x)}{Q(x)} = \frac{A_1}{a_1x + b_1} + \frac{A_2}{a_2x + b_2} + \cdots + \frac{A_n}{a_nx + b_n}}, \tag{3.18}$$

where $A_1, A_2, \ldots, A_n$, are all constants.

EXAMPLE 3.9 Write a Mathematica entry that will carry out the decomposition into partial fractions of the expression

$$\frac{6x - 30}{x^2 + 3x + 2}$$

SOLUTION ► The input and output lines are:

```
In[1]: =Clear[x]
       Apart[(6 x-30)/(x^2+3 x+2)]
Out[1] =-36/(1+x) + 42/(2+x)
```

◄

EXERCISE 3.13 ► In the study of the rate of the chemical reaction of substances A and B:

$$a\mathrm{A} + b\mathrm{B} \rightarrow \textit{products}$$

the quotient occurs.

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)}$$

where $[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ are the initial concentrations of A and B, a and b are the stoichiometric coefficients of these reactants, and x is a variable specifying the extent to which the reaction has occurred. Write a Mathematica statement to decompose the denominator into partial fractions. ◄

Solving Equations with Mathematica

Mathematica can carry out both symbolic and numerical solutions of equations, including single algebraic equations, simultaneous algebraic equations, and differential equations, which we discuss later. Mathematica contains the rules needed for the symbolic solution of polynomial equations up to the fourth degree, and can

solve some fifth-degree equations. The principal statements used to solve equations are Solve, FindRoot, Eliminate, and Reduce.

The *Solve statement* returns symbolic formulas for solutions, if they exist. For example, the input line to solve the equation $ax^2 + bx + c = 0$ is

In[1]: =**Solve[a*x^2+b*x+c==0,x]**

The name of the variable to be solved for must be included at the end of the equation and separated from it by a comma. Mathematica's third kind of equal sign, a double equal sign, must be used in equations to be solved. Another use of this equal sign is in asking Mathematica to test whether an equality if true or false. The resulting output is the standard quadratic formula:

Out[1] ={{x $\rightarrow$ $\frac{-b-\text{Sqrt}[b^2-4ac]}{2a}$}, {x $\rightarrow$ $\frac{-b+\text{Sqrt}[b^2-4ac]}{2a}$ }}

Note the use of the arrow symbol ($\rightarrow$).

If no formula can be found for a solution, you can use the *FindRoot* statement to obtain a numerical value for the root. You must provide a first estimate of the root (a). For example, to find a root for the equation

$$e^{-x} - 0.5x = 0$$

with a trial root of $x = 1$, you type the input statement:

In[1]:=**FindRoot[Exp[–x] - 0.5∗x == 0,{x,1}]**

and get the output

Out[1] ={x $\rightarrow$ 0.852606}

The trial value of the root is here represented by the 1 following the x in braces (curly parentheses, $\{\cdots\}$). If your equation is a polynomial equation, the *NSolve statement* can be used instead of FindRoot. The NSolve statement does not require a trial root, and will find all roots, while the FindRoot statement will generally cause Mathematica to converge to one root and then stop. If your equation has more than one root, you need to determine whether you have found the desired root and not one of the others.

EXAMPLE 3.10 Using the NSolve statement find the roots of the equation

$$x^4 - 5x^3 + 4x^2 - 3x + 2 = 0 \tag{3.19}$$

SOLUTION ► We enter the input statement

NSolve[x^4-5 x^3+4 x^2-3 x+2==0,x]

We press the "Enter" key and receive the output

Out[1]={{x $\rightarrow$ 0.00442308 - 0.771419ii,

{x $\rightarrow$ 0.00442308 + 0.771419ii,

{x $\rightarrow$ 0.802307}, {x $\rightarrow$ 4.18885}}

where Mathematica uses the a symbol that looks like double i (ii with a single dot) to represent the imaginary unit in its output statement. Use a capital I in an input statement containing the square root of -1. ◄

EXERCISE 3.14 ► Verify the real solutions in the preceding example by substituting them into the equation. ◄

EXERCISE 3.15 ► (a) Use the NSolve statement in Mathematica to find the numerical values of the roots of the equation

$$x^3 + 5x - 42 = 0$$

(b) Use the FindRoot statement to find the real root of the same equation. ◄

Graphing with Mathematica

Mathematica can produce sophisticated graphs, including two-dimensional graphs and perspective views of three-dimensional graphs. Graphing a function is easier than with Excel, since you do not have to fill columns with values of the variable.

EXAMPLE 3.11 Make a graph of $\sin(x)$ from $x = 0$ to $x = 2\pi$,

SOLUTION ► One enters the input
Plot[Sin[x],{x,0,2Pi}]
and presses the "Enter" key. The graph appears on the computer screen in an output statement. ◄

The graphic capabilities of Mathematica are very extensive. For example, it makes perspective views of three-dimensional graphs. You can read more about this in the book by Wolfram and in the manual that is supplied with Mathematica.

Solving Equations Numerically with Excel

Excel is a large and versatile program, and we do not have the space to discuss all of its capabilities. It has the capability to solve equations numerically, using a command called *Goal Seek*. This command causes the software to change a variable until a defined function of that variable attains a specified value. It uses a method called the Newton-Raphson method, which we will discuss in a later chapter. To find a root of an equation, one must begin with a trial root that is not too far from the desired root. You must find this by graphing or by looking for places where a table of value of the function changes sign, as we did earlier. You type in a trial root in one cell and type in the function of that variable that needs to equal zero (or some other numerical value).

EXAMPLE 3.12 Find the real roots of the equation

$$x^4 - 5x^3 + 4x^2 - 3x + 2 = 0 \tag{3.20}$$

SOLUTION ► This is the same equation that we solved with Mathematica in a previous example, so we know where the real roots are. We pretend that we know only that there is a real root near 1 and a real root near 4. We type in the value 1 in cell A1 and the value 4 in cell A2. We type the following formula in cell B1: =A1^4-5*A1^3+4*A1^2-3*A1+2 and press the "Return" key. We then drag the cursor over cells B1 and B2 and "fill down" by holding down the "Ctrl" key and typing a letter d. We could also select the two cells and choose "Fill Down" in the "Edit" menu. We then select the B1 cell and choose "Goal Seek" from the "Tools" menu. A window appears with three blanks. The first says "Set cell:" and should have B1 in the blank. The second blank

says "To value:" and we type in a zero, since we want the function to attain the value zero. The third blank says "By changing cell:" We type in A1, since that is the cell containing our trial root. We click on "OK" and the software quickly finds the root and places it in cell A1. We then select cell B2 and repeat the process, specifying that we want to vary the contents of cell A2. ◄

EXERCISE 3.16 ► Use Excel to find the real root of the equation

$$x^3 + 5x - 42 = 0 \tag{3.21}$$

◄

3.4 Simultaneous Equations: Two Equations with Two Unknowns

The simplest type of simultaneous equations is the set of two equations:

$$a_{11}x + a_{12}y = c_1 \tag{3.22}$$
$$a_{21}x + a_{22}y = c_2, \tag{3.23}$$

where the a's and the c's are constants. This set of equations is called *linear* because the unknowns x and y enter only to the first power, and is called *inhomogeneous*, because there are constant terms that do not contain x or y. If certain conditions are met, such a set of equations can be solved for a solution set consisting of a single value of x and a single value of y.

The Method of Substitution

The first step of this method is to manipulate one equation to give one variable as a function of the other. This function then is substituted into the other equation to give an equation in one unknown which can be solved. The result is then substituted into either of the original equations, which is then solved for the second variable.

EXAMPLE 3.13 Use the method of substitution on Eqs. (3.22) and (3.23).

SOLUTION ► We solve the first equation for y in terms of x:

$$y = \frac{c_1}{a_{12}} - \frac{a_{11}x}{a_{12}} \tag{3.24}$$

We substitute this into the second equation to obtain the linear equation in x:

$$a_{21}x + a_{22}\left(\frac{c_1}{a_{12}} - \frac{a_{11}x}{a_{12}}\right) = c_2 \tag{3.25}$$
$$a_{21}x - a_{22}\frac{a_{11}x}{a_{12}} = c_2 - a_{22}\frac{c_1}{a_{12}}. \tag{3.26}$$

This contains only x and not y, so it can be solved for x to give the root

$$x = \frac{c_1a_{22} - c_2a_{12}}{a_{11}a_{22} - a_{12}a_{21}}. \tag{3.27}$$

This expression can be substituted into one of our original equations and solved for y to yield

$$y = \frac{c_2a_{11} - c_1a_{21}}{a_{11}a_{22} - a_{12}a_{21}}. \tag{3.28}$$

◄

EXERCISE 3.17 ► Do the algebraic manipulations to obtain the expression for y. ◄

The method of substitution is not limited to two equations and is not limited to linear equations. In the following example, we treat a nonlinear system of two equations:

EXAMPLE 3.14 In the study of the equilibrium of a weak acid in water, the ionization of the water is generally neglected. If we cannot do this, we have the equilibrium equation for the autoionization of water

$$K_w = \frac{[\mathrm{H}^+]}{c^\circ}\frac{[\mathrm{OH}^-]}{c^\circ}$$

where $[H^+]$ is the molar concentration of hydrogen ions, where $[OH^-]$ is the molar concentration of hydroxide ions and where K_w is the equilibrium constant, equal to 1.00×10^{-14} at 25 °C. We also have the equilibrium relation for the weak acid

$$K_a = \frac{([\mathrm{H}^+]/c^\circ)([\mathrm{A}^-]/c^\circ)}{[\mathrm{HA}]/c^\circ}$$

where [HA] is the molar concentration of the unionized acid and $[\mathrm{A}^-]$ is the molar concentration of the acid anion. We let c equal the *stoichiometric molar concentration* of the acid (the concentration that would occur if no ionization occurred). Use the method substitution to obtain a single equation in $[\mathrm{H}^+]$.

SOLUTION ► We let $x = [\mathrm{H}^+]/c^\circ$ and $y = [\mathrm{OH}^-]/c^\circ$. We have the relations

$$\begin{aligned} x &= y + [\mathrm{A}^-]/c^\circ \\ [\mathrm{HA}]/c^\circ &= c/c^\circ - [\mathrm{A}^-]/c^\circ = c/c^\circ - x + y \end{aligned}$$

so that we have the simultaneous equations

$$\begin{aligned} K_w &= xy \\ K_a &= \frac{x(x-y)}{c/c^\circ - x + y}, \end{aligned}$$

Solving the first equation for y in terms of x and substituting the result into the second equation yields the equation:

$$K_a = \frac{x(x - K_w/x)}{c/c^\circ - x + K_w/x}, \tag{3.29}$$

This equation can be multiplied out to yield the cubic equation that we discussed earlier in the chapter. ◄

EXERCISE 3.18 ► Solve the pair of simultaneous equations by the method of substitution:

$$x^2 - 2xy - x = 0 \tag{3.30}$$

$$\frac{1}{x} + \frac{1}{y} = 2. \tag{3.31}$$

Hint. Multiply the second equation by xy before proceeding. ◄

In the preceding exercise there are two solution sets, since the first equation is quadratic in x. When it is solved after substituting to eliminate y, two values of x are found to satisfy the equation, and there is a root in y for each of these. Nonlinear equations are more complicated than linear equations, so we consider only linear equations for the rest of this section.

The Method of Elimination

This method is used with linear equations. It applies the process of subtracting one equation from another to obtain a simpler equation. That is, the left-hand side of the first equation is subtracted from the left-hand side of the second equation and the right-hand side of the first equation is subtracted from the right-hand side of the second to yield a new equation that is simpler.

EXAMPLE 3.15 Solve the following pair of equations:

$$\begin{aligned} x + y &= 3 \\ 2x + y &= 0. \end{aligned}$$

SOLUTION ► We subtract the first equation from the second to obtain

$$x = -3.$$

This is substituted into either of the original equations to obtain

$$y = 6.$$

◄

If necessary to get a simpler equation, you can multiply one or both of the equations by constants before taking the difference, and it is possible to add the equations instead of subtracting.

EXERCISE 3.19 ► Solve the set of equations

$$\begin{aligned} 3x + 2y &= 40 \\ 2x - y &= 10. \end{aligned}$$

◄

Consistency and Independence in Simultaneous Equations

There are two common difficulties that can arise with pairs of simultaneous equations. These are (1) that the equations might be inconsistent, and (2) that the equations might not be independent. If two equations are *inconsistent*, there is no solution that can satisfy both of them, and if the equations are not *independent*, they express the same information, so that there is really only one equation, which can be solved for one variable in terms of the other but cannot be solved to give numerical values for both variables.

EXAMPLE 3.16 Show that the pair of equations is inconsistent:

$$\begin{aligned} 2x + 3y &= 15 \\ 4x + 6y &= 45 \end{aligned}$$

SOLUTION ► We attempt a solution by elimination. We multiply the first equation by 2 and subtract the second from the first, obtaining

$$0 = -15$$

which is obviously not correct. The equations are inconsistent. ◄

EXAMPLE 3.17 Show that the equations are not independent:

$$\begin{aligned} 3x + 4y &= 7 \\ 6x + 8y &= 14 \end{aligned}$$

SOLUTION ► We attempt a solution by elimination, multiplying the first equation by 2. However, this makes the two equations identical, so that if we subtract one from the other, we obtain

$$0 = 0$$

which is correct but not useful. We have just one independent equation instead of two, so that we could solve for x in terms of y or for y in terms of x, but not for numerical values of either x or y. If one equation becomes identical to the other when it is multiplied by any constant or function, the two equations are not independent. ◄

We can understand consistency and independence in simultaneous equations by looking at the graphs of the equations. Each of the equations represents y as a function of x. With linear equations, these functions are represented by straight lines. Figure 3.3 shows the two lines representing the two equations of Example 3.15. The two equations are consistent and independent, and the lines cross at the point

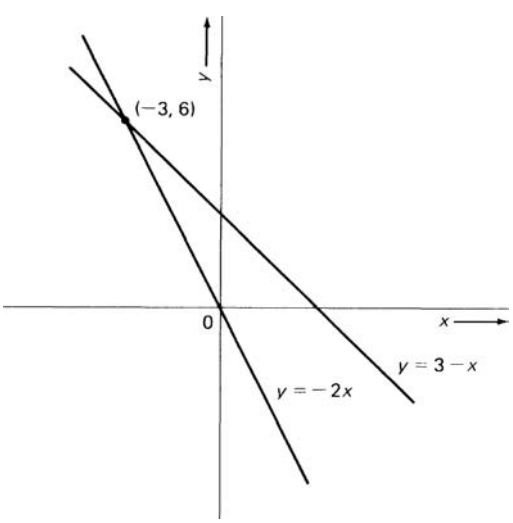

Figure 3.3 ► Graphical representation of the two consistent and linearly independent equations of Example 3.15.

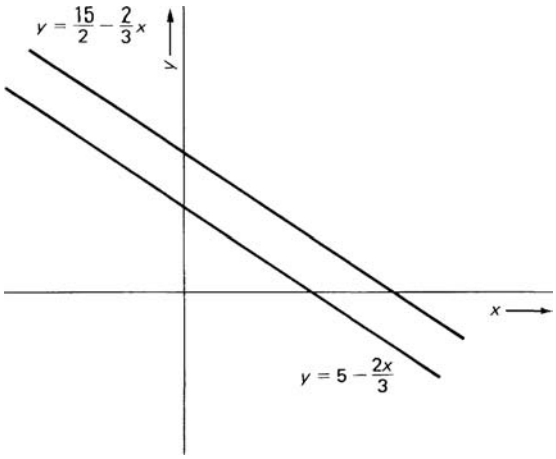

Figure 3.4 ► Graphical representation of two inconsistent equations of Example 3.16.

whose coordinates represent the solution set, consisting of a value of x and a value of y. Figure 3.4 shows the lines representing the two equations of Example 3.16. Since the lines do not cross, there is no solution to this pair of inconsistent equations. A single line represents both of the equations of Example 3.17. Any point on the line satisfies both equations, which are *linearly dependent*. Consistency and independence are more complicated when we have more than two equations, and we discuss this in a later chapter.

Homogeneous Linear Equations

The concept of linear dependence is important in the study of homogeneous linear equations. A pair of *homogeneous linear equations* is similar to those of Eq. (3.22) except that both c_1 and c_2 vanish. Consider the set of homogeneous linear equations:

$$a_{11}x + a_{12}y = 0 \tag{3.32a}$$
$$a_{21}x + a_{22}y = 0 \tag{3.32b}$$

We solve both of these equations for y in terms of x:

$$y = \frac{-a_{11}x}{a_{12}} \tag{3.32c}$$
$$y = \frac{-a_{21}x}{a_{22}} \tag{3.32d}$$

Both of these functions are represented by straight lines with zero intercept. There are two possibilities: Either the lines cross at the origin or they coincide everywhere. In other words, either $x = 0$, $y = 0$ is the solution, or else the equations are linearly dependent (are the same equation). The solution $x = 0$, $y = 0$ is called a *trivial solution*. The two equations must be linearly dependent in order for a nontrivial solution to exist. A nontrivial solution consists of specifying y as a function of x, not in finding constant values for both x and y, since there is really only one independent equation.

EXERCISE 3.20 ► Determine whether the set of equations has a nontrivial solution, and find the solution if it exists:

$$\begin{aligned} 7x + 15y &= 0 \\ 101x + 195y &= 0 \end{aligned}$$

◄

We will return to the discussion of simultaneous equations in Chapter 10.

Using Mathematica to Solve Simultaneous Equations

The Solve statement can also be used to solve simultaneous equations as well as single equations. The equations are typed inside curly brackets with commas between them, and the variables are listed inside curly brackets. To solve the equations

$$ax + by = c \tag{3.33}$$
$$gx + hy = k \tag{3.34}$$

we type the input entry

In[1]:=**Solve[{a∗x + b∗y == c, g∗x + h∗y == k},{x,y}]**

Blank spaces could be used instead of the asterisks to denote multiplication. Notice the use of braces to notify Mathematica that we have a list of two equations to be solved. The two variables to be solved for must be included inside curly brackets (braces). The output is

$$\text{Out[1]} = \{\{x \to -\frac{-c\,h + b\,k}{-b\,g + a\,h}, y \to -\frac{-c\,g + a\,k}{b\,g - a\,h}\}\}$$

which is the expression obtained from Cramer's rule. If numerical values for the coefficients are specified, Mathematica will give the numerical solution set.

EXERCISE 3.21 ► Use Mathematica to solve the simultaneous equations

$$\begin{aligned} 2x + 3y &= 13 \\ x - 4y &= -10 \end{aligned} \tag{3.35}$$

◄

The *Eliminate statement* is used to eliminate one or more of the variables in a set of simultaneous equations. For example, to obtain a single equation in x from the set of equations above, you would type the input entry (note the double equal signs):

```
Eliminate[{a x + b y == c, g x + h y == k},y]
```

and would receive the output:

```
Out[1]=b k – b g x + a h x == c h
```

we solve this equation for x by typing

```
Solve[%,x]
```

and receive the output

Out[2]={{$x \to \frac{-c\,h + b\,k}{b\,g - a\,h}$}}

SUMMARY

This chapter has dealt with solving algebraic equations. For a single equation in a single unknown, x, this means finding a value of x or a set of values of x that makes the equation into a correct numerical equation. We have discussed algebraic procedures for finding a solution, as well schemes for finding approximate solutions. If an equation cannot easily be solved, the equation itself can be approximated by neglecting terms that are small compared with other terms or by linearization. Graphical methods and numerical methods can be used to find numerical approximations to solutions. Simultaneous equations in two variables were discussed. If two equations in two unknowns are consistent and are independent, they can be solved for numerical values of the two unknowns. Linear dependence and inconsistency were discussed. The use of Excel and Mathematica to solve equations was introduced.

PROBLEMS

1. Solve the quadratic equations:

a) $x^2 - 3x + 2 = 0$

b) $x^2 - 1 = 0$

c) $x^2 + 2x + 2 = 0$

2. Solve the following equations by factoring:

a) $4x^4 - 4x^2 - x - 1 = 0$

b) $x^3 + x^2 - x - 1 = 0$

c) $x^4 - 1 = 0$

3. Find the real roots of the following equations by graphing:

a) $x^3 - x^2 + x - 1 = 0$

b) $e^{-x} - 0.5x = 0$

c) $\sin(x)/x - 0.75 = 0$

a) Using Excel, make a properly labeled graph of the function $y(x) = \ln(x) + \cos(x)$ for values of x from 0 to 2π, at intervals of $\pi/100$.

b) Repeat part a using Mathematica.

4. When expressed in terms of "reduced variables" the van der Waals equation of state is

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8T_r}{3} \tag{3.36}$$

a) Using Excel, construct a graph containing three curves of P_r as a function of V_r: one for $T_r = 0.8$, one for $T_r = 1$, and one for $T_r = 1.2$. Specify the range $0.4 < V_r < 2$.

b) Repeat part a using Mathematica.

5. The following data were taken for the thermal decomposition of N_2O_3:

t/ s	0	184	426	867	1877
$[N_2O_3]$/ mol l^{-1}	2.33	2.08	1.67	1.36	0.72

Using Excel, make three graphs: one with $\ln([N_2O_3])$ as a function of t, one with $1/[N_2O_3]$ as a function of t, and one with $1/[N_2O_3]^2$ as a function of t. Determine which graph is most nearly linear. If the first graph is most nearly linear, the reaction is first order; if the second graph is most nearly linear, the reaction is second order, and if the third graph is most nearly linear, the reaction is third order.

6. Write an Excel worksheet that will convert a list of distance measurements in meters to miles, feet, and inches. If the length in meters is typed into a cell in column A, let the corresponding length in miles appear on the same line in column B, the length in feet in column C, and the length in inches in column C.

7. The van der Waals equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{3.37}$$

where a and b are temperature-independent parameters that have different values for each gas. For carbon dioxide, $a = 0.3640\,\text{Pa}\,\text{m}^6\,\text{mol}^{-2}$ and $b = 4.267 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$.

a) Write this equation as a cubic equation in V.

b) Use the Solve statement in Mathematica to obtain a symbolic solution to the cubic equation. How would you decide which root is the one you want?

c) Use the NSolve statement in Mathematica to find the volume of 1.000 mol of carbon dioxide at $P = 1.000$ bar (100000 Pa) and $T = 298.15$ K. Notice that two of the three roots are complex, and must be ignored. Compare your result with the prediction of the ideal gas equation of state.

d) Use the FindRoot statement in Mathematica to find the real root in part c.

e) Repeat part c for $P = 10.000$ bar (1.0000×10^6 Pa) and $T = 298.15$ K. Compare your result with the prediction of the ideal gas equation of state.

f) Repeat part c for $P = 100.000$ bar (1.0000×10^7 Pa) and $T = 298.15$ K. Compare your result with the prediction of the ideal gas equation of state.

g) Make graphs showing the pressure of 1.000 mol of carbon dioxide as a function of the volume for several different temperatures. You can use the statement

```
PlotRange->{ymin,ymax}
```

as part of your Plot statement (separate it by commas) to adjust the vertical axis. Note that the symbol -> is typed with two strokes, with - and > separately typed.

h) Change variables to measure volumes in liters and pressures in atmospheres. Repeat parts a–e. Remember to change the value of R to $0.08206\,\mathrm{l\,atm\,K^{-1}\,mol^{-1}}$.

8. An approximate equation for the ionization of a weak acid, including consideration of the hydrogen ions from water is[2]

$$[\mathrm{H}^+]/c^\circ = \sqrt{K_a c/c^\circ + K_w},$$

where c is stoichiometric acid concentration. This equation is based on the assumption that the concentration of unionized acid is approximately equal to stoichiometric acid concentration. Consider a solution of HCN (hydrocyanic acid) with stoichiometric acid concentration equal to $1.00 \times 10^{-5}\,\mathrm{mol\ l^{-1}}$. $K_a = 4 \times 10^{-10}$ for HC_1N.

a) Calculate $[\mathrm{H}^+]$ using this equation.

b) Calculate $[\mathrm{H}^+]$ using Eq. (3.9) and the method of bisection.

c) Calculate $[\mathrm{H}^+]$ using Eq. (3.11). Comment on your answers.

9. Find the smallest positive root of the equation.

$$\sinh(x) - x^2 - x = 0.$$

10. Solve the cubic equation by trial and error, factoring, or by using Mathematica or Excel:

$$x^3 + x^2 - 4x - 4 = 0 \tag{3.38}$$

11. Find the real root of the equation

$$x^2 = e^{-x} \tag{3.39}$$

12. Find the root of the equation

$$x = 2\sin(x) \tag{3.40}$$

13. Find two positive roots of the equation

$$\ln(x) - 0.200x = 0 \tag{3.41}$$

14. Find the real roots of the equation

$$10x^2 - 2 = \tan(x) \tag{3.42}$$

15. In the theory of blackbody radiation, the following equation

$$x = 5(1 - e^{-x}) \tag{3.43}$$

needs to be solved to find the wavelength of maximum spectral radiant emittance. The variable x is

$$x = \frac{hc}{\lambda_{\max} k_B T} \tag{3.44}$$

[2]Henry F. Holtzclaw, Jr, William R. Robinson, and Jerone D. Odom, *General Chemistry*, 9th ed., p. 545, Heath, Lexington, MA, 1991.

where $\lambda_{\max}$ is the wavelength of maximum spectral radiant emittance, h is Planck's constant, c is the speed of light, k_B is Boltzmann's constant, and T is the absolute temperature. Solve the equation numerically for a value of x. Find the value of $\lambda_{\max}$ for $T = 6600\,\text{K}$. In what region of the electromagnetic spectrum does this value lie?

16. Solve the simultaneous equations by hand, using the method of substitution:

$$x^2 + x + 3y = 15 \tag{3.45}$$
$$3x + 4y = 18 \tag{3.46}$$

Use Mathematica to check your result. Since the first equation is a quadratic equation, there will be two solution sets.

17. Stirling's approximation for $\ln(N!)$ is

$$\ln(N!) \approx \frac{1}{2}\ln(2\pi N) + N\ln(N) - N \tag{3.47}$$

a) Determine the validity of this approximation and of the less accurate version

$$\ln(N!) \approx N\ln(N) - N \tag{3.48}$$

for several values of N up to $N = 100$. Use a calculator, Excel, or Mathematica.

b) Use Mathematica for values of N up to 2000.

18. The Dieterici equation of state is

$$P e^{a/V_m RT}(V_m - b) = RT, \tag{3.49}$$

where P is the pressure, T is the temperature, V_m is the molar volume, and R is the ideal gas constant. The constant parameters a and b have different values for different gases. For carbon dioxide, $a = 0.468\ \text{Pa m}^6\ \text{mol}^{-2}$, $b = 4.63 \times 10^{-5}\text{m}^3\ \text{mol}^{-1}$. Without linearization, find the molar volume of carbon dioxide if $T = 298.15\,\text{K}$ and $P = 10.000\,\text{atm} = 1.01325 \times 10^6\,\text{Pa}$. Use the FindRoot statement in Mathematica, Excel, or trial and error.

19. Determine which, if any, of the following sets of equations are inconsistent or linearly dependent. Draw a graph for each set of equations, showing both equations. Find the solution for any set that has a unique solution.

a)
$$x + 3y = 4$$
$$2x + 6y = 8$$

b)
$$2x + 4y = 24$$
$$x + 2y = 8$$

c)
$$3x_1 + 4x_2 = 10$$
$$4x_1 - 2x_2 = 6$$

20. Solve the set of equations using Mathematica or by hand with the method of substitution:

$$x^2 - 2xy + y^2 = 0$$
$$2x + 3y = 5$$

4

Mathematical Functions and Differential Calculus

Preview

In this chapter we discuss the concept of a mathematical function and its relationship to the behavior of physical variables. We define the derivative of a function of one independent variable and discuss its geometric interpretation. We discuss the use of derivatives in approximate calculations of changes in dependent variables and describe their use in finding minimum and maximum values of functions.

Principal Facts and Ideas

1. A mathematical function of one variable is a rule for obtaining a value of a dependent variable that corresponds to any value of an independent variable.

2. The derivative of a function is a measure of how rapidly the dependent variable changes with changes in the value of the independent variable. If Δy is the change in the dependent variable produced by a change Δx in the independent variable, then the derivative dy/dx is defined by

$$\frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{\Delta y}{\Delta x}.$$

3. The derivatives of many simple functions can be obtained by applying a few simple rules, either separately or in combination.

4. A finite increment in a dependent variable, Δy, can sometimes be calculated approximately by use of the formula

$$\Delta y \approx \frac{dy}{dx} \Delta x.$$

5. Differential calculus can be used to find maximum and minimum values of a function. A relative minimum or maximum value of a variable y which depends on x is found at a point where $dy/dx = 0$.

Objectives

After studying this chapter, you should:

1. understand the concept of a mathematical function;
2. be able to obtain a formula for the derivative of any fairly simple function without consulting a table;
3. be able to draw a rough graph of any fairly simple function and locate important features on the graph;
4. be able to find maximum and minimum values of a function of one variable.

4.1 Mathematical Functions

In Chapter 2 we introduced trigonometric functions, the logarithm function and the exponential function. We now revisit the concept of a function. Mathematical functions are useful in thermodynamics because thermodynamic variables behave exactly like mathematical functions, with some variables acting as independent variables and others as dependent variables. They are useful in quantum mechanics because all information about the state of a system is contained in a mathematical function called a wave function or state function.

One definition of a mathematical function of one variable is that it is a rule for generating a set of *ordered pairs* of numbers. This means, for example, that if you have a table with two columns of numbers in it, each number in the first column is associated with the number on the same line the other column. The choice of a number in the first column delivers a unique value from the second column. For example, thermodynamics implies that the temperature is a function of the pressure or that the pressure is a function of the temperature in a system with a single substance and two phases. A physical chemistry student might measure the vapor pressure of liquid ethanol (the pressure of a system containing only liquid ethanol and gaseous ethanol) at ten different temperatures. The student could present the results in a table. In the first column, the student puts the values of the temperature, and on the same line in the second column he or she puts the observed vapor pressure for that temperature.

Let us choose the temperature to be the *independent variable*. The vapor pressure is then the *dependent variable*. This means that if we choose a value of the temperature, the function provides the corresponding value of the vapor pressure. This is the important property of a function. It is as though the function says, "You give me a value for the independent variable, and I'll give you the corresponding value of the dependent variable." In this case, we could have chosen the temperature as the dependent variable and the pressure as the independent variable. There are also functions with more than one independent variable. In this case, a value must be specified for each of the independent variables in order for the function

to deliver a value of the dependent variable. We discuss this kind of function in Chapter 7.

A two-column table of numerical values is of course not the only way to represent a mathematical function of a single independent variable. Any rule that delivers a value of a dependent variable when a value of an independent variable is specified is a representation of a mathematical function. Two common representations of functions are mathematical formulas and graphs.

Properties of Functions Representing Physical Variables

We make the following assumptions about the behavior of physical systems:

1. Of the macroscopic variables such as temperature, pressure, volume, density, entropy, energy, and so on, only a certain number (depending on circumstances) can be independent variables. The others are dependent variables, governed by mathematical functions.

2. These mathematical functions are single-valued, except possibly at isolated points. This means that only one value of the dependent variable occurs for a given value of the independent variable.

3. These mathematical functions are continuous and differentiable, except possibly at isolated points. We will discuss later what this statement means.

Although a list of several temperatures and the corresponding several values of the vapor pressure qualifies as a mathematical function, such a function is not useful for other temperatures. We need a representation of the function that will provide a value of the vapor pressure for other temperatures. Although mathematicians frequently have exact representations of their functions, approximate representations of a function must generally be used in physical chemistry. These representations include interpolation between values in a table, use of an approximate curve in a graph, and approximate mathematical formulas. In all these approximate representations of a function we hope to make our rule for generating new values give nearly the same values as the correct function.

We assume that the exact representation of a function describing a property of a physical system is nearly always *single-valued*. A single-valued function delivers one and only one value of the dependent variable for any given value of the dependent variable. In discussing real functions of real variables, mathematicians will usually not call something a function unless it is single-valued. We also assume that a function describing a property of a physical system is nearly always *continuous*. If a function is continuous, the dependent variable does not change abruptly if the independent variable changes gradually. If you are drawing a graph of a continuous function, you will not have to draw a vertical step in your curve or take your pencil away from the paper. We define continuity in terms of mathematical limits. We say that a function $f(x)$ is continuous at $x = a$ if

$$\lim_{x \to a^+} f(x) = \lim_{x \to a^-} f(x) = f(a). \tag{4.1}$$

If the function is continuous at $x = a$, as x draws close to a from either direction, $f(x)$ smoothly draws close to $f(a)$, the value that the function has at $x = a$. If $f(x)$ approaches a different value if x approaches a from the positive side than it

does if it approaches from the negative side, the function is discontinuous at $x = a$. If $f(x)$ approaches one finite value when x approaches a from the positive side and a different finite value when x approaches a from the negative side, we say that the function has a *finite jump discontinuity*. Finite jump discontinuities are sometimes called *ordinary discontinuities*. In some cases, a function that is discontinuous at $x = a$ becomes larger and larger in magnitude without bound (diverges) as x approaches a. For example, consider the tangent function, which becomes larger and larger in the positive direction if its argument (measured in radians) approaches $\pi/2$ from the negative side. It becomes larger and larger in magnitude in the negative direction if its argument approaches $\pi/2$ from the positive direction. Some other functions can diverge in the same direction when the argument of the function approaches some value from either direction. For example, the function $1/x^2$ diverges in the positive direction as x approaches zero from either direction.

Some functions that represent physical variables are continuous over the entire range of values of the independent variable. In other cases, they are *piecewise continuous*. That is, they are continuous except at a number of isolated points, at which discontinuities in the function occur. Figure 4.1 shows schematically the density of a pure substance as a function of temperature at fixed pressure. The density is piecewise continuous. There is a large finite step discontinuity in the density at the boiling temperature, T_b, and a smaller finite step discontinuity at the freezing temperature, T_f. If T is made to approach T_f from the positive side the density smoothly approaches the density of the liquid at T_f. If T is made to approach T_f from the negative side the density smoothly approaches the density of the solid at this temperature. The system can exist either as a solid or as a liquid at the freezing temperature T_f, or the two phases can coexist, each having a different value of the density. The function representing the density is not single-valued at the freezing temperature. A similar situation occurs at the boiling temperature T_b. At this temperature the liquid and gas phases can coexist.

If a mathematician wants to discuss a function of a variable x, he or she would write

$$y = f(x), \tag{4.2}$$

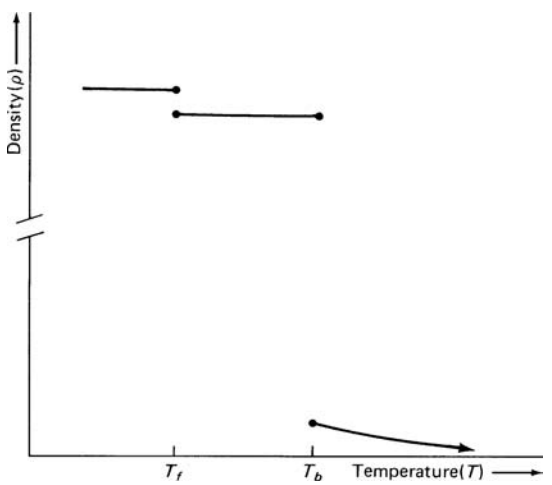

Figure 4.1 ► The density of a pure substance as a function of temperature (schematic).

using the letter y to represent the dependent variable and the letter f to represent the function that provides values of y. We will follow a different policy, writing for example for the density as a function of temperature

$$\rho = \rho(T), \tag{4.3}$$

where the letter ρ stands both for the density and for the function that provides values of the density. The main reason for this policy is that we have a lot of variables to discuss and only a limited supply of letters.

Graphical Representations of Functions

One way to communicate quickly the general behavior of a function is with a graph. A rough graph can quickly show the general behavior of a dependent variable. An accurate graph can be read to provide good approximate values of the dependent variable for specific values of the independent variable. A graph containing data points and a curve drawn through or near the points can also reveal the presence of an inaccurate data point.

EXERCISE 4.1 ▶ The following is a set of data for the vapor pressure of ethanol. Plot these points by hand on graph paper, with the temperature on the horizontal axis (the *abscissa*) and the vapor pressure on the vertical axis (the *ordinate*). Decide if there are any bad data points. Draw a smooth curve nearly through the points, disregarding any bad points. Use Excel to construct another graph and notice how much work the spreadsheet saves you.

Temperature/°C	**Vapor pressure/torr**
25.00	55.9
30.00	70.0
35.00	97.0
40.00	117.5
45.00	154.1
50.00	190.7
55.00	241.9

◀

Important Families of Functions

There are a number of important families of functions that occur frequently in physical chemistry. A *family of functions* is a set of related functions. A family of functions is frequently represented by a single formula that contains other symbols besides the one for the independent variable. These quantities are sometimes called *parameters*. The choice of a set of values for these quantities specifies which member of the family of functions is meant.

Linear Functions

The following formula represents the family of linear functions:

$$y = mx + b \tag{4.4}$$

This is a family of *linear functions* or *first-degree polynomials*. In this family, we have a different function for each set of values of the parameters m and b. The graph of each such function is a straight line, so Eq. (4.4) represents a family of different straight lines. The constant b is called the *intercept*. It equals the value of the function for $x = 0$. The constant m is called the *slope*. It gives the steepness of the line, or the relative rate at which the dependent variable changes as the independent variable varies.

Figure 4.2 shows two particular values of x, called x_1 and x_2, and their corresponding values of y, called y_1 and y_2. A line is drawn through the two points. If $m > 0$, then $y_2 > y_1$ and the line slopes upward to the right. If $m < 0$, then $y_2 < y_1$ and the line slopes downward to the right.

EXAMPLE 4.1 For a linear function let y_1 be the value of y corresponding to $x_1$and y_2 be the value of y corresponding to x_2. Show that the slope is given by

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\Delta y}{\Delta x}. \tag{4.5}$$

where we introduce the common notation for a difference:

$$\Delta x = x_2 - x_1 \tag{4.6}$$

$$\Delta y = y_2 - y_1 \tag{4.7}$$

SOLUTION ►

$$y_2 - y_1 = mx_2 + b - (mx_1 + b) = m(x_2 - x_1)$$

or

$$m = \frac{y_2 - y_1}{x_2 - x_1}.$$

◄

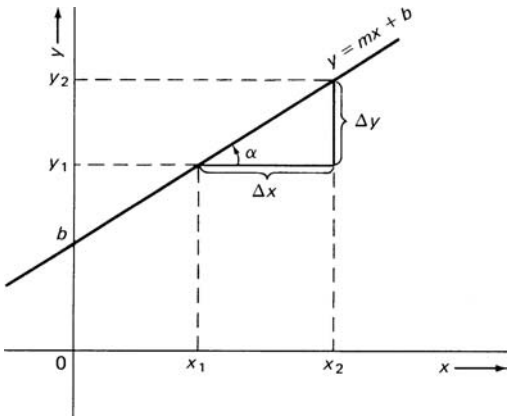

Figure 4.2 ► The graph of the linear function $y = mx + b$.

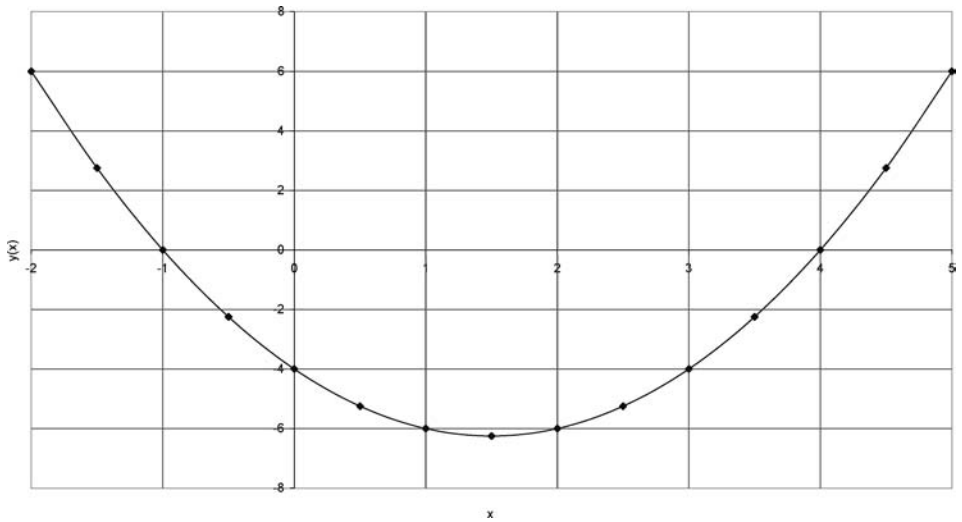

Figure 4.3 ► Graph of the quadratic function $y = x^2 - 3x - 4$.

Another important property of the slope is that the slope is the tangent of the angle between the horizontal axis and the straight line representing the function

$$m = \tan(\alpha). \tag{4.8}$$

The angle α is taken to lie between $-90°$ and $90°$ and the slope can range from $-\infty$ to ∞.

Quadratic Functions

Another important family of functions is the *quadratic function* or *second-degree polynomial*:

$$y = ax^2 + bx + c. \tag{4.9}$$

The graph of a function from this family is a *parabola*. Figure 4.3 depicts the parabola representing the function

$$y(x) = x^2 - 3x - 4 \tag{4.10}$$

Notice that the parabola rapidly rises on both sides of the minimum.

Trigonometric Functions

There are several families of trigonometric functions. We have already discussed them in Chapter 2. You should be familiar with the graphs of the trigonometric functions that are shown in Figs. 2.2 through 2.4.

Exponential and Logarithmic Functions

We have also discussed these two families of functions in Chapter 2. You should be familiar with their properties. An important property of the exponential function

is that it increases very rapidly for large values of its independent variable. An important property of the logarithm function is that is increases only very slowly for large values of its independent variable.

Gaussian Functions

Another important family of functions is the family of *Gaussian functions*, named for Karl Friedrich Gauss (1777–1855), a great German mathematician. A Gaussian function is represented by the formula

$$y = ce^{-(x-\mu)^2/2\sigma^2}. \tag{4.11}$$

The constant c can be given a specific value to achieve *normalization*, which we discuss later. The constant μ is called the *mean*, and the constant σ is called the *standard deviation* and is a measure of the width of the "hump" in the curve. The graph of this function shown in Fig. 4.4 corresponds to $\mu = 0$. The curve in this graph is sometimes called a *bell-curve*.

This function is proportional to the probability that a value of x will occur in a number of statistical applications and is discussed in Chapter 11.

Generating Approximate Graphs

A graph that represents a function is useful in helping us to visualize the behavior of the function, even if it is only a rough graph. Sketching a rough graph of a function is often useful in understanding the function. The families of functions that we have listed form a repertoire of functions that you can use to generate approximate graphs of functions that are products of other functions. To do this, you need to recognize the factors as members of the families that we have studied and to figure out what a graph of the product of the factors will be like from graphs of the factors. The two most important facts are that if any of the factors vanishes, the product vanishes and that if either factor diverges (becomes infinite) the product diverges.

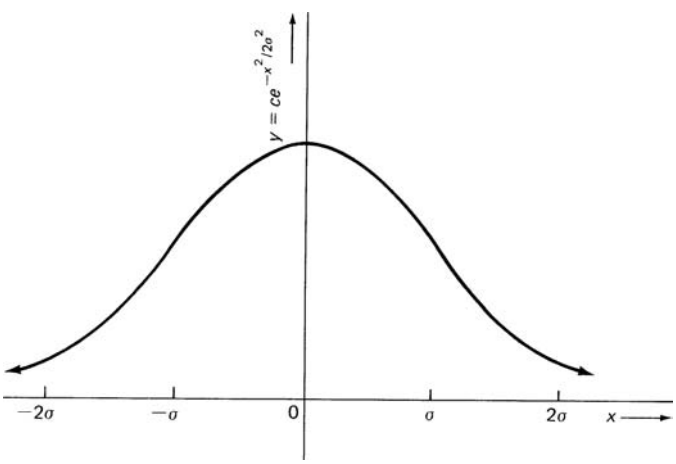

Figure 4.4 ► The graph of the Gaussian function.

EXAMPLE 4.2 Sketch a rough graph of the function

$$y = x\cos(\pi x)$$

SOLUTION ► This function is a product of the function x, which is shown in Fig. 4.5a, and the function $\cos(\pi x)$, which is shown in Fig. 4.5b. The desired rough graph can be constructed by inspection of the graphs of the two factors. The first thing to do is to find where the function vanishes, using that fact that if either factor vanishes, the product vanishes. The factor x vanishes at the origin and the factor $\cos(x)$ vanishes when $x = \frac{\pi}{2}, \frac{3\pi}{2}$, and so on. Since the cosine oscillates between -1 and $+1$, the product oscillates between x and $+x$. A rough graph of the product is shown in Fig. 4.4c. ◄

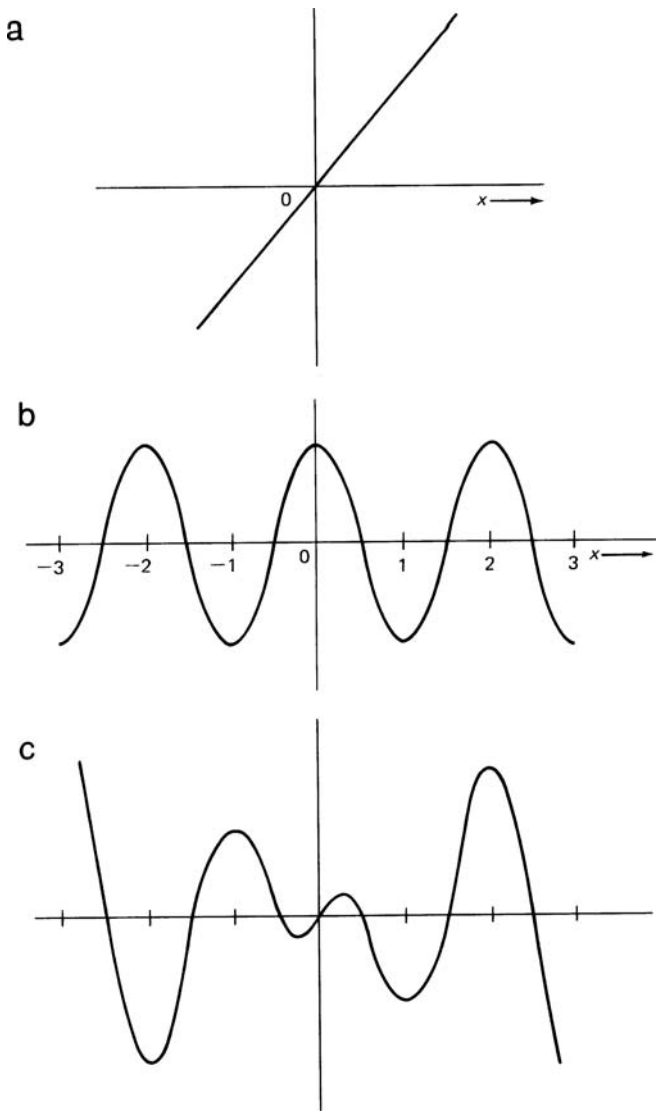

Figure 4.5 ► (a) The first factor in the function of Example 4.2. (b) The second factor in the function of Example 4.2. (c) The function of Example 4.2.

EXERCISE 4.2 ► Sketch rough graphs of the following functions. Verify your graphs using Excel or Mathematica if possible.

(a) $e^{-x}\sin(x)$ (b) $\sin^2(x) = \sin(x)^2$

(c) $x^2 e^{-x/2}$ (d) $1/x^2$

(e) $(1-x)\,e^{-x}$ (f) xe^{-x^2}

◄

4.2 The Tangent Line and the Derivative of a Function

A function other than a linear function has a graph with a curve other than a straight line. Such a curve has a different direction (different steepness) at different points on the curve.

The Line Tangent to a Curve

Consider the graph of some nonlinear function of x, as is shown in Fig. 4.6. The figure also shows the line that is tangent to the curve representing the function at $x = x_1$. At most points on such a curve, the tangent to the curve at that point is the line that has the point in common with the curve but does not cross it at that point, as shown in Fig. 4.6. There are points called inflection points at which the tangent line does cross the curve, and we will discuss them later. We can say that the curve at $x = x_1$ has the same direction as the tangent line at that point.

If the tangent line is represented by the formula

$$y = mx + b,$$

then the slope of the tangent line is equal to m. In the figure, we have labeled another point at $x = x_2$. In addition to the tangent line, the figure includes a horizontal line intersecting the curve at $x = x_1$. At $x = x_2$, the vertical distance

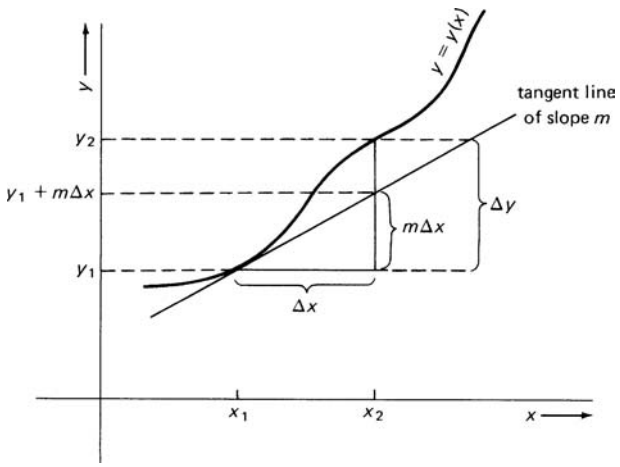

Figure 4.6 ► The curve representing the function $y = y(x)$ and its tangent line.

from the horizontal line to the tangent line is given by $m(x_2 - x_1) = m\Delta x$, where

$$\Delta x = x_2 - x_1$$

The distance $m\Delta x$ is not necessarily equal to the distance from the horizontal line to the curve, which is given by

$$y\,(x_2) - y\,(x_1) = y_2 - y_1 = \Delta y.$$

EXERCISE 4.3 ▶ Using graph paper plot the curve representing $y = \sin(x)$ for values of x lying between 0 and $\pi/2$ radians. Using a ruler, draw the tangent line at $x = \pi/4$. By drawing a right triangle on your graph and measuring its sides, find the slope of the tangent line. ◀

There is a case in which the definition of the tangent line to a curve at a point x_1 is more complicated than in the case shown in Fig. 4.6. In this case, the point x_1 lies between a region in which the curve is concave downward and a region in which the curve is concave upward. Such a point is called an *inflection point*. For such a point, we must consider tangent lines at points that are taken closer and closer to x_1. As we approach closer and closer to x_1 from either direction, the tangent line will approach more and more closely to a line that is the tangent line at x_1. This line does cross the curve at the point that it shares with the curve.

The Derivative of a Function

The *derivative of a function* is a quantity that represents the rate of change of a function and the steepness of the curve in a graph representing the function. Consider a nonlinear function $y = y(x)$. We have already asserted that Δy is not necessarily equal to $m\,\Delta x$, where m is the slope of the tangent to the curve. However, if Δx is not too large, we can write as an approximation

$$\Delta y \approx m\,\Delta x. \tag{4.12}$$

We divide both sides of Eq. (4.12) by Δx and write

$$m \approx \frac{\Delta y}{\Delta x} = \frac{y\,(x_2) - y\,(x_1)}{x_2 - x_1} = \frac{y_2 - y_1}{x_2 - x_1}. \tag{4.13}$$

If the curve is smooth, this equation becomes a better and better approximation as Δx becomes smaller, and if we take the mathematical limit as $\Delta x \to 0$, it becomes exact:

$$\boxed{m = \lim_{x_2 \to x_1} \frac{y(x_2) - y(x_1)}{x_2 - x_1}}. \tag{4.14}$$

DEFINITION ♦ If the limit in Eq. (4.14) exists and has the same value when x_2 approaches x_1 from either side, it is called the *derivative* of the function at $x = x_1$. If the derivative exists, it is equal to the slope of the tangent line at the given point. The derivative is denoted by the symbol dy/dx. The symbol y' is also used. ♦

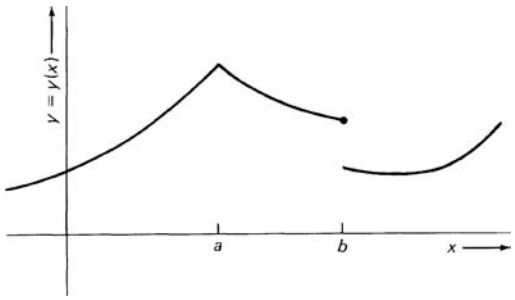

Figure 4.7 ► A function that is not differentiable at $x = a$ and at $y = b$.

The symbol y' has the advantage that the value of x at which the derivative is evaluated can easily be specified. If the derivative is to be evaluated at x_1, we would write $y'(x_1)$. The value of x at which dy/dx is to be evaluated can be denoted by a subscript, as in $(dy/dx)_{x_1}$. The symbol (dy/dx) resembles a fraction, but you should remember that a derivative is *not* a fraction. It is a limit that a fraction approaches. It is not permissible to cancel what looks like a numerator or a denominator against another factor.

If the limit in Eq. 4.14 does not exist, the function is not *differentiable* and its derivative does not exist at $x = x_1$. If $y(x)$ has a discontinuity at $x = x_1$, the limit does not exist at that point and a function is not differentiable at that point. A function is also not differentiable at a *cusp*, which corresponds to a "corner" or abrupt change in direction of a curve representing a function. At a cusp the function is continuous, but the tangent to the curve has different values on the two sides of the cusp. If the function has a cusp at $x = x_1$, the limit has a different value if $x_2 > x_1$ than it does if $x_2 < x_1$.

Figure 4.7 shows the graph of a function that is discontinuous at $x = b$ and has a cusp at $x = a$ and is not differentiable at these points, although it is differentiable elsewhere in the region shown in the graph.

EXAMPLE 4.3 Decide where the following functions are differentiable and where they are not differentiable:

(a) $y = |x|$ (b) $y = \sqrt{x}$.

SOLUTION ► (a) Differentiable everywhere except at $x = 0$, where there is a cusp. The limit has different values when $x = 0$ is approached from the two different directions.

(b) This function has real values for $x \geq 0$. It is differentiable for all positive values of x, but the limit does not exist at $x = 0$, so it is not differentiable at $x = 0$. The tangent to the curve at $x = 0$ is vertical.

◄

EXERCISE 4.4 ► Decide where the following functions are differentiable.

(a) $y = \frac{1}{1-x}$ (b) $y = x + 2\sqrt{x}$

(c) $y = \tan(x)$

◄

Derivatives of Specific Functions

Now that we have defined the derivative, we can see how derivatives of particular functions are found by using the definition of the derivative.

EXAMPLE 4.4 Find the derivative of the function

$$y = y(x) = ax^2.$$

SOLUTION ►

$$\begin{aligned}
\Delta y &= y(x_2) - y(x_1) = y_2 - y_1 = ax_2^2 - ax_1^2 = a\,(x_1 + \Delta x)^2 - ax_1^2 \\
&= a\left[x_1^2 + 2x_1\Delta x + (\Delta x)^2\right] - ax_1^2 \\
&= 2ax_1\Delta x + (\Delta x)^2 \\
\frac{\Delta y}{\Delta x} &= 2ax_1 + \Delta x.
\end{aligned}$$

We now take the limit as $x_2 \to x_1$ ($\Delta x \to 0$). The first term, $2ax_1$ is not affected. The second term, Δx, vanishes. Thus, if we use the symbol x instead of x_1

$$\frac{d\left(ax^2\right)}{dx} = \lim_{\Delta x \to 0} \frac{\Delta y}{\Delta x} = 2ax. \tag{4.15}$$

◄

Figure 4.8 shows a graph of the function $y = ax^2$ and a graph of its derivative, $dy/dx = 2ax$.

This graph exhibits some important general characteristics of derivatives:

1. Where the function has a horizontal tangent line, the derivative is equal to zero.
2. The derivative is positive in regions where the function increases as x increases.
3. A positive derivative is larger when the tangent line is steeper.
4. The derivative is negative where the function decreases as x increases, as it does in this example for negative values of x.

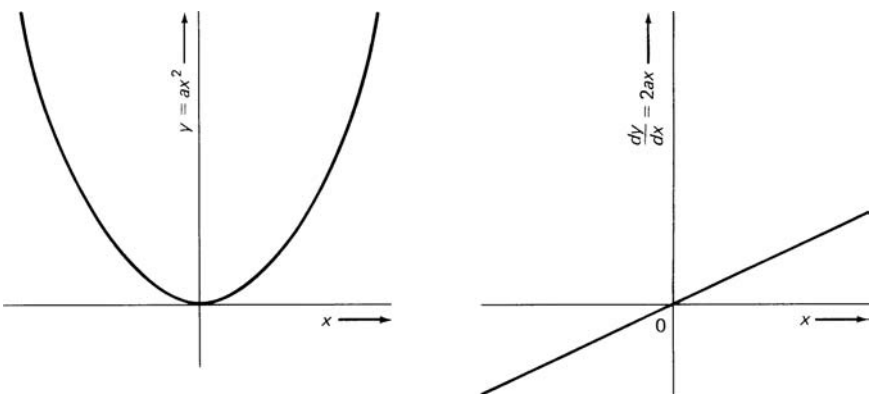

Figure 4.8 ► A graph of a function and its derivative.

5. A negative derivative is more negative (has a larger magnitude) when the tangent line is steeper.

The derivative of any differentiable function can be obtained by using the definition of the derivative.

EXERCISE 4.5 ► Show that the derivative of $ay(x)$ is equal to $a\,dy/dx$ where $y(x)$ is a differentiable function of x and where a is a constant. ◄

EXERCISE 4.6 ► The exponential function can be represented by the following power series

$$e^{bx} = 1 + bx + \frac{1}{2!}b^2x^2 + \frac{1}{3!}b^3x^3 + ... + \frac{1}{n!}b^nx^n ...,$$

where the ellipsis $(\cdots)$ indicates that additional terms follow. The notation $n!$ stands for *n factorial,* which is defined to equal $n\,(n-1)\,(n-2)\,...(3)(2)(1)$. Use this representation to derive the expression for the derivative of e^{bx}. ◄

Table 4.1 gives the derivatives of some simple functions, derived in much the same way as Eq. (4.15). Additional derivatives are given in Appendix D.

TABLE 4.1 ► Some Elementary Functions and Their Derivatives.*

Function, $y = y(x)$	**Derivative**, $dy/dx = y'(x)$
ax^n	nax^{n-1}
ae^{bx}	abe^{bx}
a	0
$a \sin(bx)$	$ab \cos(x)$
$a \cos(bx)$	$-ab \sin(bx)$
$a \ln(x)$	a/x

*In these formulas, a, b, and n are constants. not necessarily integers.

The derivative of a function is the rate of change of the dependent variable with respect to the independent variable. Because it is the slope of the tangent line, it has a large magnitude when the curve is steep and a small magnitude when the curve is nearly horizontal.

EXERCISE 4.7 ► Make rough graphs of several functions from Table 4.1. Below each graph, on the same sheet of paper, make a rough graph of the derivative of the same function. ◄

4.3 Differentials

In Section 4.2, we talked about a change in a dependent variable produced by a change in an independent variable. If y is a function of x, we wrote in Eq. (4.12)

$$\Delta y \approx m\,\Delta x, \tag{4.16}$$

where $\Delta x = y(x_2) - y(x_1)$, $\Delta x = x_2 - x_1$, and m was the slope of the tangent line at $x = x_1$. Using Eq. (4.14) this becomes

$$\Delta y \approx \left(\frac{dy}{dx}\right)\Delta x. \tag{4.17}$$

This approximate equality will generally be more nearly correct when Δx is made smaller.

EXAMPLE 4.5 Using Eq. (4.17), estimate the change in the pressure of 1.000 mol of an ideal gas at 0 °C when its volume is changed from 22.414 l to 21.414 l.

SOLUTION ► An ideal gas obeys the equation

$$P = \frac{nRT}{V} \tag{4.18}$$

so that if n and T are kept fixed, we can differentiate with respect to V:

$$\begin{aligned} \frac{dP}{dV} &= \frac{-nRT}{V^2} \\ &= \frac{-(1.000\,\text{mol})(0.08206\,\text{l atm mol}^{-1}\,\text{K}^{-1})(273.15\,\text{K})}{(22.414\,\text{l})^2} \\ &= -0.0446\,\text{atm l}^{-1}\,. \end{aligned} \tag{4.19}$$

We can approximate an increment in P:

$$\begin{aligned} \Delta P &\approx \left(\frac{dP}{dV}\right)\Delta V = \left(-0.0446\,\text{atm l}^{-1}\right)(-1.000\,\text{l}) \\ &\approx 0.0446\,\text{atm}\,. \end{aligned}$$

◄

EXAMPLE 4.6 Determine the accuracy of the result of Example 4.5.

SOLUTION ►

$$\begin{aligned} \Delta P &= P(21.414\,\text{l}) - P(22.414\,\text{l}) = 1.0468\,\text{atm} - 1.0000\,\text{atm} \\ &= 0.0468\,\text{atm}\,. \end{aligned}$$

Our estimate in Example 4.5 was wrong by about 5%. If the change in volume had been 0.1 l, the error would have been about 0.5%. ◄

Since Eq. (4.17) becomes more nearly exact as Δx is made smaller, we make it into an exact equation by making Δx become smaller than any finite quantity that anyone can name. We do not make Δx strictly vanish, but we say that we make it become *infinitesimal*. That is, we make it smaller in magnitude than any nonzero quantity one might specify. In this limit, Δx is called the *differential* dx and we write

$$\boxed{dy = \left(\frac{dy}{dx}\right) dx} \tag{4.20}$$

The infinitesimal quantity dy is the *differential* of the dependent variable y. It is the change in y that results from the infinitesimal increment dx in x. It is proportional to dx and to the slope of the tangent line, which is equal to dy/dx. Since x is an independent variable, dx is arbitrary, or subject to our control. Since y is a dependent variable, its differential dy is determined by dx, as specified by Eq. (4.20) and is not under our control once we have chosen a value for dx. Note that Eq. (4.20) has the appearance of an equation in which the dx in the denominator is canceled by the dx in the numerator. This cancellation cannot occur, although the equation

is valid. The symbol dy/dx is *not* a fraction or a ratio. It is the limit that a ratio approaches, which is not the same thing.

In numerical calculations, differentials are not of direct use, since they are smaller than any finite quantities that you can specify. Their use lies in the construction of formulas, especially through the process of integration, in which infinitely many infinitesimal quantities are added up to produce something finite. We discuss integration in the next chapter.

EXERCISE 4.8 ▶ The number of atoms of a radioactive substance at time t is given by

$$N(t) = N_o e^{-t/\tau},$$

where N_o is the initial number of atoms and τ is the relaxation time. For ^{14}C, $\tau = 8320\,y$. Calculate the fraction of an initial sample of ^{14}C that remains after 10.0 years, using Eq. (4.17). Calculate the correct fraction and compare it with your first answer. ◀

EXERCISE 4.9 ▶ Assume that $y = 3x^2 - 4x + 10$. If $x = 4$ and $\Delta x = 0.5$, Find the value of Δy using Eq. (4.17). Find the correct value of Δy. ◀

4.4 Some Useful Facts About Derivatives

In this section we present some useful identities involving derivatives, which, together with the formulas for the derivatives of simple functions presented in Table 4.1, will enable you to obtain the derivative of almost any function that you will encounter in physical chemistry.

The Derivative of a Product of Two Functions

If y and z are both functions of x,

$$\boxed{\frac{d(yz)}{dx} = y\frac{dz}{dx} + z\frac{dy}{dx}}. \tag{4.21}$$

The Derivative of the Sum of Two Functions

If y and z are both functions of x,

$$\boxed{\frac{d(y+z)}{dx} = \frac{dy}{dx} + \frac{dz}{dx}}. \tag{4.22}$$

The Derivative of the Difference of Two Functions

If y and z are both functions of x,

$$\boxed{\frac{d(y-z)}{dx} = \frac{dy}{dx} - \frac{dz}{dx}}. \tag{4.23}$$

The Derivative of the Quotient of Two Functions

If y and z are both functions of x, and z is not zero.

$$\boxed{\frac{d\,(y/z)}{dx} = \frac{x\left(\frac{dy}{dx}\right) - y\left(\frac{dz}{dx}\right)}{z^2}}. \tag{4.24}$$

An equivalent result can be obtained by considering y/z to be a product of $1/z$ and y and using Eq. (4.21),

$$\boxed{\frac{d}{dx}\left(y\frac{1}{z}\right) = \frac{1}{z}\frac{dy}{dx} - y\frac{1}{z^2}\frac{dz}{dx}}. \tag{4.25}$$

Many people think that Eq. (4.25) is more convenient to use than Eq. (4.24).

The Derivative of a Constant

If c is a constant,

$$\boxed{\frac{dc}{dx} = 0}. \tag{4.26}$$

From this follows the simple but important fact:

$$\boxed{\frac{d\,(y+c)}{dx} = \frac{dy}{dx}}. \tag{4.27}$$

If we add any constant to a function, we do not change its derivative.

The Derivative of a Function Times a Constant

If y is a function of x and c is a constant,

$$\boxed{\frac{d\,(cy)}{dx} = c\frac{dy}{dx}}. \tag{4.28}$$

This can be deduced by substituting into the definition of the derivative, or by using Eqs. (4.21) and (4.26).

The Derivative of a Function of a Function (the Chain Rule)

If u is a differentiable function of x, and f is a differentiable function of u,

$$\boxed{\frac{df}{dx} = \frac{df}{du}\frac{du}{dx}}. \tag{4.29}$$

The function f is sometimes referred to as a *composite function*. It is a function of x, because x is a function of u. Specifying a value of x specifies a value of u,

which specifies a value of f. This can be communicated by the notation

$$f(x) = f[u(x)]. \tag{4.30}$$

Here we have used the same letter for the function f whether it is expressed as a function of u or of x.

We now illustrate how these facts about derivatives can be used to obtain formulas for the derivatives of various functions.

EXAMPLE 4.7 Find the derivative of $\tan(ax)$ by using the formulas for the derivatives of the sine and cosine.

SOLUTION ►

$$\begin{aligned}\frac{d}{dx}\tan(ax) &= \frac{d}{dx}\left[\frac{\sin(ax)}{\cos(ax)}\right] \\ &= \frac{\cos(ax)\,a\cos(ax) + \sin(ax)\,a\sin(ax)}{\cos^2(ax)} \\ &= a\left[\frac{\cos^2(ax)+\sin^2(ax)}{\cos^2(ax)}\right] = \frac{a}{\cos^2(ax)} \\ &= a\sec^2(ax)\end{aligned}$$

We have used several trigonometric identities in the solution. ◄

EXAMPLE 4.8 Find dP/dT if $P(T) = ke^{-Q/T}$.

SOLUTION ► Let $u = -Q/T$. From the chain rule,

$$\begin{aligned}\frac{dP}{dT} &= \frac{dP}{du}\frac{du}{dT} = ke^{u}\frac{Q}{T^2} \\ &= ke^{-Q/T}\left(\frac{Q}{T}\right).\end{aligned}$$

◄

EXERCISE 4.10 ► Find the following derivatives. All letters stand for constants except for the dependent and independent variables indicated.

(a) $\frac{dy}{dx}$, where $y = (ax^2+bx+c)^{-3/2}$ (b) $\frac{d\ln(P)}{dT}$, where $P = ke^{-Q/T}$

(c) $\frac{dy}{dx}$, where $y = a\cos(bx^3)$

◄

Newton's Method

This method, which is also called the *Newton–Raphson method*, is an *iterative procedure* for obtaining a numerical solution to an algebraic equation. An iterative procedure is one that is repeated until the desired degree of accuracy is attained. The procedure is illustrated in Fig. 4.9. We assume that we have an equation written in the form

$$f(x) = 0$$

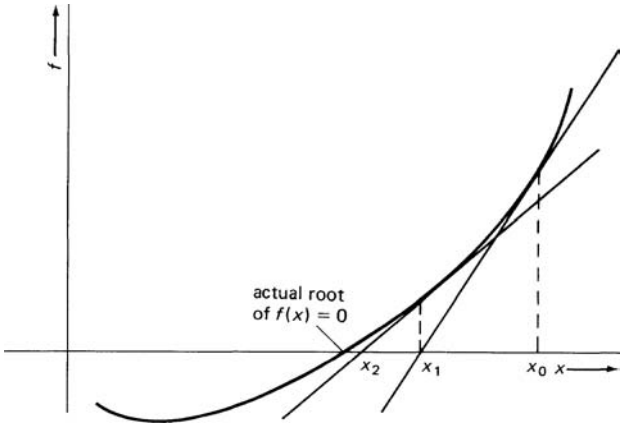

Figure 4.9 ► Graph to illustrate Newton's method.

The process is as follows:

Step 1. Guess at a value, x_0, which is "not too far" from the actual root. A rough graph of the function $f(x)$ can help you to choose a good value for x_0.

Step 2. Find the value of $f(x)$ and the value of df/dx at $x = x_0$.

Step 3. Using the value of $f(x)$ and df/dx, find the value of x at which the tangent line to the curve at $x = x_0$ crosses the axis. This value of x, which we call x_1, is our next approximation to the root. It is given by

$$x_1 = x_0 - \frac{f(x_0)}{f'(x_0)}, \tag{4.31}$$

where we use the notation

$$f'(x_0) = \left.\frac{df}{dx}\right|_{x=x_0}.$$

for the derivative evaluated at $x = x_0$.

Step 4. Repeat the process until you are satisfied with the accuracy obtained. The nth approximation is given by

$$\boxed{x_n = x_{n-1} - \frac{f(x_{n-1})}{f'(x_{n-1})}} \tag{4.32}$$

EXERCISE 4.11 ► Using the definition of the derivative, show that Eqs. (4.31) and (4.32) are correct. ◄

You must decide when to stop your iteration. If the graph of the function $f(x)$ crosses the x axis at the root, you can probably stop when the difference between x_n and x_{n+1} is smaller than the error you can tolerate. However, if the curve becomes tangent to the x axis at the root, the method may converge very slowly near the root. It may be necessary to pick another trial root on the other side of the root and to compare the results from the two iterations. Another possibility is to take the

derivative of the function, set that equal to zero, and solve for that root, since the first derivative changes sign if the function is tangent to the x axis.

You should not demand too much of Newton's method. A poor choice of x_0 can make the method converge to the wrong root, especially if the function is oscillatory. If your choice of x_0 is near a local maximum or a local minimum, the first application of the procedure might give a value of x_1 that is nowhere near the desired root. These kinds of problems can be especially troublesome when you are using a computer to do the iterations, because you might not see the values of x_1, x_2, and so on, until the program has finished execution. Remember the *first maxim of computing*: "Garbage in, garbage out." Carrying out an approximate graphical solution before you start is a good idea so that you can make a good choice for your first approximation to the root and so that you can know if you found the desired root instead of some other root.

EXERCISE 4.12 ► Carry out the Newton–Raphson method to find the smallest positive root of the equation

$$5x - e^x = 0 \tag{4.33}$$

Do the calculation by hand or use a spreadsheet. The Goal Seek command in Excel carries out the Newton-Raphson method automatically. See Chapter 3.

◄

4.5 Higher-Order Derivatives

Since the derivative of a function is itself a function, a derivative of a differentiable function is usually differentiable. The derivative of a derivative is called a *second derivative*, and the derivative of a second derivative is called a *third derivative*, and so on. We use the notation

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left(\frac{dy}{dx}\right) \tag{4.34}$$

and

$$\frac{d^3y}{dx^3} = \frac{d}{dx}\left(\frac{d^2y}{dx^2}\right), \tag{4.35}$$

and so on. The nth-order derivative is

$$\frac{d^ny}{dx^n} = \frac{d}{dx}\left(\frac{d^{n-1}y}{dx^{n-1}}\right). \tag{4.36}$$

The notation $y''(x)$ is sometimes used for the second derivative. The third and higher order derivatives are sometimes denoted by a lowercase roman numeral superscript in parentheses, as $y^{(iii)}$, $y^{(iv)}$, and so on.

EXAMPLE 4.9 Find d^2y/dx^2 if $y = a\sin(bx)$.

SOLUTION ►

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left[ab\cos(bx)\right] = -ab^2\sin(bx).$$

◄

The result of this example is sometimes useful: the sine is proportional to the negative of its second derivative. The cosine has the same behavior. The exponential function is proportional to all of its derivatives.

EXERCISE 4.13 ► Find the second and third derivatives of the following functions. All letters stand for constants except for the indicated dependent and independent variables. Treat all symbols except for the specified independent variable as constants.

(a) $y = y(x) = ax^n$

(b) $y = y(x) = ae^{bx}$

(c) $v_{\text{rms}} = v_{\text{rms}}(T) = \sqrt{\frac{3RT}{M}}$

(d) $P = P(V) = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$

(e) $\eta = \eta(\lambda) = \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda kT}-1)}$.

◄

The Curvature of a Function

Figure 4.10 shows a rough graph of a function in the interval $a < x < g$.

A rough graph of the first derivative of the function and a rough graph of the second derivative of the function in the interval are also included. Where the function is concave downward, the second derivative is negative, and where the function is concave upward, the second derivative is positive. Where the graph of the function is more sharply curved, the magnitude of the second derivative is larger. The second derivative therefore provides a measure of the curvature of the function curve.

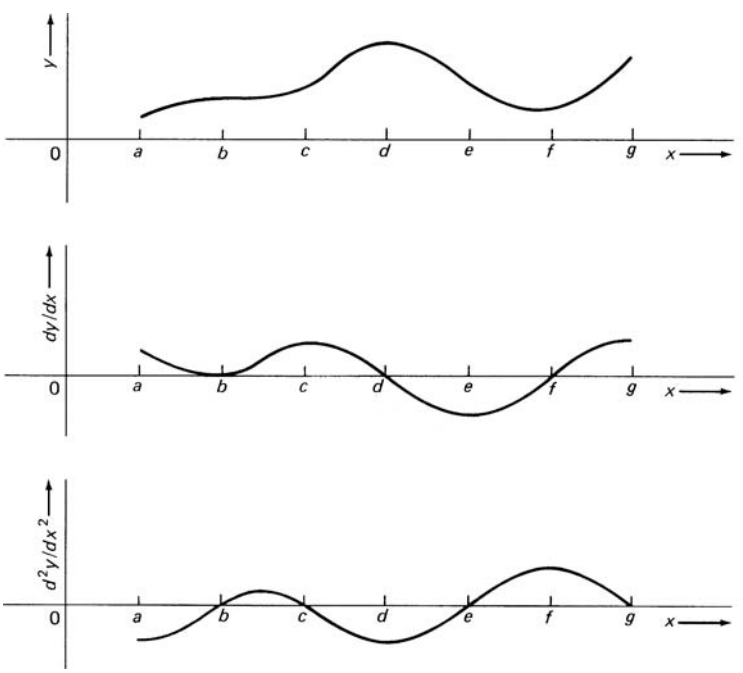

Figure 4.10 ► A function and its first and second derivative.

For any function that possesses a second derivative, the *curvature* K is defined by

$$K = \frac{d^2y/dx^2}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}}. \tag{4.37}$$

The curvature is positive if the curve representing the function is concave upward, and is negative if the curve is concave downward. The magnitude of the curvature is equal to the reciprocal of the radius of the circle that fits the curve at that point. If the curvature is larger the circle is smaller. At a point where the first derivative is zero, the curvature is equal to the second derivative. Since the denominator in Eq. (4.37) is always positive, the curvature has the same sign as the second derivative.

EXAMPLE 4.10 Find the curvature of the function $y = x^2$ at $x = 0$ and at $x = 2$.

SOLUTION ►

$$\frac{d^2y}{dx^2} = \frac{d}{dx}(2x) = 2$$

$$K = \frac{2}{(1 + 4x^2)^{3/2}} = \begin{cases} 2 & \text{at } x = 0 \\ 0.0285 & \text{at } x = 2 \end{cases}.$$

◄

EXERCISE 4.14 ►

(a) Find the curvature of the function $\cos(x)$ at $x = 0$ and at $x = \pi/2$.

(b) Find a formula for the curvature of the function

$$P(V) = \frac{nRT}{V - nb} - \frac{an^2}{V^2},$$

where n, R, a, b, and T are treated as constants.

◄

4.6 Maximum-Minimum Problems

Sometimes you want to find the largest or smallest value that a function attains or approaches in a certain interval, or to find the value of the independent variable at which this happens. The *minimum value* of a function means the most negative value of the function, not necessarily the smallest magnitude. The *maximum value* means the most positive value of the function, not necessarily the largest magnitude. Both a maximum and a minimum are called an *extremum*. If a function happens to be negative in all parts of some interval, the maximum value in that interval will correspond to the smallest magnitude and the minimum value will correspond to the largest magnitude. We now state the fact that enables us to find

maximum and minimum values of a differentiable function in a given interval: *The minimum or maximum value of a differentiable function in an interval will either occur at an end of the interval or at a point where the first derivative of the function vanishes.*

We illustrate the process of finding the maximum and minimum values of a function in an interval in Fig. 4.10. In the interval shown there are three points at which the curve has a horizontal tangent, labeled b, d, and f. The first derivative vanishes at these points. The points at which we might have the maximum value of the function include these three points and the ends of the interval, labeled a and g. At $x = f$ we have a *relative minimum*, also called a *local minimum*. At such a point the function has a smaller value than at any other point in the immediate vicinity. At point d we have a *relative maximum* or a *local maximum*, at which the function has a larger value than at any other point in the immediate vicinity. The first derivative also vanishes at point b, but this is an *inflection point* with a horizontal tangent line.

To find the maximum value we must compare the value of the function at point d and at the ends of the interval. Inspection of the graph indicates that the function has a greater value at point d than at the ends of the interval, and this point is the *absolute maximum* of the function in the interval shown. The possible points for the minimum value of the function are the ends of the interval and point f. Inspection of the graph indicates that the left end of the interval (point a) is the *absolute minimum*.

In our discussion of Fig. 4.10, we were guided by inspection of the graph. If you don't have a graph, you can distinguish relative minima, relative maxima, and inflection points from each other by finding the sign of the curvature, which is equal to the second derivative at a point with zero first derivative. At a relative minimum, the second derivative is positive. At a relative maximum, the second derivative is negative. At an inflection point with horizontal tangent line, the second derivative vanishes. To find the absolute maximum of a function in an interval, you evaluate the function at each relative maximum and at the ends of the interval and then choose the point with the largest value of the function. To find the absolute minimum of a function in an interval, you evaluate the function at each relative minimum and at the ends of the interval and then choose the point with the smallest (most negative) value.

If you don't want to go to the trouble of evaluating the second derivatives, you can use the following procedure for a differentiable function:

1. Find all the points in the interval at which the first derivative vanishes.

2. Evaluate the function at all of these points and at the ends of the interval. The largest value in the list is the maximum value and the smallest value is the minimum.

If a function is not differentiable at all points in an interval, you must add all points at which the function is not differentiable to your list of possible maxima or minima. For example, there might be a discontinuity or a cusp at which the function has a larger value than at any other point in the interval.

EXAMPLE 4.11 Find the maximum and minimum values of the function

$$y = x^2 - 4x + 6$$

in the interval $0 < x < 5$.

SOLUTION ► The derivative is

$$\frac{dy}{dx} = 2x - 4.$$

There is only one point at which $dy/dx = 0$. Call it x_m.

$$2x_m - 4 = 0 \qquad \text{or} \qquad x_m = 2.$$

We evaluate the function at the ends of the interval and at $x = x_m$:

$$\begin{aligned} y(0) &= 6 \\ y(x_m) &= y(2) = 2 \\ y(5) &= 11. \end{aligned}$$

The maximum value of the function is at $x = 5$, the end of the interval. The minimum value is at $x = 2$. ◄

EXERCISE 4.15 ► For the interval $10 < x < 10$, find the maximum and minimum values of

$$y = -x^3 + 3x^2 - 3x + 8.$$

◄

EXERCISE 4.16 ► The probability that a molecule in a gas will have a speed v is proportional to the function

$$f_v(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(\frac{-v^2}{2mk_B T}\right),$$

where m is the mass of the molecule, k_B is Boltzmann's constant, and T is the temperature on the Kelvin scale. The most probable speed is the speed for which this function is at a maximum. Find the expression for the most probable speed and find its value for nitrogen molecules at $T = 298\,\text{K}$. Remember to use the mass of a molecule, not the mass of a mole. ◄

EXERCISE 4.17 ► According to the Planck theory of black-body radiation, the *radiant spectral emittance* is given by the formula

$$\eta = \eta(\lambda) = \frac{2\pi hc^2}{\lambda^5 \left(e^{hc/\lambda kT} - 1\right)},$$

where h is Planck's constant, k_B is Boltzmann's constant, c is the speed of light, and T is the temperature on the Kelvin scale. Treat T as a constant and find an equation that will give the wavelength of maximum emittance. ◄

EXERCISE 4.18 ▶ Find the maximum and minimum values of the function

$$y = x^3 + 4x^2 - 10x + 25|x^3|$$

in the interval $-5 < x < 5$. Note the cusp at $x = 0$. ◀

4.7 Limiting Values of Functions: L'Hôpital's Rule

We have already defined mathematical limits. The limit of y as x approaches a is denoted by

$$\lim_{x \to a} \left[y\,(x) \right]$$

and is defined as the value that y approaches ever more closely as x approaches ever more closely to a, if such a number exists. The value a is not required to be finite, and a limit such as

$$\lim_{x \to \infty} \left[y\,(x) \right]$$

exists if $y(x)$ approaches more closely to some value as x is made larger and larger without bound. In some cases it matters whether the limit is approached from the right or from the left. This occurs when there is a discontinuity or a cusp at the limiting point. An example of a limit that does not exist is

$$\lim_{x \to a} \left(\frac{1}{x - a} \right). \tag{4.38}$$

As x approaches closer to a, $1/(x - a)$ becomes larger without bound if x approaches a from the right (from values larger than a) and $1/(x - a)$ becomes more negative without bound if x approaches a from the left.

Another limit that does not exist is

$$\lim_{x \to \infty} [\sin\,(x)]. \tag{4.39}$$

The sine function continues to oscillate between -1 and 1 as x becomes larger and larger. An example of a limit that does exist as x approaches infinity is

$$\lim_{x \to \infty} \left(1 - e^{-x} \right) = 1. \tag{4.40}$$

EXERCISE 4.19 ▶ Decide which of the following limits exist and find the values of those that do exist.

(a) $\lim_{x \to 0} \left(1 - e^{-x} \right)$ (b) $\lim_{x \to \infty} \left(e^{-x^2} \right)$

(c) $\lim_{x \to \pi/2} [x \tan\,(x)]$ (d) $\lim_{x \to 0} [\ln\,(x)]$.

◀

Sometimes a limit exists but cannot be evaluated in a straightforward way by substituting into the expression the limiting value of the independent variable. For example, if we try to determine the limit

$$\lim_{x \to 0} \left[\frac{\sin\,(x)}{x} \right] \tag{4.41}$$

we find that for $x = 0$ both the numerator and denominator of the expression vanish. If an expression appears to approach $0/0$, it might approach 0, it might approach a finite constant of either sign, or it might diverge in either direction (approach $-\infty$ or $+\infty$). The same is true if it appears to approach ∞/∞ or $0 \times \infty$.

The *rule of l'Hôpital* provides a way to determine the limit in such cases. This rule can be stated: *If the numerator and denominator of a quotient both approach zero or both approach infinity in some limit, the limit of the quotient is equal to the limit of the quotient of the derivatives of the numerator and denominator if this limit exists. That is, if the limits exist, then*

$$\boxed{\lim_{x\to a}\left[\frac{f(x)}{g(x)}\right]=\lim_{x\to a}\left[\frac{df/dx}{dg/dx}\right]=\lim_{x\to a}\left[\frac{f'(x)}{g'(x)}\right]} \tag{4.42}$$

EXAMPLE 4.12 Find the value of the limit in Eq. (4.41) by use of l'Hôpital's rule.

SOLUTION ►

$$\lim_{x\to 0}\left[\frac{\sin(x)}{x}\right]=\lim_{x\to 0}\left[\frac{d\sin(x)/dx}{dx/dx}\right]=\lim_{x\to 0}\left[\frac{\cos(x)}{1}\right]=1. \tag{4.43}$$

◄

l'Hôpital's rule does not necessarily give the correct limit if it is applied to a case in which the limit does not appear to approach $0/0$ *or* ∞/∞ *or* $0 \times \infty$. *One author put it: "As a rule of thumb, l'Hôpital's rule applies when you need it, and not when you do not need it."*

If the expression appears to approach $0 \times \infty$, it can be put into a form that appears to approach $0/0$ or ∞/∞ by using the expression for the reciprocal of one factor. In the following example, we use this technique, as well as illustrating the fact that sometimes the rule must be applied more than once in order to find the value of the limit.

EXAMPLE 4.13 Find the limit

$$\lim_{x\to\infty}\left(x^3e^{-x}\right).$$

SOLUTION ►

$$\begin{aligned}\lim_{x\to\infty}\left(x^3e^{-x}\right) &= \lim_{x\to\infty}\left(\frac{x^3}{e^x}\right)=\lim_{x\to\infty}\left(\frac{3x^2}{e^x}\right)\\ &= \lim_{x\to\infty}\left(\frac{6x}{e^x}\right)=\lim_{x\to\infty}\left(\frac{6}{e^x}\right)=0.\end{aligned} \tag{4.44}$$

◄

By applying l'Hôpital's rule n times, we can show

$$\boxed{\lim_{x\to\infty}\left(x^ne^{-x}\right)=0} \tag{4.45}$$

for any finite value of n. The exponential function e^{-x} approaches zero so rapidly that it overwhelms any finite power of x in the limit that x becomes large.

EXERCISE 4.20 ► Investigate the limit

$$\lim_{x\to\infty}\left(x^{-n}e^{x}\right)$$

for any finite value of n. ◄

Another interesting limit is that of the next example.

EXAMPLE 4.14 Find the limit

$$\lim_{x\to\infty}\left(\frac{\ln(x)}{x}\right).$$

SOLUTION ►

$$\lim_{x\to\infty}\left(\frac{\ln(x)}{x}\right)=\lim_{x\to\infty}\left(\frac{1/x}{1}\right)=0. \tag{4.46}$$

◄

EXERCISE 4.21 ► Find the limit

$$\lim_{x\to\infty}\left[\frac{\ln(x)}{\sqrt{x}}\right].$$

◄

EXERCISE 4.22 ► A collection of N harmonic oscillators at thermal equilibrium at absolute temperature T is shown by statistical mechanics to have the thermodynamic energy

$$U=\frac{Nh\nu}{e^{h\nu/k_BT}-1} \tag{4.47}$$

where k_B is Boltzmann's constant, h is Planck's constant, T is the absolute temperature, and ν is the vibrational frequency.

(a) Find the limit of U as $\nu\to 0$. (b) Find the limit of U as $T\to 0$.

◄

There are a number of applications of limits in physical chemistry, and l'Hôpital's rule is useful in some of them.[1]

EXERCISE 4.23 ► Draw a rough graph of the function

$$y=\frac{\tan(x)}{x}$$

in the interval $-\pi < x < \pi$. Use l'Hôpital's rule to evaluate the function at $x=0$. ◄

[1]Missen, Ronald W., "Applications of the l'Hôpital–Bernoulli Rule in Chemical Systems," *J. Chem. Educ.* **54**, 448 (1977).

SUMMARY

A function is a rule that provides a value for a dependent variable for any given value of a dependent variable. The derivative of a function is another function of the same independent variable, which specifies the rate of change of the first function with respect to the independent variable. The first derivative of the function $y(x)$ is defined by

$$\frac{dy}{dx} = y' = \lim_{x_2 \to x_1} \frac{y\,(x_2) - y\,(x_1)}{x_2 - x_1}$$

if this limit exists. The derivative is equal to the slope of the tangent line to a curve representing the function. The first derivative vanishes at a relative maximum or minimum and can be used to locate these points. The second derivative is the derivative of the first derivative

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left(\frac{dy}{dx}\right)$$

The second derivative determines the curvature of a function. Higher derivatives were defined. Derivatives are useful in applying the rule of l'Hôpital:

$$\lim_{x \to a}\left[\frac{f\,(x)}{g\,(x)}\right] = \lim_{x \to a}\left[\frac{df/dx}{dg/dx}\right] = \lim_{x \to a}\left[\frac{f'(x)}{g'(x)}\right]$$

PROBLEMS

1. The sine and cosine functions are represented by the two series

$$\begin{aligned} \sin(x) &= x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots . \\ \cos(x) &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{4^6}{6!} + \cdots . \end{aligned} \tag{4.48}$$

Differentiate each series to show that

$$\frac{d\sin(x)}{dx} = \cos(x)$$

and

$$\frac{d\cos(x)}{dx} = -\sin(x)$$

2. The natural logarithm of $1 + x$ is represented by the series

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \cdots (x^2 < 1 \text{ and } x = 1).$$

Use the identity

$$\frac{d\ln(x)}{dx} = \frac{1}{x}.$$

to find a series to represent $1/(1+x)$.

3. Use the definition of the derivative to derive the formula

$$\frac{d(yz)}{dx} = y\frac{dz}{dx} + z\frac{dy}{dx}$$

where y and z are both functions of x.

4. Find the first and second derivatives of the following functions

a) $P = P(V_m) = RT(1/V_m + B/V_m^2 + C/V_m^3)$ where R, B, and C are constants

b) $G = G(x) = G^\circ + RTx\ln(x) + RT(1-x)\ln(1-x)$, where G°, R, and T are constants

c) $y = y(x) = a\ln(x^{1/3})$, where a is a constant

a) $y = y(x) = 3x^3\ln(x)$

b) $y = y(x) = 1/(c - x^2)$, where c is a constant

c) $y = y(x) = ce^{-a\cos(bx)}$, where a, b, and c are constants

5. Find the first and second derivatives of the following functions.

a) $y = \ln[\tan(2x)]$

b) $y = (1/x)\,(1/(1+x))$

c) $f = f(v) = ce^{-mv^2/(2kT)}$ where m, c, k, and T are constants

6. Find the first and second derivatives of the following functions.

a) $y = 3\sin^2(2x) = 3\sin(2x)^2$

b) $y = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + a_5x^5$, where a_0, a_1, and so on, are constants

c) $y = a\cos(e^{-bx})$, where a and b are constants

7. Find the following derivatives and evaluate them at the points indicated.

a) $(dy/dx)_{x=0}$ if $y = \sin(bx)$, where b is a constant

b) $(df/dt)_{t=0}$ if $f = Ae^{-kt}$, where A and k are constants

8. Find the following derivatives and evaluate them at the points indicated.

a) $(dy/dx)_{x=1}$, if $y = \left(ax^3 + bx^2 + cx + 1\right)^{-1/2}$, where a, b, and c are constants

b) $\left(d^2y/dx^2\right)_{x=0}$, if $y = ae^{-bx}$, where a and b are constants

9. Find the following derivatives

a) $\frac{d(yz)}{dx}$, where $y = ax^2$, $z = \sin(bx)$

b) $\frac{dP}{dV}$, where $P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$

c) $\frac{d\eta}{d\lambda}$, where $\eta = \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda kT}-1)}$

10. The volume of a cube is given by

$$V = V(a) = a^3,$$

where a is the length of a side. Estimate the percent error in the volume if a 1% error is made in measuring the length, using the formula

$$\Delta V \approx \left(\frac{dV}{da}\right)\Delta a.$$

Check the accuracy of this estimate by comparing $V(a)$ and $V(1.01a)$.

11. Draw a rough graph of the function

$$y = y(x) = e^{-|x|}$$

Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

12. Draw a rough graph of the function

$$y = y(x) = \sin(|x|)$$

Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

13. Draw a rough graph of the function

$$y = y(x) = \cos(|x|)$$

Is the function differentiable at $x = 0$? Draw a rough graph of the derivative of the function.

14. Show that the function $\psi = \psi(x) = A\sin(kx)$ satisfies the equation

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

if A and k are constants.

15. Show that the function $\psi = \psi(x) = \cos(kx)$ satisfies the equation

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

if A and k are constants.

16. Draw rough graphs of the third and fourth derivatives of the function whose graph is given in Fig. 4.10.

17. The Gibbs energy of a mixture of two *enantiomorphs* (optical isomers of the same substance) is given by

$$G = G(x) = G^\circ + RTx\ln(x) + RT(x_0 - x)\ln(x_0 - x)$$

where x_0 is the sum of the concentrations of the enantiomorphs and x is the concentration of one of them. G° is a constant, R is the gas constant, and T is the temperature. If the temperature is maintained constant, what is the concentration of each enantiomorph when G has its minimum value? What is the maximum value of G in the interval $0 < x < x_0$?

a) A rancher wants to enclose a rectangular part of a large pasture so that $1.000\,\text{km}^2$ is enclosed with the minimum amount of fence. Find the dimensions of the rectangle that he should choose. The area is

$$A = xy$$

but A is fixed at $1.000\,\text{km}^2$, so that $y = A/x$.

b) The rancher now decides that the fenced area must lie along a road and finds that the fence costs \$20 per meter along the road and \$10 per meter along the other edges. Find the dimensions of the rectangle that would minimize the cost of the fence.

18. Using

$$\Delta y \approx \left(\frac{dy}{dx}\right)\Delta x$$

show that

$$e^{\Delta x} - 1 \approx \Delta x \quad \text{if } \Delta x \ll 1.$$

19. The sum of two nonnegative numbers is 100. Find their values if their product plus twice the square of the first is to be a maximum.

20. A cylindrical tank in a chemical factory is to contain $2.000\,\text{m}^3$ of a corrosive liquid. Because of the cost of the material, it is desirable to minimize the area of the tank. Find the optimum radius and height and find the resulting area.

21. Find the following limits.

a) $\lim_{x\to\infty}[\ln(x)/x^2]$

b) $\lim_{x\to 3}\left[(x^3-27)/(x^2-9)\right]$

c) $\lim_{x\to\infty}[x\ln(\frac{1}{1+x})]$

22. Find the following limits.

a) $\lim_{x\to 0^+}\left[\frac{\ln(1+x)}{\sin(x)}\right]$

b) $\lim_{x\to 0^+}[\sin(x)\ln(x)]$

23. Find the following limits

a) $\lim_{x\to\infty}\left(e^{-x^2}/e^{-x}\right)$

b) $\lim_{x\to 0}\left[x^2/(1-\cos(2x))\right]$

c) $\lim_{x\to\pi}\left[\sin(x)/\sin(3x/2)\right]$.

24. If a hydrogen atom is in a $2s$ state, the probability of finding the electron at a distance r from the nucleus is proportional to $4\pi r^2\psi_{2s}^2$, where ψ represents the orbital (wave function):

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/a_0},$$

where a_0 is a constant known as the Bohr radius, equal to $0.529\times 10^{-10}\,\text{m}$.

a) Locate the maxima and minima of ψ_{2s}.
b) Draw a rough graph of ψ_{2s}.
c) Locate the maxima and minima of ψ_{2s}^2.
d) Draw a rough graph of ψ_{2s}^2.
e) Locate the maxima and minima of $4\pi r^2 \psi_{2s}^2$.
f) Draw a rough graph of $4\pi r^2 \psi_{2s}^2$.

25. The thermodynamic energy of a collection of N harmonic oscillators (approximate representations of molecular vibrations) is given by

$$U = \frac{Nh\nu}{e^{h\nu/k_BT} - 1} \tag{4.49}$$

a) Draw a rough sketch of the thermodynamic energy as a function of T.
b) The heat capacity of this system is given by

$$C = \frac{dU}{dT}.$$

c) Show that the heat capacity is given by

$$C = Nk_B \left(\frac{h\nu}{k_BT}\right)^2 \frac{e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT} - 1\right)^2}.$$

d) Find the limit of the heat capacity as $T \to 0$ and as $T \to \infty$. Note that the limit as $T \to \infty$ is the same as the limit $\nu \to 0$.
e) Draw a graph of C as a function of T.

26. Find the relative maxima and minima of the function $f(x) = x^3 + 3x^2 - 2x$ for all real values of x.

27. The van der Waals equation of state is

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

When the temperature of a given gas is equal to its critical temperature, the gas has a state at which the pressure as a function of V at constant T and n exhibits an inflection point at which $dP/dV = 0$ and $d^2P/dV^2 = 0$. This inflection point corresponds to the critical point of the gas. Write P as a function of T, V, and n and write expressions for dP/dV and d^2P/dV^2, treating T and n as constants. Set these two expressions equal to zero and solve the simultaneous equations to find an expression for the pressure at the critical point.

28. Solve the following equations by hand, using the Newton-Raphson method. Verify your results using Excel or Mathematica:

a) $x^3 - x^2 + x - 1 = 0$
b) $e^{-x} - 0.5x = 0$
c) $\sin(x)/x - 0.75 = 0$

29. Use the Newton-Raphson method to calculate the pH of a 0.01 molar solution of lactic acid, $C_3H_6O_3$ at 25°C. The acid dissociation constant, K_a, is equal to 1.38×10^{-4} at this temperature. Use Eqs. (3.10) and (3.11) to calculate the pH and comment on the accuracy of these two approximations.

5

Integral Calculus

Preview

In this chapter we first discuss the antiderivative, a function that possesses a given derivative. We then define integration as the limit of a summation process and discuss the process of constructing a finite increment in a function from knowledge of its derivative. We discuss the role of the antiderivative as an indefinite integral and the use of tables of indefinite and definite integrals. We discuss several methods of working out integrals without the use of a table. Finally, we discuss the use of integration to find mean values with a probability distribution.

Principal Facts and Ideas

1. The antiderivative $F(x)$ of a function $f(x)$ is the function such that $dF/dx = f(x)$.
2. An indefinite integral is the same thing as the antiderivative function.
3. A definite integral is the limit of a sum of terms $f(x)\Delta x$ in the limit that Δx approaches zero, where $f(x)$ is the integrand function.
4. A definite integral equals the indefinite integral evaluated at the upper limit minus the indefinite integral evaluated at the lower limit:

$$\int_a^b f(x)\,dx = F(b) - F(a).$$

5. An improper integral has at least one infinite limit or has an integrand function that is infinite somewhere in the interval of integration. If an improper integral has a finite value it is said to converge. Otherwise it is said to diverge.
6. Analytical methods can be used to transform an integral into a more easily computed form.
7. Numerical methods exist to compute accurate approximations to integrals that cannot be analytically performed.
8. A mean value of a continuously distributed variable can be computed as an integral using a probability distribution.

Objectives

After studying this chapter, you should be able to:

1. obtain the indefinite integral of an integrand function using a table;
2. calculate a definite integral using the indefinite integral and understand its role as an increment in the antiderivative function;
3. understand the relationship of a definite integral to an area in a graph of the integrand function;
4. obtain an approximate value for a definite integral using numerical analysis;
5. manipulate integrals into tractable forms by use of partial integration, the method of substitution, and the method of partial fractions;
6. calculate mean values of quantities using a probability distribution with one random variable.

5.1 The Antiderivative of a Function

In Chapter 4, we discussed the derivative of a function. We consider the inverse problem, finding a function that possesses a specific function as its derivative. We begin with a particular example.

Position, Velocity, and Acceleration

The position of a particle is represented by its *position vector*, which we denote by **r**. If a particle moves only in the vertical direction, we can express its position as a function of time by the z component of this vector, which is a function of time.

$$z = z(t), \tag{5.1}$$

The *velocity* is the derivative of the position vector with respect to time. The velocity is a vector which we denote by **v**. The z component of the velocity is

$$v_z = v_z(t) = \frac{dz}{dt} \tag{5.2}$$

The *acceleration* is the derivative of the velocity with respect to time, or the second derivative of the position vector. The z component of the acceleration is

$$a_z = \frac{dv_z}{dt} = \frac{d^2z}{dt^2}. \tag{5.3}$$

The x and y components are defined in the same way if the particle moves in three dimensions.

EXAMPLE 5.1 According to *classical mechanics* (*Newtonian mechanics*) particle falling vertically in a vacuum near the surface of the earth has a position given by

$$z = z(t) = z(0) + v_z(0)t - \frac{gt^2}{2},$$

where $z(0)$ is the position at $t = 0$, $v_z(0)$ is the velocity at $t = 0$, and g is the *acceleration due to gravity*,[a] equal to $9.80\,\mathrm{m\,s^{-2}}$. Find the velocity and the acceleration.

[a]The acceleration due to gravity varies slightly with latitude. This value holds for the latitude of Washington, DC, or San Francisco.

SOLUTION ►

$$v_z(t) = \frac{dz}{dt} = v_z(0) - gt \tag{5.4}$$

$$a_z(t) = \frac{d^2z}{dt^2} = -g \tag{5.5}$$

◄

The Antiderivative Function

Now consider the reverse problem from that of the previous example. If we are given the acceleration as a function of time, how do we find the velocity? If we are given the velocity as a function of time, how do we find the position? In the following example, we see that the answer to these questions involves the *antiderivative function*, which is a function that possesses a particular derivative.

EXAMPLE 5.2 Given that a particle moves in the z direction and that its acceleration is $a_z = -g$, find its velocity and position.

SOLUTION ► We know that $-gt$ is a function that possesses $-g$ as its derivative, so that one possibility for the velocity is

$$v_z(t) = -gt.$$

However, the derivative of any constant is zero, so the most general possibility is

$$v_z(t) = v_z(0) - gt, \tag{5.6}$$

where $v_z(0)$ is a constant. Equation (5.6) represents a family of functions, one for each value of this constant. Every function in this family is an antiderivative of the given acceleration. To find the position, we seek a function that has $v_z(0) - gt$ as its derivative. We know that

$$\frac{d}{dx}\left(ax^2\right) = 2ax \qquad \text{and} \qquad \frac{d}{dx}(ax) = a \tag{5.7}$$

so that the second family of antiderivative functions that we need is

$$z = z(t) = z(0) + v_z(0)t - \frac{gt^2}{2}, \tag{5.8}$$

where $z(0)$ is again a constant. We have arrived at the beginning point of the previous example. Equation (5.8) represents a family of functions that includes all of the functions that give the position z as a function of time such that $-g$ is the acceleration in the z direction. Since we went through two stages of antiderivatives, there are two arbitrary constants, $z(0)$ and $v_z(0)$, that would be assigned values to correspond to any particular case, as in the following example. ◄

EXAMPLE 5.3 Find the expression for the velocity of a particle falling near the surface of the earth in a vacuum, given that the velocity at $t = 1.000\,\text{s}$ is $10.00\,\text{m s}^{-1}$.

SOLUTION ► The necessary family of functions is given by Eq. (5.6), with $v_z(0) = 19.80\,\text{m s}^{-1}$:

$$v_z(t) = 19.80\,\text{m s}^{-1} - (9.80\,\text{m s}^{-2})t. \tag{5.9}$$

In order to find the position as a function of time, we would need to know the initial position. ◄

EXAMPLE 5.4 Find the antiderivative of

$$f(x) = a\sin(bx),$$

where a and b are constants.

SOLUTION ► The antiderivative function is, from Table 4.1,

$$F(x) = -\frac{a}{b}\cos(bx) + c, \tag{5.10}$$

where c is an arbitrary constant. You can differentiate to verify that

$$\frac{dF}{dx} = f(x). \tag{5.11}$$

◄

EXERCISE 5.1 ► Find the family of functions whose derivative is ae^{bx}. ◄

EXERCISE 5.2 ► Find the function whose derivative is $-10e^{-5x}$ and whose value at $x = 0$ is 10. ◄

5.2 The Process of Integration

In the previous examples we have identified an antiderivative function by inspection of the well-known formulas for derivatives. We now consider the general problem of constructing a function that possesses a certain derivative. Say that we have a function $f = f(x)$, and we want to find its antiderivative function, which we call $F(x)$. That is,

$$\frac{dF}{dx} = f(x). \tag{5.12}$$

We first describe a process of finding the value of $F(x_1) - F(x_0)$ where x_0 and x_1 are two values of x and where the value of F at $x = x_0$ is known. In Section 4.4, we discussed the approximate calculation of an increment in a function, using the slope of the tangent line, which is equal to the derivative of the function. Equation (4.17) is

$$\Delta F = F(x_1) - F(x_0) \approx \left(\frac{dF}{dx}\right)_{x=x_0} \Delta x, \tag{5.13}$$

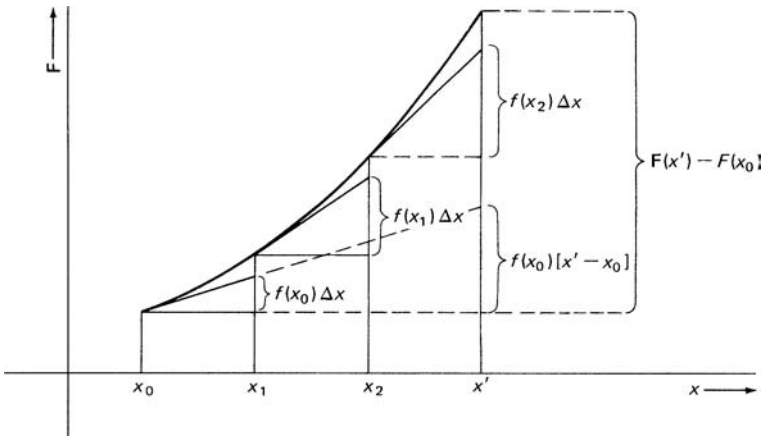

Figure 5.1 ► Figure to illustrate Eq. (5.14).

where $\Delta x = x_1 - x_0$. This approximation becomes more and more nearly exact as Δx is made smaller.

If we want the value of F at some point that is not close to $x = x_0$, we can get a better approximation by using Eq. (5.13) several times for smaller values of Δx. Say that we want the value of F at $x = x'$. We divide the interval (x_0, x') into n equal subintervals. This is shown in Fig. 5.1, with n equal to 3. We now write

$$F\left(x'\right) - F\left(x_0\right) \approx \left(\frac{dF}{dx}\right)_{x=x_0} \Delta x + \left(\frac{dF}{dx}\right)_{x=x_1} \Delta x + \left(\frac{dF}{dx}\right)_{x=x_2} \Delta x + \cdots + \left(\frac{dF}{dx}\right)_{x=x_{n-1}} \Delta x, \tag{5.14}$$

where Δx is the length of each subinterval:

$$\Delta x = x_1 - x_0 = x_2 - x_1 = x_3 - x_2 = \cdots = x' - x_{n-1}. \tag{5.15}$$

This approximation to $F(x') - F(x_0)$ is generally a better approximation than the one obtained by multiplying the slope at the beginning of the interval by the length of the whole interval, as you can see in Fig. 5.1. In fact, if we make n fairly large, we can make the approximation nearly exact.

Let us now rewrite Eq. (5.14), using the symbol $f = f(x)$ instead of dF/dx,

$$F(x') - F(x_0) \approx f(x_0)\Delta x + f(x_1)\Delta x + f(x_2)\Delta x + \cdots + f(x_{n-1})\Delta x \tag{5.16}$$

$$\approx \sum_{k=0}^{n-1} f\left(x_k\right)\, \Delta x. \tag{5.17}$$

In Eq. (5.17), we have introduced the standard notation for a sum, a capital Greek sigma (Σ). The letter k is called the *summation index*. Its initial value is given under the capital sigma and its final value is given above it. Unless otherwise stated, k is incremented by unity for each term. There are n terms indicated in this sum.

We can use Eq. (5.15) to write

$$x_k = x_0 + k\Delta x \tag{5.18}$$

and use this in Eq. (5.17):

$$F(x') - F(x_0) \approx \sum_{k=0}^{n-1} f\ (x_0 + k\Delta x)\ \Delta x. \tag{5.19}$$

We now make Eq. (5.19) into an exact equation by taking the limit as n becomes larger and larger without bound, meanwhile making Δx smaller and smaller so that $n\ \Delta x$ remains fixed and equal to $x' - x_0$.

$$F(x') - F(x_0) = \lim_{\substack{\Delta x \to 0, n \to \infty, \\ n\Delta x = x' - x_0}} \left[\sum_{k=0}^{n-1} f\ (x_0 + k\Delta x)\ \Delta x \right]. \tag{5.20}$$

The limiting value of the right-hand side of Eq. (5.20) is called a *definite integral*. The function $f(x)$ is called the *integrand function*. The notation in this equation is cumbersome, so another symbol is used:

$$\lim_{\substack{\Delta x \to 0, n \to \infty, \\ n\Delta x = x' - x_0}} \left[\sum_{k=0}^{n-1} f\ (x_0 + k\Delta x)\ \Delta x \right] = \int_{x_0}^{x'} f\ (x)\ dx. \tag{5.21}$$

The *integral sign* on the right-hand side of Eq. (5.21) is a stretched-out letter "S," for sum. However, an integral is not just a sum. It is the limit that a sum approaches as the number of terms in the sum becomes infinite in a particular way. The value x_0 at the bottom of the integral sign is called the *lower limit of integration*, and the value x at the top is called the *upper limit of integration*. Equation (5.20) is now

$$\boxed{F(x') - F(x_0) = \int_{x_0}^{x'} f\ (x)\ dx}. \tag{5.22}$$

The finite increment $F(x') - F(x_0)$ is equal to the sum of infinitely many infinitesimal increments, each given by the differential $dF = (dF/dx)dx = f(x)dx$ evaluated at the appropriate value of x. The integral on the right-hand side of Eq. (5.22) is called a *definite integral*, because the limits of integration are definite values. Equation (5.22) is often called the *fundamental theorem of integral calculus*. It is equivalent to saying that a finite increment in F is constructed by adding up infinitely many infinitesimal increments. The antiderivative function F is called the *indefinite integral* of the integrand function f.

Equation (5.22) is an important equation. In many applications of calculus to physical chemistry, we will be faced with an integral equivalent to the right-hand side of this equation. If we can by inspection or by use of a table find the function F that possesses the function f as its derivative, we can evaluate the function F at the two limits of integration and take the difference to obtain the value of the integral. In other cases, we might not be able to identify the antiderivative function, but can numerically construct a change in its value using this equation.

EXAMPLE 5.5 Find the value of the definite integral

$$\int_0^{\pi} \sin(x)\, dx.$$

SOLUTION ► From our table of derivatives we find that the antiderivative of $\sin(x)$ is

$$-\cos(x) + C = F(x),$$

where C is an arbitrary constant. The integral is the difference between the value of the antiderivative function at the upper limit and at the lower limit:

$$\begin{aligned} I &= F(\pi) - F(0) = -\cos(\pi) + C - [-\cos(0) + C] \\ &= -\cos(\pi) + \cos(0) = -(-1) + 1 = 2. \end{aligned}$$

The constant C cancels because it occurs with the same value in both occurrences of the antiderivative function. ◄

This example illustrates an important fact: A definite integral is not a function of its integration variable, called x in this case. Its value depends only on what values are chosen for the limits and on what function occurs under the integral sign. It is called a *functional*, or a function of a function, because its value depends on what function is chosen for the integrand function.

EXERCISE 5.3 ► Find the numerical value of the definite integral

$$\int_0^{1} e^x\, dx.$$

◄

The Definite Integral as an Area

We will now show that a definite integral is equal in value to an area between the x axis and the curve representing the integrand function in a graph. We return to Eq. (5.17), which gives an approximation to a definite integral. Figure 5.2 shows the situation with $n = 3$.

The curve in the figure is the curve representing the integrand function $f(x)$. Each term in the sum is equal to the area of a rectangle with height $f(x_k)$ and width Δx, so that the sum is equal to the shaded area under the bar graph in the figure. As the limit of Eq. (5.20) is taken, the number of bars between $x = x_0$ and $x = x'$ becomes larger and larger, while the width Δx becomes smaller and smaller. The roughly triangular areas between the bar graph and the curve become smaller and smaller, and although there are more and more of them their total area shrinks to zero as the limit is taken. The integral thus becomes equal to the area bounded by the x axis, the curve of the integrand function, and the vertical lines at the limits $x = x_0$ and $x = x'$.

Figure 5.2 shows a case in which all values of the integrand function are positive. If $x_0 < x'$, the increment Δx is always taken as positive. If the integrand function is negative in some region, we must take the area in that region as negative.

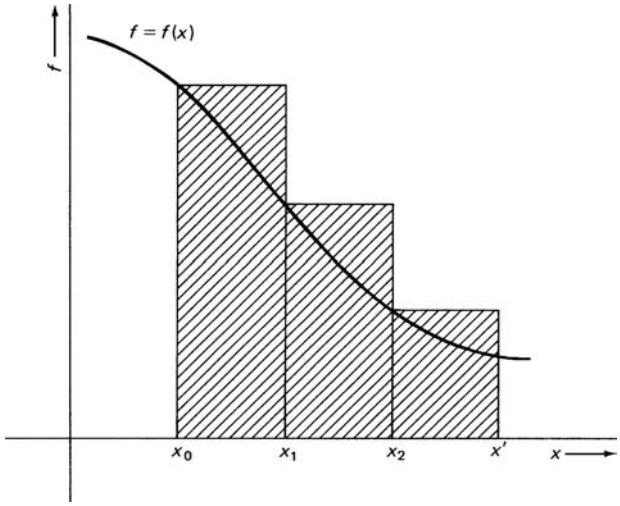

Figure 5.2 ► The area under a bar graph and the area under a curve.

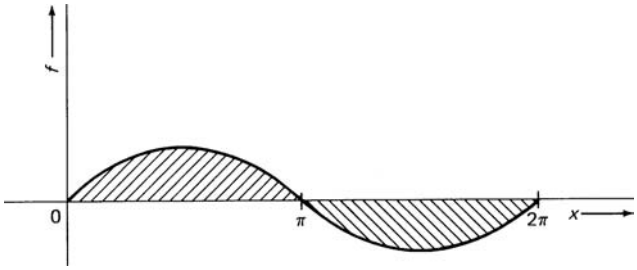

Figure 5.3 ► A graph of $f = \sin(x)$ for Example 5.6

EXAMPLE 5.6 Find the area bounded by the x axis and the curve representing

$$f(x) = \sin(x),$$

(a) between $x = 0$ and $x = 2\pi$. (b) between $x = 0$ and $x = \pi$

SOLUTION ► The graph of the function is shown in Fig. 5.3.

(a)

$$\begin{aligned} area &= \int_0^{\pi} \sin(x)\, dx = -\cos(\pi) - [-\cos(0)] \\ &= 2. \end{aligned}$$

(b)

$$\begin{aligned} area &= \int_0^{2\pi} \sin(x)\, dx = -\cos(2\pi) - [-\cos(0)] \\ &= -(1) - [-(-1)] = 0. \end{aligned}$$

◄

When we found the value of the integral from the antiderivative function, we omitted the constant term that generally must be present in the antiderivative function. This constant would have canceled out, so we left it out from the beginning.

EXERCISE 5.4 ▶ Find the following areas by computing the values of definite integrals:

(a) The area bounded by the curve representing $y = x^3$, the positive x axis, and the line $x = 3$.

(b) The area bounded by the straight line $y = 2x + 3$, the x axis, the line $x = 1$, and the line $x = 4$.

(c) The area bounded by the parabola $y = 4 - x^2$ and the x axis. You will have to find the limits of integration.

◀

Before the advent of programmable computers and electronic calculators, numerical approximations to integrals were sometimes made by drawing an accurate graph of the integrand function and directly measuring the appropriate area in the graph. There were three practical ways to do this. One was by simply counting squares on the graph paper. Another was by cutting out the area to be determined and weighing this piece of graph paper and also weighing another piece of known area from the same sheet. A third was by using a mechanical device called a *planimeter*, which registers an area on a dial after a stylus is moved around the boundary of the area.

Such procedures are now seldom used, since numerical approximations can be done quickly and easily with computer software.

EXERCISE 5.5 ▶ Find the approximate value of the integral

$$\int_0^1 e^{-x^2} dx$$

by making a graph of the integrand function and measuring an area. ◀

Rules about Integrals

The following rules can be understood by considering the relation between integrals and areas in graphs of integrand functions:

1. A definite integral over the interval (a, c) is the sum of the definite integrals over the intervals (a, b) and (b, c):

$$\int_a^c f(x)\,dx = \int_a^b f(x)\,dx + \int_b^c f(x)\,dx. \tag{5.23}$$

This fact is illustrated in Fig. 5.4. The integral on the left-hand side of Eq. (5.23) is equal to the entire area shown, and each of the two terms on the right-hand side is equal to one of the two differently shaded areas that combine to make the entire area.

2. If the two limits of integration are interchanged, the resulting integral is the negative of the original integral. In Eq. (5.22), we assumed that $x_0 < x'$, so that Δx would be positive. If the lower limit x_0 is larger than the upper limit of integration x', Δx must be taken as negative, reversing the sign of the area

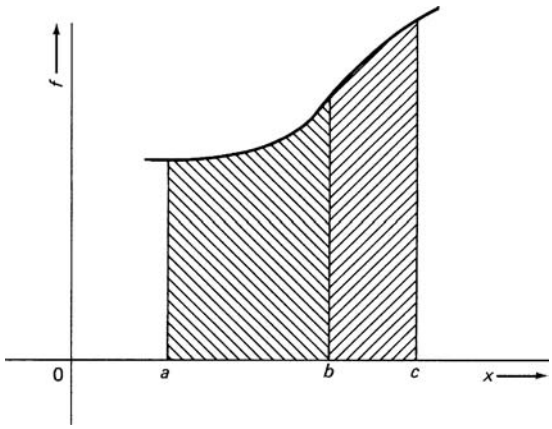

Figure 5.4 ► Figure to illustrate Eq. (5.23).

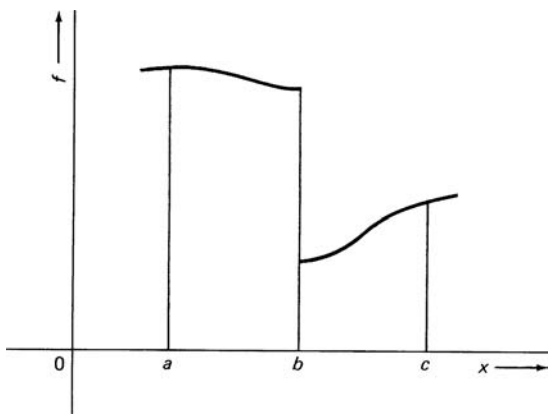

Figure 5.5 ► An integrand function that is discontinuous at $x = b$.

in the graph. Therefore,

$$\int_a^b f(x)dx = -\int_b^a f(x)\,dx. \tag{5.24}$$

Use of this fact makes Eq. (5.23) usable for any real values of a, b, and c. It is not necessary for b to lie between a and c.

3. The presence of a finite step discontinuity in an integrand function does not prevent us from carrying out the process of integration. In this regard, integration differs from differentiation. Figure 5.5 illustrates the situation. If the discontinuity is at $x = b$, we simply apply Eq. (5.23) and find that the integral is given by the integral up to $x = b$ plus the integral from $x = b$ to the end of the interval.

4. If an integrand function consists of a constant times some other function, the constant can be factored out of the integral:

$$\int_a^b cf(x)\,dx = c\int_a^b f(x)\,dx. \tag{5.25}$$

5. An *odd function* is one that obeys the relation

$$f(-x) = -f(x). \tag{5.26}$$

The integral of an odd function from $-c$ to c vanishes, where c is a constant. In this case, the area above the axis exactly cancels the area below the axis, so that

$$\int_{-c}^{c} f(x)\,dx = 0 \quad (f(x) \text{ odd}), \tag{5.27}$$

The sine function and the tangent function are examples of odd functions, as defined in Eqs. (2.10) and (2.12).

EXERCISE 5.6 ▶ Draw a rough graph of $f(x) = xe^{-x^2}$ and satisfy yourself that this is an odd function. Identify the area in this graph that is equal to the following integral and satisfy yourself that the integral vanishes:

$$\int_{-2}^{2} xe^{-x^2}\,dx = 0.$$

◀

6. An *even function* is one that obeys the relation

$$f(-x) = f(x). \tag{5.28}$$

The integral of an even function from $-c$ to c is twice the integral from 0 to c. In this case the area between c and 0 is equal to the area between 0 and c, so that

$$\int_{-c}^{c} f(x)\,dx = 2\int_{0}^{c} f(x)\,dx \quad (f(x) \text{ even}), \tag{5.29}$$

where c is any real constant. The cosine function is an example of an even function.

EXERCISE 5.7 ▶ Draw a rough graph of $f(x) = e^{-x^2}$. Satisfy yourself that this is an even function. Identify the area in the graph that is equal to the definite integral

$$I_1 = \int_{-1}^{1} e^{-x^2}\,dx$$

and satisfy yourself that this integral is equal to twice the integral

$$I_2 = \int_{0}^{1} e^{-x^2}\,dx.$$

◀

If you have an integrand that is a product of several factors, you can use the following facts:

a. The product of two even functions is an even function.

b. The product of two odd functions is an even function.

c. The product of an odd function and an even function is an odd function.

The rules about odd and even functions are valid if the function is either even or odd about the center of the integration interval, even if the center of the interval is not at the origin.

EXERCISE 5.8 ▶ The quantum-mechanical wave functions of a particle in a box of length a are either even or odd functions. For example, if the box extends from $x = 0$ to $x = a$, the two lowest-energy wave functions are

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$
$$\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$$

(a) By drawing rough graphs, satisfy yourself that ψ_1 is even about the center of the box—that is, $\psi_1(x) = \psi_1(a - x)$. Satisfy yourself that ψ_2 is odd about the center of box.

(b) Draw a rough graph of the product $\psi_1\psi_2$ and satisfy yourself that the integral of this product from $x = 0$ to $x = a$ vanishes.

◀

If the upper limit of a definite integral is considered to be a variable, we can write

$$\frac{d}{db}\left[\int_a^b f(x)\,dx\right] = f(b), \tag{5.30}$$

where a is considered to be a constant. If the lower limit is considered to be a variable, we can write

$$\frac{d}{da}\left[\int_a^b f(x)\,dx\right] = -f(a), \tag{5.31}$$

where b is considered to be a constant. If a and b are functions of some variable c (not the variable of integration, x), then

$$\boxed{\frac{d}{dc}\left[\int_a^b f(x)\,dx\right] = f(b)\frac{db}{dc} - f(a)\frac{da}{dc}}. \tag{5.32}$$

These equations follow from Eq. (5.22). Equation (5.32) also comes from the chain rule, Eq. (4.29), p. 105.

5.3 Indefinite Integrals: Tables of Integrals

Let us consider the upper limit x' in Eq. (5.22) to be variable and the lower limit to be fixed and equal to a:

$$\int_a^{x'} f(x)\,dx = F(x') + C.$$

The quantity C is a constant that is equal to $-f(a)$. It is called the *constant of integration*. Its value is arbitrary if a is arbitrary. We omit mention of a and write

$$\int^{x'} f(x)\,dx = F(x') + C. \tag{5.33}$$

This integral is called an *indefinite integral*, since the lower limit is unspecified and the upper limit is variable. The indefinite integral is the same as the antiderivative function. Large tables of indefinite integrals have been compiled. Appendix E is a brief version of such a table. In most such tables, the notation of Eq. (5.33) is not maintained. The entries are written in the form

$$\int f(x)\,dx = F(x). \tag{5.34}$$

This equation is an abbreviation for Eq. (5.33). The upper limit and the constant of integration are usually omitted from table entries, and the same symbol is usually used for the variable of integration and for the argument of the integral function F. However, you should remember that an arbitrary constant C can be added to the right-hand side of Eq. (5.34).

The same information is contained in a table of indefinite integrals as is contained in a table of derivatives. However, we can get by with a fairly short table of derivatives, since we have the chain rule and other facts listed in Section 4.4. Antiderivatives are harder to find, so it is good to have a separate table of indefinite integrals, arranged so that similar integrand functions occur together.

EXAMPLE 5.7 Using a table, find the indefinite integrals:

(a) $\displaystyle\int \frac{dx}{a^2 + x^2}$ (b) $\displaystyle\int x \sin^2(x)\,dx$

(c) $\displaystyle\int xe^{ax}\,dx$

SOLUTION ► From Appendix E or any published table of indefinite integrals,

(a) $\displaystyle\int^{x'} \frac{dx}{a^2 + x^2} = \frac{1}{a}\arctan\left(\frac{x'}{a}\right) + C$

(b) $\displaystyle\int^{x'} x \sin^2(x)\,dx = \frac{x'^2}{4} - \frac{x' \sin(2x')}{4} - \frac{\cos(2x')}{8} + C$

(c) $\displaystyle\int^{x'} xe^{ax}\,dx = \frac{e^{ax'}}{a^2}(ax' - 1) + C.$

◄

EXERCISE 5.9 ► Show by differentiation that the functions on the right-hand sides of the equations in Example 5.7 yield the integrand functions when differentiated. ◄

Since the indefinite integral is the antiderivative function, it is used to find a definite integral in the same way as in Section 5.2. If x_1 and x_2 are the limits of the definite integral,

$$\begin{aligned}\int_{x_1}^{x_2} f(x)\,dx &= \int_{x_1}^{a} f(x)\,dx + \int_{a}^{x_2} f(x)\,dx = \int_{a}^{x_2} f(x)\,dx - \int_{a}^{x_1} f(x)\,dx \\ &= F(x_2) - C - [F(x_1) - C] = F(x_2) - F(x_1).\end{aligned} \tag{5.35}$$

Equation (5.35) is the same as Eq. (5.22).

EXAMPLE 5.8 Using a table of indefinite integrals, find the definite integral

$$\int_0^{\pi/2} \sin(x)\cos(x)\,dx.$$

SOLUTION ► From Appendix C we find that the indefinite integral is $\sin^2(x)/2$,

$$\int_0^{\pi/2} \sin(x)\cos(x)\,dx = \left.\frac{\sin^2(x)}{2}\right|_0^{\pi/2} = \frac{1}{2}\left[\sin^2\left(\frac{\pi}{2}\right) - \sin^2(0)\right]$$
$$= \frac{1}{2}(1-0) = \frac{1}{2}.$$

We have used the common notation

$$F(x)\Big|_a^b = F(b) - F(a). \tag{5.36}$$

◄

EXERCISE 5.10 ► Using a table of indefinite integrals, find the definite integrals.

(a) $\displaystyle\int_0^3 \cosh(2x)\,dx$ (b) $\displaystyle\int_1^2 \frac{\ln(3x)}{x}\,dx$

(c) $\displaystyle\int_0^5 4^x\,dx.$

◄

In addition to tables of indefinite integrals, there are tables of definite integrals. Some tables are listed at the end of the book, and Appendix F is a short version of such a table. Some of the entries in these tables are integrals that could be worked out by using a table of indefinite integrals, but others are integrals that cannot be obtained as indefinite integrals, but by some particular method can be worked out for one set of limits. An example of such an integral is worked out in Appendix G. Tables of definite integrals usually include only sets of limits such as $(0, 1)$, $(0, \pi)$, $(0, \frac{\pi}{2})$, and $(0, \infty)$. The last set of limits corresponds to an improper integral, which is discussed in the next section.

5.4 Improper Integrals

So far we have assumed that both limits of a definite integral are finite and that the integrand function does not become infinite inside the interval of integration. If either of these conditions is not met, an integral is said to be an *improper integral*. For example,

$$I = \int_0^\infty f(x)\,dx \tag{5.37}$$

is an improper integral because its upper limit is infinite. We must decide what is meant by the infinite upper limit in Eq. (5.37), because Eq. (5.20) cannot always

be modified by inserting ∞ into the equation instead of x'. We define

$$\int_0^\infty f(x)\,dx = \lim_{b\to\infty} \int_0^b f(x)\,dx. \tag{5.38}$$

In this mathematical limit, the upper limit of integration becomes larger and larger without bound. Notice that the word "limit" has several definitions, and two of them unfortunately occur here in the same sentence.

If the integral approaches more and more closely to some finite value as the upper limit is made larger and larger, we say that the limit exists and that the improper integral is equal to this finite value. The improper integral is said to *converge* to the value that is approached. Some improper integrals do not converge. The magnitude of the integral can become larger and larger without bound as the limit of integration is made larger and larger. In other cases, the integral oscillates repeatedly in value as the limit of integration is made larger and larger. We say in both of these cases that the integral *diverges*.

In addition to the type of improper integral shown in Eq. (5.37), some improper integrals have a lower limit of integration that is made to approach $-\infty$, while the upper limit is finite. Other improper integrals have a lower limit that is made to approach $-\infty$, while the upper limit is made to approach $+\infty$. Just as in the case of Eq. (5.38), if the integral approaches a finite value more and more closely as the limit or limits approach infinite magnitude, the improper integral is said to converge to that value.

Another kind of improper integral has an integrand function that becomes infinite somewhere in the interval of integration. For example,

$$I = \int_0^1 \frac{1}{x^2}\,dx \tag{5.39}$$

is an improper integral because the integrand function becomes infinite at $x = 0$. This improper integral is defined by

$$\int_0^1 \frac{1}{x^2}\,dx = \lim_{a\to 0^+} \int_a^1 \frac{1}{x^2}\,dx. \tag{5.40}$$

Just as in the other cases, if the integral grows larger and larger in magnitude as the limit is taken, we say that it diverges. If the limit exists, we say that the improper integral converges to that limit. The situation is similar if the point at which the integrand becomes infinite is at the upper limit of integration. If it is within the interval of integration, break the interval into two subintervals so that the point at which the integrand function diverges is at the lower limit of one subinterval and at the upper end of the other subinterval.

The two principal questions that we need to ask about an improper integral are:

1. Does it converge?
2. If so, what is its value?

EXAMPLE 5.9 Determine whether the following improper integral converges, and if so, find its value:

$$\int_0^\infty e^{-x}\,dx.$$

SOLUTION ►

$$\int_0^\infty e^{-x}\,dx = \lim_{b\to\infty}\int_0^b e^{-x}\,dx = \lim_{b\to\infty}\left[-e^{-x}\right]\Big|_0^b$$
$$= \lim_{b\to\infty} -\left(e^{-b}-1\right) = 0+1 = 1.$$

The integral converges to the value 1. ◄

EXERCISE 5.11 ► Determine whether each of the following improper integrals converges, and if so, determine its value:

(a) $\int_0^1 \left(\frac{1}{x}\right)\,dx$ (b) $\int_0^\infty \sin(x)\,dx$

(c) $\int_0^\infty \left(\frac{1}{1+x}\right)\,dx$ (d) $\int_0^\infty \frac{1}{x^3}\,dx$

(e) $\int_{-\infty}^0 e^x\,dx$

◄

5.5 Methods of Integration

In this section, we discuss three methods that can be used to transform an integral that is not exactly like any integral you can find in a table into one that is.

The Method of Substitution

In this method a *change of variables* is performed in order to obtain a simpler integral. The integrand function is expressed in terms of the new independent variable, which then becomes the variable of integration.

EXAMPLE 5.10 Find the integral

$$\int_0^\infty xe^{-x^2}\,dx$$

without using a table of integrals.

SOLUTION ► We have x^2 in the exponent, which suggests using $y = x^2$ as a new variable. If $y = x^2$, then $dy = 2x\,dx$, or $x\,dx = \frac{1}{2}dy$,

$$\int_0^\infty xe^{-x^2}\,dx = \frac{1}{2}\int_{x=0}^{x=\infty} e^{-y}\,dy = \frac{1}{2}\int_0^\infty e^{-y}\,dy$$
$$= -\frac{1}{2}e^{-y}\Big|_0^\infty = -\frac{1}{2}(0-1) = \frac{1}{2}.$$

To review the solution of this example: First a new variable was chosen that looked as though it would give a simpler integrand function. Next, the integrand function was expressed in terms of this variable. The differential of the integration variable was also reexpressed. The limits of integration were then expressed in terms of the new variable, making the limits equal to the values of the new variable that correspond to the values of the old variable at the old limits. The final step was to compute the new integral, which is equal to the old integral. ◄

EXAMPLE 5.11 Find the integral

$$\int_0^{1/2} \frac{dx}{2-2x}$$

without using a table of integrals.

SOLUTION ► We let $y = 2-2x$, in order to get a simple denominator. With this, $dy = -2dx$, or $dx = -dy/2$. When $x = 0$, $y = 2$, and when $x = \frac{1}{2}$, $y = 1$,

$$\begin{aligned}\int_0^{1/2} \frac{1}{2-2x}\,dx &= -\frac{1}{2}\int_2^1 \frac{1}{y}\,dy = \frac{1}{2}\int_1^2 \frac{1}{y}\,dy \\ &= \frac{1}{2}\ln(y)\Big|_1^2 = \frac{1}{2}[\ln(2) - \ln(1)] \\ &= \frac{1}{2}\ln(2)\,.\end{aligned}$$

◄

EXERCISE 5.12 ► Find the integral

$$\int_0^{\pi} e^{\sin(\theta)}\cos(\theta)\;d\theta$$

without using a table of integrals. ◄

Integration by Parts

This method, which is also called *partial integration*, consists of application of the formula

$$\boxed{\int u\frac{dv}{dx}\,dx = uv - \int v\frac{du}{dx} + C} \tag{5.41}$$

or the corresponding formula for definite integrals

$$\boxed{\int_a^b u\frac{dv}{dx}\,dx = u(x)\,v(x)|_a^b - \int_a^b v\frac{du}{dx}}. \tag{5.42}$$

In these formulas, u and v must be functions of x that are differentiable everywhere in the interval of integration.

We can derive Eq. (5.41) by use of Eq. (4.21), which gives the derivative of the product of two functions:

$$\frac{d}{dx}(uv) = u\frac{dv}{dx} + v\frac{du}{dx}.$$

The antiderivative of either side of this equation is just $uv + C$, where C is an arbitrary constant. We can write the indefinite integral

$$\int \frac{d(uv)}{dx}\,dx = \int u\frac{dv}{dx}\,dx + \int v\frac{du}{dx}\,dx = u(x)\,v(x) + C.$$

This is the same as Eq. (5.41).

EXAMPLE 5.12 Find the indefinite integral

$$\int x \sin(x)\, dx$$

without using a table.

SOLUTION ► There are two choices. We could let $u(x) = x$ and $\sin(x) = dv/dx$, or we could let $u(x) = \sin(x)$ and $x = dv/dx$. We make the first choice because the antiderivative of x is $x^2/2$, which will lead to a more complicated integral than the one containing x. With this choice

$$\begin{aligned} \frac{du}{dx} &= 1 \qquad \text{and} \qquad v = -\cos(x) \\ \int x \sin(x)\, dx &= -x\cos(x) + \int \cos(x)\, dx \\ &= -x\cos(x) + \sin(x) + C. \end{aligned}$$

◄

EXERCISE 5.13 ► Find the integral

$$\int_0^{\pi} x^2 \sin(x)\, dx$$

without using a table. You will have to apply partial integration twice. ◄

The fundamental equation of partial integration, Eq. (5.41), is sometimes written with differentials instead of derivatives:

$$\boxed{\int u\, dv = uv - \int v\, du + C} \tag{5.43}$$

The Method of Partial Fractions

This method uses an algebraic procedure for turning a difficult integrand into a sum of two or more easier functions. It works with an integral of the type

$$I = \int \frac{P(x)}{Q(x)}\, dx, \tag{5.44}$$

where $P(x)$ and $Q(x)$ are polynomials in x. The highest power of x in P must be lower than the highest power of x in Q. However, if this is not the case, you can proceed by performing a long division, obtaining a polynomial plus a remainder, which will be a quotient of polynomials that does obey the condition. The polynomial can be integrated easily, and the remainder quotient can be handled with the method of partial fractions.

The first step in the procedure is to factor the denominator, $Q(x)$, into a product of polynomials of degree 1 and 2. A polynomial of degree 1 is an expression of the form $ax + b$, and a polynomial of degree 2 is $ax^2 + bx + c$. We first assume that all of the factors are of degree 1, so that

$$Q(x) = (a_1x + b_1)(a_2x + b_2)(a_3x + b_3)\cdots(a_nx + b_n), \tag{5.45}$$

where all the a's and b's are constants.

The fundamental formula of the method of partial fractions is a theorem of algebra that says that if $Q(x)$ is given by Eq. (5.45) and $P(x)$ is of lower degree than $Q(x)$, then

$$\boxed{\frac{P(x)}{Q(x)} = \frac{A_1}{a_1x + b_1} + \frac{A_2}{a_2x + b_2} + \cdots + \frac{A_n}{a_nx + b_n}}, \tag{5.46}$$

where $A_1, A_2, \ldots, A_n$, are all constants.

Equation (5.46) is applicable only if all the factors in $Q(x)$ are distinct from each other. If the same factor occurs more than once, Eq. (5.46) must be modified. If the factor $a_1x + b_1$ occurs m times in the denominator, we write

$$\frac{P(x)}{(a_1x + b_1)^m} = \frac{A_1}{a_1x + b_1} + \frac{A_2}{(a_1x + b_1)^2} + \cdots + \frac{A_m}{(a_1x + b_1)^m} \tag{5.47}$$

If other factors occur in the denominator, we must add other terms as in Eq. (5.46).

Sometimes a factor of degree 2 occurs that cannot easily be factored. If $Q = a_1x^2 + b_1x + c_1$, we must write

$$\frac{P(x)}{Q(x)} = \frac{A_1x + B_1}{a_1x^2 + b_1x + c_1} + \text{other terms as in Eqs. (5.46) and (5.47)} \tag{5.48}$$

If Q contains other factors we must add other terms as in Eqs. (5.46) and (5.47).

EXAMPLE 5.13 Apply Eq. (5.46) to

$$\int \frac{6x - 30}{x^2 + 3x + 2}\,dx.$$

SOLUTION ► The denominator can be factored, so we write

$$\frac{6x - 30}{x^2 + 3x + 2} = \frac{A_1}{x + 2} + \frac{A_2}{x + 1}.$$

We need to solve for A_1 and A_2 so that this equation will be satisfied for all values of x. We multiply both sides of the equation by $(x + 2)(x - 1)$:

$$6x - 30 = A_1(x + 1) + A_2(x + 2).$$

Since this equation must be valid for all values of x, we can get a different equation for each value of x. If we let $x = 0$, we get

$$-30 = A_1 + 2A_2. \tag{5.49}$$

If we let x become very large, so that the constant terms can be neglected, we obtain

$$6x = A_1x + A_2x$$

or

$$6 = A_1 + A_2. \tag{5.50}$$

Equations (5.49) and (5.50) can be solved simultaneously to obtain

$$A_1 = 42, \quad A_2 = -36. \tag{5.51}$$

Our result is

$$\int \frac{6x - 30}{x^2 + 3x + 2} = \int \frac{42}{x + 2}\,dx - \int \frac{36}{x + 1}\,dx. \tag{5.52}$$

◄

EXERCISE 5.14 ► Solve Eq. (5.49) and (5.50) simultaneously to obtain Eq. (5.51). ◄

EXERCISE 5.15 ► Find the indefinite integrals on the right-hand side of Eq. (5.52). ◄

The Apart statement in Mathematica carries out the decomposition into partial fractions automatically. See Chapter 3.

EXERCISE 5.16 ► Use Mathematica to verify the partial fractions in the above example. ◄

The following example shows a case in the study of chemical reaction rates that requires the use of partial fractions.

EXAMPLE 5.14 Consider a chemical reaction

$$a\mathrm{A}+b\mathrm{B} \longrightarrow c\mathrm{C},$$

where the capital letters are abbreviations for some chemical formulas and the lowercase letters are abbreviations for the stoichiometric coefficients that balance the equation. Assume that the rate of the reaction is given by the *rate law*

$$-\frac{1}{a}\frac{d\,[\mathrm{A}]}{dt} = k_f\,[\mathrm{A}]\,[\mathrm{B}]\,,$$

where k_f is a function of temperature called the *rate constant* and where [A] represents the molar concentration of A and [B] represents the molar concentration of B. This rate law is said to be *second order overall, first order in A,* and *first order in B.* Carry out the integration of this rate law using the method of partial fractions.

SOLUTION ► In order to proceed, we express [A] and [B] in terms of a single variable:

$$[\mathrm{A}] = [\mathrm{A}]_0 - ax$$

and

$$[\mathrm{B}] = [\mathrm{B}]_0 - bx,$$

where the initial values of the concentrations are labeled with a subscript 0. We have

$$-\frac{1}{a}\frac{d\,[\mathrm{A}]}{dt} = \frac{dx}{dt}.$$

In the case that the reactants are not mixed in the stoichiometric ratio, we manipulate the rate expression into the form, where we have multiplied by dt and recognized that $(dx/dt)\,dt = dx$,

$$\frac{1}{([\mathrm{A}]_0 - ax)\,([\mathrm{B}]_0 - bx)}\,dx = k_f\,dt.$$

We write

$$\frac{1}{([\mathrm{A}]_0 - ax)\,([\mathrm{B}]_0 - bx)} = \frac{G}{[\mathrm{A}]_0 - ax} + \frac{H}{[\mathrm{B}]_0 - bx}.$$

The constants G and H are found to be

$$G = \frac{1}{[\mathrm{B}]_0 - b\,[\mathrm{A}]_0\,/a} \qquad \text{and} \qquad H = \frac{1}{[\mathrm{A}]_0 - a\,[\mathrm{B}]_0\,/b}.$$

When these expressions are substituted into the rate expression, a definite integration gives

$$\frac{1}{a\,[\mathrm{B}]_0 - b\,[\mathrm{A}]_0}\ln\left(\frac{[\mathrm{B}]_t\,[\mathrm{A}]_0}{[\mathrm{A}]_t\,[\mathrm{B}]_0}\right) = k_f t.$$

◄

EXERCISE 5.17 ► Show that the expressions for G and H are correct. Verify your result using Mathematica if it is available. ◄

The methods presented thus far in this chapter provide an adequate set of tools for the calculation of most integrals that will be found in a physical chemistry course. In applying these methods, it is probably best to proceed as follows:

1. If the limits are 0 and ∞ or 0 and π, or something else quite simple, look first in a table of definite integrals.

2. If this does not work, or if the limits were not suitable, look in a table of indefinite integrals.

3. If you do not find the integral in a table, try the method of substitution.

4. If you still have not obtained the integral, see if the method of partial fractions is applicable and use it if you can.

5. If this did not work, manipulate the integrand into a product of two factors and try the method of partial integration.

6. If all these things have failed, or if they could not be attempted, do a numerical approximation to the integral. This is discussed in the next section.

Integration with Mathematica

Mathematica can carry out indefinite integrals symbolically. For example, the input and output statements for the indefinite integral of sin(x) are

```
In[1]: =Clear[x]
       Integrate[Sin[x],x]
Out[1] =–Cos[x]
```

Mathematica appears to contain just about every indefinite integral that exists in tables. However, if you specify an integrand for which no indefinite integral exists or one that is not in Mathematica's tables, Mathematica will print out what you gave it.

Mathematica can also carry out definite integrals. Definite integrals are obtained by adding the limits to the input entry. To obtain the definite integral of sin(x) from $x = 0$ to $x = \pi$, the input and output statements are

```
In[1]: =Clear[x]
       Integrate[Sin[x],{x,0,Pi}]
Out[1] =2
```

5.6 Numerical Integration

There are two cases for which a numerical approximation to a definite integral must be used. In one case the integrand function does not possess an antiderivative function that you can find in a table or can work out. For example, one integrand function for which no antiderivative functions exists is e^{-x^2} (see Appendix G). In the other case the integrand function is represented approximately by a set of data points instead of by a formula. In ether case, there are several approximation methods that we can use to obtain a definite integral.

The Bar-Graph Approximation

We begin with Eq. (5.21):

$$\int_a^b f(x)\,dx = \lim_{\substack{\Delta x\to 0, n\to\infty, \\ (n\Delta x = x' - x_0)}} \sum_{k=0}^{n-1} f\,(a + j\Delta x)\;\Delta x. \tag{5.53}$$

If we do not take the limit but allow n to be some convenient finite number, the resulting equation will be approximately correct. Let us consider an example the integral of e^{-x^2} from $x = 1$ to $x = 2$. We apply an approximate version of Eq. (5.53) with $n = 10$. The result is

$$\int_1^2 e^{-x^2}\,dx \approx \sum_{j=0}^{9} \exp\left[-(1 + 0.1j)^2\right](0.1) = 0.15329. \tag{5.54}$$

This result is represented by the area under a bar graph with bars of unit width such as in Fig. 5.2. We call this approximation the *bar-graph approximation*. The integral is equal to the area under the graph of the integrand function, so the bar-graph approximation is in error by the area of the roughly triangular areas between the bar graph and the curve representing the integrand function. The error in Eq. (5.54) is about 15%, since the correct value of this integral is 0.13525726 to eight significant digits.

Each bar in Fig. 5.2 is called a *panel*. The bar-graph approximation can be made more nearly accurate by increasing the number of panels and decreasing their width, but the rate of improvement can be quite slow. For example, if we take $n = 20$ and $\Delta x = 0.05$, we get 0.14413 for the bar-graph approximation to the integral in Eq. (5.54), which is still in error by about 6%. If we take $n = 100$ and $\Delta x = 0.01$, we get 0.13701, which is still wrong by about 1%.

The Trapezoidal Approximation

One way to improve on the bar-graph approximation is to take the height of the rectangles as equal to the value of the integrand function near the middle of the panel. In the *trapezoidal approximation* the height of the bar is taken as the average of the values of the function at the two sides of the panel. This gives an area for the panel that is the same as that of a trapezoid whose upper corners match the integrand function at the sides of the panel, as shown in Fig. 5.6.

$$\int_a^b f(x)\,dx \approx \frac{f\,(a)\,\Delta x}{2} + \sum_{k=1}^{n-1} f\,(a + k\Delta x)\,\Delta x + \frac{f\,(b)\,\Delta x}{2}. \tag{5.55}$$

As expected, the trapezoidal approximation gives more nearly correct values than does the bar-graph approximation, for the same number of panels. For 10 panels, the trapezoidal approximation gives a result of 0.135810 for the integral in Eq. (5.54). For 100 panels, the trapezoidal approximation is correct to five significant digits.

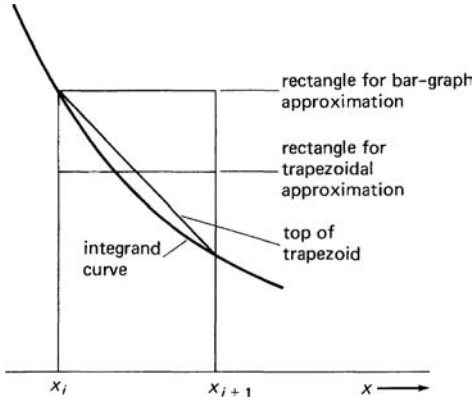

Figure 5.6 ► Figure to illustrate the trapezoidal approximation (enlarged view of one panel shown).

EXERCISE 5.18 ► Using the trapezoidal approximation with five panels, calculate the value of the integral

$$\int_{10}^{20} 2x^2\,dx.$$

Calculate the exact value of the integral for comparison. ◄

Simpson's Rule

In the bar-graph approximation, we used only one value of the integrand for each panel. In the trapezoidal approximation, we used two values for each panel, corresponding to a line segment fitting the integrand curve at the edges of the panel. If three points in a plane are given, there is one and only one parabola that can be drawn through all three. In *Simpson's rule*, we take the panels two at a time, construct a parabola through the three points, find the area under the parabola, and sum these areas to approximate the integral. A parabolic curve is likely to fall closer to the integrand curve than a straight line, so we expect this to give a better approximation than the trapezoidal approximation, and it usually does. We must have an even number of panels to use this method.

We let $f_0 = f(a)$, $f_1 = f(a + \Delta x)$, $f_2 = f(a + 2\Delta x)$, and so on, and use the formula for the area under a parabola to obtain as our final result

$$\int_a^b f(x)\,dx \approx \frac{(f_0 + 4f_1 + 2f_2 + 4f_3 + \cdots + 4f_{n-1} + f_n)\,\Delta x}{3}. \qquad (5.56)$$

Notice the pattern, with alternating coefficients of 2 and 4, except for the first and last values of the integrand.

This version of Simpson's rule is sometimes called *Simpson's one-third rule* because of the 3 in the denominator. There is another version, called *Simpson's five-eighths rule*, which corresponds to fitting third-degree polynomials to four points at a time.

EXERCISE 5.19 ► Apply Simpson's rule to the integral of Exercise 5.18, using two panels. Since the integrand curve is a parabola, your result should be exactly correct. ◄

There is another widely used way to obtain a numerical approximation to a definite integral, known as *Gauss quadrature*. In this method, the integrand function must be evaluated at particular unequally spaced points on the interval of integration. We will not discuss this method, but you can read about it in books on numerical analysis.

So far, we have assumed that the integrand function was known so that it could be evaluated at the required points. Most of the applications of numerical integration in physical chemistry are to integrals where the integrand function is not known exactly, but is known only approximately from experimental measurements at a few points on the interval of integration. If there are an odd number of data points that are equally spaced, we can apply Simpson's rule.

EXERCISE 5.20 ► In thermodynamics, it is shown that the entropy change of a system that is heated at constant pressure from temperature T_1 to temperature T_2 is given by

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p}{T}\, dT, \tag{5.57}$$

where C_p is the constant-pressure heat capacity and T is the temperature on the Kelvin scale. Calculate ΔS for the heating of 1.00 mol of solid zinc from 20.0 K to 100.0 K, using the following data:

T / K	$C_{\mathbf{p}}$ / J K^{-1}mol^{-1}	T / K	$C_{\mathbf{p}}$ / J K^{-1}mol^{-1}
20	1.70	70	15.43
30	4.966	80	16.87
40	8.171	90	18.11
50	11.18	100	19.15
60	13.60		

◄

Numerical Integration with Mathematica

If you give Mathematica a definite integral with an integrand that has no indefinite integral in Mathematica's tables, Mathematica will simply return your input statement. To carry out a numerical approximation to the integral and obtain a numerical value, use the NIntegrate statement, which has the form:

NIntegrate[integrand function, {x,lower limit,upper limit}].

EXAMPLE 5.15 Use Mathematica to obtain the integral

$$\frac{2}{\sqrt{\pi}} \int_0^1 e^{-x^2} dx \tag{5.58}$$

SOLUTION ► We type the input statements:

```
Clear[x]
```

NIntegrate[(2/Sqrt[Pi])Exp[-x^2],{x,0,1}]

and press the "Enter" key. We obtain the output

Out[1]=0.842701

which is the value of erf(1). ◄

EXERCISE 5.21 ► Write Mathematica entries to obtain the following integrals:

(a) $\int \cos^3(x)dx$ (b) $\int_1^2 e^{5x^2}dx$

(c) $\int_0^{\pi} \sin[\cos(x)]dx$

◄

5.7 Probability Distributions and Mean Values

In this section, we discuss how to obtain certain average values using integration. There are several kinds of averages in common use. One type is the *median*, which is the value such that half of the set of values is greater than the median and half of the set is smaller than the median. The *mode* is the value that occurs most frequently in the set. We now discuss the calculation of a mean value by integration. The *mean* of a set of N values is defined as

$$\boxed{\bar{x} = \frac{1}{N}(x_1 + x_2 + x_3 + x_4 + \cdots + x_N)}, \tag{5.59}$$

where x_1, x_2, x_3, and so on, are the values to be averaged. The notation $\langle x \rangle$ is also used for the mean value.

EXERCISE 5.22 ► Calculate the mean of the integers beginning with 10 and ending with 20. ◄

There is another way to write the mean of a set of values if several of the members of the list are equal to each other. Let us arrange the members of our list so that the first M members of the list are all different from each other, and each of the other $N - M$ members is equal to some member of the first subset. Let N_i be the total number of members of the entire list that are equal to x_i, where x_i is one of the distinct values in the first subset. Equation (5.59) can be rewritten

$$\bar{x} = \frac{1}{N}(N_1x_1 + N_2x_2 + N_3x_3 + N_4x_4 + \cdots + N_Mx_M) \tag{5.60}$$

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{M} N_i x_i = \sum_{i=1}^{M} p_i x_i. \tag{5.61}$$

We again use the standard notation of a capital Greek sigma ($\sum$) for a sum, introduced in Eq. (5.17). The quantity p_i is equal to N_i/N and is the fraction of the members of the entire list that are equal to x_i. If we were to sample the entire list by choosing a member at random, the *probability* that this member would equal x_i

is given by p_i. The set of probabilities that we have defined adds up to unity:

$$\sum_{i=1}^{M} p_i = \sum_{i=1}^{M} \frac{N_i}{N} = \frac{1}{N} \sum_{i=1}^{M} N_i = 1. \tag{5.62}$$

A set of probabilities that adds up to unity is said to be *normalized*.

EXAMPLE 5.16 A quiz was given in a class with 100 members. The scores were as follows:

Score	# of students	Score	# of students
100	8	70	23
90	11	60	14
80	35	50	9

Find the mean score.

SOLUTION ►

$$\bar{s} = (0.08)(100) + (0.11)(90) + (0.35)(80) + (0.23)\,(70) + (0.14)(60) + (0.09)(50) = 74.9.$$

◄

If you have a set of values with considerable duplication, Eq. (5.61) is quicker and easier to use than Eq. (5.59).

It is also possible to take the mean of a function of the values in our set. For example, to form the mean of the squares of the values, we have

$$\overline{x^2} = \frac{1}{N}\left(x_1^2 + x_2^2 + x_3^2 + x_4^2 + \cdots + x_N^2\right) \tag{5.63}$$

$$= \frac{1}{N} \sum_{i=1}^{M} N_i x_i^2 = \sum_{i=1}^{M} p_i x_i^2. \tag{5.64}$$

Similarly, if $g = g(x)$ is any function defined for all values of x that occur in our list, the mean value of this function is given by

$$\boxed{\overline{g\,(x)} = \sum_{i=1}^{M} p_i g\,(x_i)}. \tag{5.65}$$

EXERCISE 5.23 ► Find the mean of the squares of the scores given in Example 5.16. Find also the square root of this mean, which is called the *root-mean-square* score. The *root-mean-square (rms)* value is another type of average. ◄

Probability Distributions

One of the important quantities in gas kinetic theory is the mean speed of molecules in a gas. The calculation of such a mean is a little more complicated than the case

of Eq. (5.61). The reasons for this are: (1) the speed of a molecule can take on any real nonnegative value, and (2) there are many molecules in almost any sample of a gas. Let's develop formulas to handle cases like this. Consider a variable x, which can take on any real values between $x = a$ and $x = b$. We divide the interval (a, b) into n subintervals. Look at the subinterval (x_i, x_{i+1}), which is the same as saying $x_i < x < x_{i+1}$. The interval can also be written $(x_i, x_i + \Delta x_i)$, where

$$\Delta x = x_{i+1} - x_i. \tag{5.66}$$

Let the fraction of all members of our sample that have values of x lying between x_i and x_{i+1} be called p_i. If Δx is quite small, p_i will be very nearly proportional to Δx. We write

$$p_i = f_i \Delta x. \tag{5.67}$$

The quantity f_i will not depend strongly on Δx. The mean value of x is given by Eq. (5.61):

$$\bar{x} \approx \sum_{i=0}^{n-1} p_i x_i = \sum_{i=0}^{n-1} x_i f_i \Delta x. \tag{5.68}$$

This equation is only approximately true, because we have multiplied the probability that x is in the subinterval $(x_i, x_i + \Delta x)$ by x_i, which is only one of the values of x in the subinterval. However, Eq. (5.68) can be made more and more nearly exact by making n larger and larger and Δx smaller and smaller in such a way that $n\Delta x$ is constant. In this limit, f_i becomes independent of Δx. We replace the symbol f_i by $f(x_i)$ and assume that $f(x_i)$ is an integrable function of x_i. It must be at least piecewise continuous. Our formula for the mean value of x now becomes an integral as defined in Eq. (5.21):

$$\bar{x} = \lim_{\substack{\Delta x \to 0, n \to \infty, \\ n\Delta x = b - a}} \sum_{i-0}^{n-1} x_i f(x_i)\, \Delta x = \int_a^b x f\,(x)\; dx. \tag{5.69}$$

The function $f(x)$ is called the *probability density*, or *probability distribution*, or sometimes the *distribution function*.

If we desire the mean value of a function of x—say, $g(x)$—the formula is analogous to Eq. (5.65),

$$\boxed{\overline{g\,(x)} = \int_a^b g(x) f(x)\, dx}. \tag{5.70}$$

For example, the mean of x^2 is given by

$$\overline{x^2} = \int_a^b x^2 f(x)\, dx. \tag{5.71}$$

As defined above, the probability density is *normalized*, which now means that

$$\int_a^b f(x)\, dx = 1. \tag{5.72}$$

It is possible to use a probability density that is not normalized, but if you do this, you must modify Eq. (5.70). For an unnormalized probability distribution

$$\boxed{\overline{g(x)} = \frac{\int_a^b g(x) f(x)\, dx}{\int_a^b f(x)\, dx} \qquad \begin{matrix}(\text{unnormalized} \\ \text{probability distribution})\end{matrix}}. \tag{5.73}$$

For a normalized probability distribution, the probability that x lies in the infinitesimal interval $(x, x + dx)$ is $f(x)\, dx$, which is the probability per unit length times the length of the infinitesimal interval. The fact that $f(x)$ is a probability per unit length is the reason for using the name "probability density" for it. Since all continuously variable values of x in some range are possible, a continuous probability distribution must apply to a set of infinitely many members. Such a set is called the *population* to which the distribution applies. The probability $f(x')\, dx$ is the fraction of the population that has its value of x lying in the region between x and $x' + dx$.

The most commonly used measure of the "spread" of a probability distribution is the *standard deviation*, σ_x, defined by

$$\boxed{\sigma_x = \left[\overline{x^2} - (\bar{x})^2\right]^{1/2}}. \tag{5.74}$$

We label the standard deviation with a subscript to indicate what variable is being considered. Generally, about two-thirds of a population will have their values of x within one standard deviation of the mean—that is, within the interval $(\bar{x} - \sigma_x, \bar{x} + \sigma_x)$.

EXAMPLE 5.17 If all values of x between a and b are equally probable, find the mean value of x, the root-mean-square value of x, and the standard deviation of x.

SOLUTION ► In order to be normalized, the probability density is

$$f(x) = \frac{1}{b-a}$$

so that

$$\begin{aligned} \bar{x} &= \int_a^b x \frac{1}{b-a}\, dx = \frac{1}{2(b-a)}\left(b^2 - a^2\right) = \frac{1}{2}(b+a) \\ \overline{x^2} &= \int_a^b x^2 \frac{1}{b-a}\, dx = \frac{1}{3(b-a)}\left(b^3 - a^3\right) = \frac{1}{3}\left(b^2 + ab + a^2\right). \end{aligned}$$

The root-mean-square value of x is

$$\left(\overline{x^2}\right)^{1/2} = \left[\frac{1}{3}\left(b^2 + ab + a^2\right)\right]^{1/2}.$$

The standard deviation is found as

$$\begin{aligned}\sigma_x^2 &= \overline{x^2} - \bar{x}^2 = \frac{1}{3}\left(b^2 + ab + a^2\right) - \frac{1}{4}\left(b^2 + 2ab + a^2\right) \\ &= \frac{1}{12}(a-b)^2 \\ \sigma_x &= \sqrt{\frac{1}{12}}(a-b)\,.\end{aligned}$$

◄

EXERCISE 5.24 ► From the results of the preceding example, find the numerical values of $\bar{x}$, $\left(\overline{x^2}\right)^{1/2}$, and σ_x for $a = 0$ and $b = 10$. Comment on your values. What fraction of the total probability is found between $\bar{x} - \sigma_x$ and $\bar{x} + \sigma_x$? ◄

EXERCISE 5.25 ► If x ranges from 0 to 10 and if $f(x) = cx^2$, find the value of c so that $f(x)$ is normalized. Find the mean value of x and the root-mean-square value of x. ◄

The Gaussian Distribution

The most important probability distribution is the *Gaussian distribution*, which is represented by the formula

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right], \tag{5.75}$$

where μ is the mean value of x and where σ is the standard deviation. This distribution is also called the *normal distribution*. If $\sigma = 1$, then the distribution is called the *standard normal distribution*. The Gaussian distribution is assumed to describe populations of various kinds, including the IQ scores of people and velocities of molecules in a gas.[1]

EXAMPLE 5.18 Show that the distribution in Eq. (5.75) satisfies the normalization condition of Eq. (5.72) with the limits of integration equal to $-\infty$ and $+\infty$.

SOLUTION ► We have the following integral, which we modify by the method of substitution, and then look up in Appendix G:

$$\int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-\mu)^2/2\sigma^2}\, dx = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2}\, dt = 1.$$

◄

EXERCISE 5.26 ► Calculate the mean and standard deviation of the Gaussian distribution, showing that μ is the mean and that σ is the standard deviation. ◄

[1] The Gaussian distribution is named after Carl Friedrich Gauss, 1777–1855, a great German mathematician who made a number of important discoveries in addition to this one.

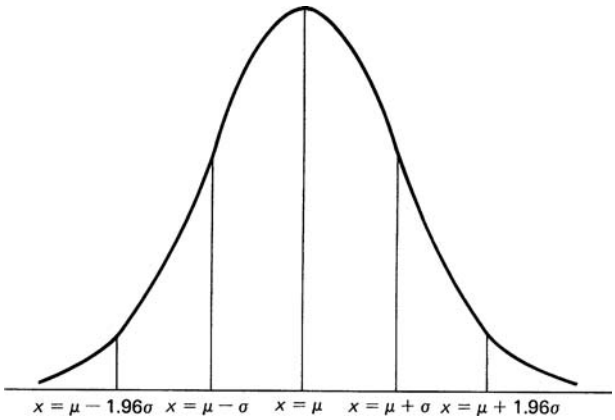

Figure 5.7 ► The Gaussian probability distribution.

Figure 5.7 shows a graph of the Gaussian distribution. Five values of x have been marked on the x axis: $x = \mu - 1.96\sigma$, $x = \mu - \sigma$, $x = \mu$, $x = \mu + \sigma$, and $x = \mu + 1.96\sigma$.

EXAMPLE 5.19 Assuming the Gaussian distribution, calculate the fraction of the population with x lying between $x = \mu - \sigma$ and $x = \mu + \sigma$.

SOLUTION ► By integration of Eq. (5.75), we obtain

$$\begin{aligned}(\text{fraction between } \mu-\sigma \text{ and } \mu+\sigma) &= \int_{\mu-\sigma}^{\mu+\sigma} \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-\mu)^2/2\sigma^2}\, dx \\ &= \int_{-\sigma}^{+\sigma} \frac{1}{\sqrt{2\pi}\sigma} e^{-y^2/2\sigma^2}\, dy \\ &= \frac{2}{\sqrt{\pi}} \int_0^{1/\sqrt{2}} e^{-t^2}\, dt.\end{aligned}$$

◄

The last integral in this example is the *error function* with argument $1/\sqrt{2}$. The integrand function e^{-t^2} does not possess an indefinite integral that can be written with a single formula, so the error function must be approximated numerically unless the upper limit is infinite, in which case the error function is equal to 1. The error function is described in Appendix G. From the table of values in that appendix,

$$\begin{aligned}(\text{fraction between } \mu-\sigma \text{ and } \mu+\sigma) &= \text{erf}\left(\frac{1}{\sqrt{2}}\right) \\ &= \text{erf}(0.707\ldots) = 0.683\ldots\end{aligned}$$

in agreement with our assertion that roughly two-thirds of the members of a population lie within one standard deviation of the mean.

EXERCISE 5.27 ► Show that the fraction of a population lying between $\mu - 1.96\sigma$ and $\mu + 1.96\sigma$ is equal to 0.95 if the population is described by the Gaussian distribution. ◄

You should remember the following facts: With a Gaussian distribution, 68% of the population lies within one standard deviation of the mean, 95% of the population lies within 1.96 standard deviations of the mean, and 99% of the population lies within 2.67 standard deviations of the mean. For other intervals, we can write

$$(\text{fraction between } \mu - x_i \text{ and } \mu + x_i) = \text{erf}\left(\frac{x_i}{\sqrt{2}\sigma}\right). \tag{5.76}$$

There are a number of other common probability distributions in addition to the Gaussian distribution, including the binomial distribution, the Poisson distribution, and the Lorentzian distribution.[2] However, the Gaussian distribution is generally used in discussing experimental errors, and we return to this topic in Chapter 11.

Probability Distributions in Gas Kinetic Theory

In gas kinetic theory, the probability density for a component of the molecular velocity is a Gaussian distribution. The normalized probability distribution for v_x, the x component of the velocity, is given by

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m v_x^2}{2k_B T}\right), \tag{5.77}$$

where m is the molecular mass, T the temperature on the Kelvin scale, and k_B is Boltzmann's constant.

EXERCISE 5.28 ▶

(a) Show that the mean value of v_x is equal to zero. Explain this fact in physical terms.

(b) Find the expression for $\left(\overline{v_x^2}\right)^{1/2}$, the root-mean-square value of v_x.

(c) Find the expression for the standard deviation of v_x.

◀

The speed v is the magnitude of the velocity. Since velocities with the same magnitude but different directions are included in the same speed, the distribution of speeds is different from the velocity distribution of Eq. (5.77). We denote the speed distribution by $f_v(v)$. It is given by[3]

$$f_v(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2k_B T}\right). \tag{5.78}$$

A graph of this function is shown in Fig. 5.8. The speed is never negative, so that the graph does not extend to the left of the origin. In ordinary gas kinetic theory, the requirements of special relativity are ignored, and speeds approaching infinity are included. The error due to this inclusion is insignificant at ordinary temperatures, because of the low probability ascribed to high speeds.

[2] See Philip R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, Chap. 3, McGraw-Hill, New York, 1969, or Hugh D. Young, *Statistical Treatment of Experimental Data*, McGraw-Hill, New York, 1962, for discussions of various distributions.

[3] Robert G. Mortimer, *Physical Chemistry*, 2nd ed., Academic Press, San Diego, CA, 2000, p. 335.

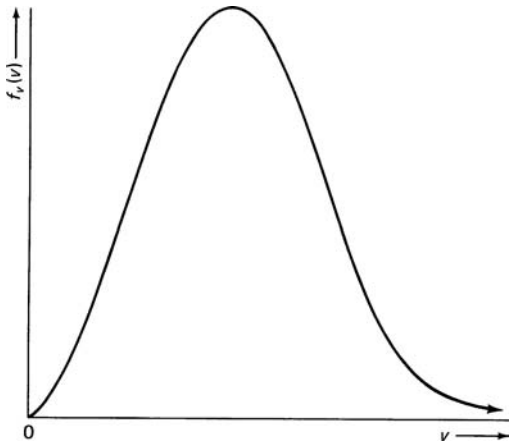

Figure 5.8 ► A graph of the probability density for speeds of molecules in a gas.

The mean speed is given by

$$\bar{v} = \int_0^\infty v\, f_v(v)\, dv. \tag{5.79}$$

EXAMPLE 5.20 Obtain a formula for the mean speed of molecules in a gas.

SOLUTION ►

$$\bar{v} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2k_B T}\right) dv. \tag{5.80}$$

This integral can be obtained from Eq. (A.6) of Appendix G:

$$\bar{v} = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{(2k_B T)^2}{2m^2} = \left(\frac{8k_B T}{\pi m}\right)^{1/2}. \tag{5.81}$$

◄

EXERCISE 5.29 ► Find the value of $\bar{v}$ for N_2 gas at 298 K. ◄

EXAMPLE 5.21 Find a formula for the mean of the square of the speed of molecules in a gas and for the root-mean-square speed.

SOLUTION ►

$$\begin{aligned} \overline{v^2} &= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2k_B T}\right) dv \\ &= \frac{3k_B T}{m} \\ v_{rms} &= \left(\overline{v^2}\right)^{1/2} = \left(\frac{3k_B T}{m}\right)^{1/2}. \end{aligned}$$

◄

EXERCISE 5.30 ► For molecules in a gas, find the formula for σ_v and find its value for N_2 gas at 298 K. ◄

Time Averages

If $g = g(t)$, the time average of g is defined as

$$\overline{g(t)} = \int_{t_1}^{t_2} g(t) f(t)\, dt, \tag{5.82}$$

where we call $f(t)$ the *weighting function*. It plays the same role as a probability density, specifying the importance of different times. Most time averages are unweighted, which means that $f(t)$ is a constant equal to $1/(t_2 - t_1)$:

$$\overline{g(t)} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} g(t)\, dt. \tag{5.83}$$

Equation (5.83) is a version of the *mean value theorem* of integral calculus, which states that the mean value of a function is equal to the integral of the function divided by the length of the interval over which the mean is taken.

EXAMPLE 5.22 A particle falls in a vacuum near the surface of the earth. Find the average z component of the velocity during the first 10.00 s of fall if the initial speed is zero.

SOLUTION ► From Eq. (5.6),

$$v_z = -gt,$$

where g is the acceleration due to gravity, $9.80\,\mathrm{m\,s^{-2}}$,

$$\begin{aligned} \overline{v}_z &= -\frac{1}{10}\int_0^{10} gt\, dt = -\frac{g}{10}\left.\frac{t^2}{2}\right|_0^{10} = -5g \\ &= -5\left(9.80\,\mathrm{m\,s^{-2}}\right) = -49.0\,\mathrm{m\,s^{-1}}. \end{aligned}$$

◄

EXERCISE 5.31 ► Find the time-average value of the z coordinate of the particle in the previous example for the first 10.00 s of fall if the initial position is $z = 0.00\,\mathrm{m}$. ◄

SUMMARY

Integration is one of the two fundamental processes of calculus. It is essentially the reverse of differentiation, the other important process. The first kind of an integral is the indefinite integral, which is the antiderivative of the integrand function. The second kind of an integral is the definite integral, which is constructed as the sum of very many small increments of the antiderivative function F, constructed from the integrand function f according to the formula from Chapter 4,

$$dF = f(x)\, dx = \frac{dF}{dx}\, dx$$

The definite integral has a lower limit of integration, at which the summation process starts, and an upper limit, at which the process ends. The definite integral

is therefore equal to the value of the antiderivative function (indefinite integral) at the upper limit minus its value at the lower limit

$$\int_a^b f(x)\,dx = F(b) - F(a).$$

Extensive tables of indefinite integrals exist, as well as tables of definite integrals. Some integrals have infinite limits or have integrands that attain infinite values, and such integrals are called improper integrals. Many such integrals diverge (have undefined values), but some improper integrals have finite values and are said to converge.

There are several techniques for manipulating integrals into a form that you can recognize or which you can look up in a table, and we presented a few of these. Some integrals cannot be worked out mathematically, but must be approximated numerically. We discussed some elementary techniques for carrying out this approximation, including Simpson's rule, the most commonly used technique, and finally presented a simple computer program for implementing Simpson's rule.

Mean values of variables that take on all real values in a certain interval are calculated as integrals of the form

$$g = \int_a^b g\,(x)\; f\,(x)\; dx,$$

where $g(x)$ is the function to be averaged and $f(x)$ is the probability distribution, or probability density, or distribution function.

PROBLEMS

1. Find the indefinite integrals without using a table:

a) $\int x \ln(x)\; dx$

b) $\int x \sin^2(x)\; dx$

c) $\int \dfrac{1}{x\,(x-a)}\, dx$

d) $\int x^3 \ln\left(x^2\right)\; dx$

2. Find the definite integrals:

a) $\int_0^{2\pi} \sin(x)\; dx$

b) $\int_1^2 x \ln(x)\, dx$

c) $\int_0^{\pi/2} \sin^2(x) \cos(x)\; dx$

3. Find the definite integrals:

a) $\int_0^{2\pi} \sin^2(x)\; dx$

b) $\int_2^{10} x \ln(x)\, dx$

c) $\int_0^{\pi/2} \sin(x) \cos^2(x)\; dx$

4. Find the definite integrals:

a) $\int_0^{\pi/2} x \sin(x^2)\ dx$

b) $\int_0^{\pi/2} x \sin\left(x^2\right) \cos\left(x^2\right)\ dx$

c) $\int_0^{2\pi} x \cos(x) dx$

5. Determine whether the following improper integrals converge. Evaluate the convergent integrals.

a) $\int_1^{\infty} \left(\frac{1}{x^2}\right) dx$

b) $\int_1^{\pi/2} \tan(x)\, dx$

c) $\int_0^1 \frac{1}{x \ln(x)} dx$

6. Determine whether the following improper integrals converge. Evaluate the convergent integrals.

a) $\int_1^{\infty} \left(\frac{1}{x}\right) dx$

b) $\int_0^{\pi} \tan(x)\, dx$

c) $\int_0^{\pi/2} \tan(x)\, dx$

7. Determine whether the following improper integrals converge. Evaluate the convergent integrals.

a) $\int_0^1 \left(\frac{1}{x}\right) dx$

b) $\int_0^{\infty} \sin(x)\, dx$

c) $\int_{-\pi/2}^{\pi/2} \tan(x)\, dx$

8. At 298 K, what fraction of nitrogen molecules has speeds lying between 0 and the mean speed? Do a numerical approximation to the integral or use the identity

$$\int_0^{\infty} t^2 e^{-at^2}\, dt = \frac{\sqrt{x}}{4a^{3/2}} \operatorname{erf}\left(\sqrt{a}x\right) - \frac{x}{2a} e^{-ax^2}.$$

9. Approximate the integral

$$\int_0^{\infty} e^{-x^2}\, dx$$

using Simpson's rule. You will have to take a finite upper limit, choosing a value large enough so that the error caused by using the wrong limit is negligible. The correct answer is $\sqrt{\pi}/2 = 0.886226926\cdots$.

10. Using Simpson's rule, evaluate $\operatorname{erf}(2)$.

$$\operatorname{erf}(2) = \frac{2}{\sqrt{\pi}} \int_0^2 e^{-t^2} dt$$

Compare your answer with the correct value from the table in Appendix G.

11. Find the integrals.

a) $\int \sin\left[x\,(x+1)\right](2x+1)\,dx$

b) $\int_0^{\pi} \sin\left[\cos\,(x)\right]\sin\,(x)\;dx$

12. When a gas expands reversibly, the work that it does on its surroundings is given by the integral

$$w_{surr} = \int_{V_1}^{V_2} P\,dV,$$

where V_1 is the initial volume, V_2 the final volume, and P the pressure of the gas. Certain nonideal gases are described quite well by the van der Waals equation of state,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

where V is the volume, n is the amount of gas in moles, T is the temperature on the Kelvin scale, and a and b are constants. R is usually taken to be the ideal gas constant, $8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

a) Obtain a formula for the work done if 1.000 mol of such a gas expands reversibly at constant temperature from a volume V_1 to a volume V_2.

b) If $T = 298\,\mathrm{K}$, $V_1 = 1.00\,\mathrm{l}$ $(1.000 \times 10^{-3}\,\mathrm{m^3})$, and $V_2 = 100.0\,\mathrm{l} = 0.100\,\mathrm{m^3}$, find the value of the work done for 1.000 mol of CO_2, which has $a = 0.3640\,\mathrm{Pa\,m^6\,mol^{-2}}$, and $b = 4.267 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$. The ideal gas constant, $R = 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

c) Calculate the work done in the process of part b if the gas is assumed to be ideal.

13. The entropy change to bring a sample from 0 K (absolute zero) to a given state is called the *absolute entropy* of the sample in that state. Using Simpson's rule, calculate the absolute entropy of 1.000 mol of solid silver at 270 K. For the region 0 K to 30 K, use the approximate relation

$$C_P = aT^3,$$

where a is a constant that you can evaluate from the value of C_P at 30 K. For the region 30 K to 270 K, use the following data:[4]

T/ K	$C_{\mathbf{P}}$/ $\mathrm{J\,K^{-1}\,mol^{-1}}$	T/ K	$C_{\mathbf{P}}$/ $\mathrm{J\,K^{-1}\,mol^{-1}}$
30	4.77	170	23.61
50	11.65	190	24.09
70	16.33	210	24.42
90	19.13	230	24.73
110	20.96	250	25.03
130	22.13	270	25.31
150	22.97		

[4] P.F. Meads, W.R. Forsythe, and W.F. Giaque, *J. Am. Chem. Soc*. **63**, 1902 (1941).

14. Use Simpson's rule with at least 10 panels to evaluate the following definite integrals. Use Mathematica to check your results.

a) $\int_0^2 e^{3x^3} dx$

b) $\int_1^3 e^{x^2} dx$

6

Mathematical Series and Transforms

Preview

A *mathematical series* is a sum of terms. A series can have a finite number of terms or can have an infinite number of terms. If a series has an infinite number of terms, an important question is whether it approaches a finite limit as more and more terms of the series are included (in which case we say that it *converges*) or whether it becomes infinite in magnitude or oscillates endlessly (in which case we say that it *diverges*). A *constant series* has terms that are constants, so that it equals a constant if it converges. A *functional series* has terms that are functions of one or more independent variables, so that the series is a function of the same independent variables if it converges. Each term of a functional series contains a constant coefficient that multiplies a function from a set of *basis functions*. The process of constructing a functional series to represent a specific function is the process of determining the coefficients. We discuss two common types of functional series, power series and Fourier series.

An *integral transform* is similar to a functional series, except that it contains an integration instead of a summation, which corresponds to an integration variable instead of a summation index. The integrand contains two factors, as does a term of a functional series. The first factor is the transform, which plays the same role as the coefficients of a power series. The second factor is the basis function, which plays the same role as the set of basis functions in a functional series. We discuss two types of transforms, Fourier transforms and Laplace transforms.

Principal Facts and Ideas

1. A mathematical series is a sum of terms, either with a finite number of terms or an infinite number of terms.

2. A constant series has terms that are constants, and a functional series has terms that are functions.

3. An infinite series converges if the sum approaches a finite limit ever more closely as ever more terms are summed, or diverges if the series does not approach such a limit.
4. An infinite functional series represents a function if it converges.
5. A Taylor series is a sum of terms that consist of coefficients times powers of $x - h$, where x is a variable and h is a constant. The coefficients can be determined to represent any analytic function within a region of convergence.
6. A Fourier series is an infinite series of terms that consist of coefficients times sine and cosine functions. It can represent almost any periodic function.
7. A Fourier transform is a representation of a function as an integral instead of a sum. Many modern instruments use Fourier transforms to produce spectra from raw data in another form.
8. A Laplace transform is a representation of a function that is similar to a Fourier transform.

Objectives

After studying this chapter, you should be able to:

1. determine whether an infinite constant series converges,
2. determine how large a partial sum must be taken to approximate a series to a specified accuracy,
3. compute the coefficients for a power series to represent a given function,
4. determine the region of convergence of a power series,
5. determine the coefficients of a Fourier series to represent some elementary functions,
6. determine the Fourier transform of some elementary functions,
7. determine the Laplace transform of some elementary functions,
8. manipulate Laplace transforms using various theorems.

6.1 Constant Series

A *sequence* is a set of numerical quantities with a rule for generating one member of the set from the previous one. If the members of a sequence are added together, the result is a *series*. A *finite series* has a finite number of terms, and an *infinite series* has a infinite number of terms. If a series has terms that are constants, it is a *constant series*. Such a series can be written

$$s = a_0 + a_1 + a_2 + a_3 + a_4 + \cdots + a_n + \cdots \tag{6.1}$$

For an infinite series, we define the *nth partial sum* as the sum of the first n terms:

$$S_n = a_0 + a_1 + a_2 + a_3 + \cdots + a_{n-1}. \tag{6.2}$$

The entire infinite series is the limit

$$s = \lim_{n\to\infty} S_n. \tag{6.3}$$

If this limit exists and is finite, we say that the series *converges*. If the magnitude of S_n becomes larger and larger without bound as n becomes large, or if S_n continues to oscillate without approaching a fixed value as n becomes large, we say that the series *diverges*.

The two questions that we generally ask about an infinite constant series are: (1) Does the series converge? (2) What is the value of the series if it does converge? Sometimes it is difficult to find the value of a convergent infinite series, and we then might ask how well we can approximate the series with a partial sum.

Some Convergent Series

Let us consider a well-known convergent constant series:

$$s = 1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \cdots + \frac{1}{2^n} + \cdots = \sum_{n=0}^{\infty} \frac{1}{2^n}. \tag{6.4}$$

There is no general method that is capable of finding the value of every series.[1] However, the value of this series is calculated in the following example.

EXAMPLE 6.1 Find the value of the series in Eq. (6.4).

SOLUTION ► We write the sum as the first term plus the other terms, with a factor of $\frac{1}{2}$ factored out of all the other terms:

$$s = 1 + \frac{1}{2}\left(1 + \frac{1}{2} + \frac{1}{4} + \frac{1}{8} + \cdots\right).$$

The series in the parentheses is just the same as the original series. There is no problem due to the apparent difference that the series in the parentheses seems to have one less term than the original series, because both series have an infinite number of terms. We now write

$$s = 1 + \frac{1}{2}s$$

which can be solved to give

$$s = 2. \tag{6.5}$$

◄

EXERCISE 6.1 ► Show that in the series of Eq. (6.4) any term of the series is equal to the sum of all the terms following it. (*Hint*: Factor a factor out of all of the following terms so that they will equal this factor times the original series, whose value is now known.) ◄

The result of this exercise is of interest in seeing how a series can be approximated by a partial sum. For the series of Eq. (6.4), we can write

$$s = S_n + a_{n-1}. \tag{6.6}$$

[1] See A. D. Wheelon, "On the Summation of Infinite Series," *J. Appl. Phys*., **25**, 113 (1954), for a method that can be applied to a large number of series.

In some cases it is necessary to approximate a series with a partial sum, and sometimes Eq. (6.6) can be applied to other series as a rough measure of the error in approximating s by S_n.

EXAMPLE 6.2 Determine which partial sum approximates the series of Eq. (6.4) to (a) 1% and (b) 0.001%.

SOLUTION ► Since 1% of 2 is equal to 0.02, we find the first term of the series that is equal to or smaller than 0.02, and take the partial sum that ends with that term. We have

$$\frac{1}{2^6} = \frac{1}{64} = 0.015625,$$

so that the partial sum required is the one ending with $\frac{1}{64}$, or S_7. Its value is

$$S_7 = 1.984375.$$

Since 0.001% of 2 is 2×10^{-5}, and $1/2^n$ has the value 1.5259×10^{-5} when $n = 16$, we need the partial sum S_{17}, which has the value $S_{17} = 1.999984741$. ◄

EXERCISE 6.2 ► Consider the series

$$s = 1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \cdots + \frac{1}{n^2} + \cdots$$

which is known to be convergent. Using Eq. (6.6) as an approximation, determine which partial sum approximates the series to (a) 1% and (b) 0.001%. ◄

The Geometric Series

The series of Eq. (6.4) is an example of a *geometric series*, which is defined to be

$$\begin{aligned} s &= a + ar + ar^2 + ar^3 + ar^4 + \cdots + ar^n + \cdots && \text{(6.7a)} \\ &= ar\left(1 + r + r^2 + r^3 + \cdots + r^n + \cdots\right), && \text{(6.7b)} \end{aligned}$$

where a and r are constants. In order for the infinite series of Eq. (6.7a) to converge, the magnitude of r must be less than unity. Otherwise, each term would be equal to or larger than the previous term, causing the sum to grow without bound (diverge) as more and more terms are added. However, r can be positive or negative. If r is negative, the sum has terms of alternating sign, but still converges only if $|r| < 1$.

The value of a geometric series can be obtained in the same way as was the value of the series in Eq. (6.4),

$$\begin{aligned} s &= a + r\left(a + ar + ar^2 + ar^3 + \cdots\right) \\ &= a + rs \end{aligned}$$

or

$$\boxed{s = \frac{a}{1-r}} \qquad (|r| < 1)\,. \qquad \text{(6.8)}$$

The partial sums of the geometric series are given by

$$\boxed{S_n = a + ar + ar^2 + \cdots + ar^{n-1} = a\frac{1-r^n}{1-r}}. \tag{6.9}$$

Equation (6.9) is valid for any value of r, since a finite series always converges.

Instead of writing a series in the form used up to now, in which various terms are exhibited, we can use a standard symbol for a sum, a capital Greek sigma, which we introduced in Chapter 5. For example, the geometric series can be written as

$$s = \sum_{n=0}^{\infty} a^n$$

where the summation index n ranges from 0 to ∞. The nth partial sum is written as

$$S_n = \sum_{n=0}^{n-1} a^n$$

EXAMPLE 6.3 The *molecular partition function* z is defined in the statistical mechanics of noninteracting molecules as the sum over all the states of one molecule

$$z = \sum_{i=0}^{\infty} \exp\left(\frac{-E_i}{k_B T}\right), \tag{6.10}$$

where i is an index specifying the state, E_i is the energy that the molecule has when in state number i, k_B is Boltzmann's constant, and T is the absolute temperature. If we consider only the vibration of a diatomic molecule, to a good approximation

$$E_i = E_v = h\nu\left(v + \frac{1}{2}\right), \tag{6.11}$$

where ν is the vibrational frequency; v is the vibrational quantum number, which can take on the integral values 0, 1, 2, 3, etc.; and h is Planck's constant. Use Eq. (6.8) to find the value of the partition function for vibration.

SOLUTION ►

$$\begin{aligned} z_{vib} &= \sum_{v=0}^{\infty} \exp\left[\frac{-h\nu\left(v+\frac{1}{2}\right)}{k_B T}\right] \\ &= \exp\left(\frac{-h\nu}{2k_B T}\right)\sum_{v=0}^{\infty}\left[\exp\left(\frac{h\nu}{k_B T}\right)\right]^v \\ &= e^{-x/2}\sum_{v=0}^{\infty}\left(e^{-x}\right)^v, \end{aligned}$$

where $h\nu/k_B T = x$, a positive quantity. The sum is a geometric series, so

$$z_{vib} = \frac{e^{-x/2}}{1-e^{-x}} \tag{6.12}$$

The series is convergent, because e^{-x} is smaller than unity for all positive values of x and is never negative. ◄

EXERCISE 6.3 ▶ Find the value of the infinite series

$$\sum_{n=0}^{\infty}[\ln(2)]^n$$

Determine how well this series is approximated by S_2, S_5, and S_{10}. ◀

A Divergent Series

The *harmonic series* is defined to be

$$s = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \cdots + \frac{1}{n} + \cdots . \tag{6.13}$$

Here are a few partial sums of this series:

$$\begin{aligned} S_1 &= 1 \\ S_2 &= 1.5 \\ S_{200} &= 6.87803 \\ S_{1000} &= 8.48547 \\ S_{100,000} &= 13.0902. \end{aligned}$$

However, the harmonic series diverges.

$$s = \lim_{n\to\infty} S_n = \infty.$$

Many people are surprised when they first learn that this series diverges, because the terms keep on getting smaller as you go further into the series. This is a necessary condition for a series to converge, but it is not sufficient. We will show that the harmonic series is divergent when we introduce tests for convergence.

EXERCISE 6.4 ▶ Use a spreadsheet or a computer program to evaluate partial sums of the harmonic series and use it to verify the foregoing values. ◀

There are a number of constant series listed in Appendix C, and additional series can be found in the references listed at the end of the chapter.

Tests for Convergence of a Series

There are several tests that will usually tell us whether an infinite series converges or not.

1. *The Comparison Test.* If a series has terms that are each smaller in magnitude than the corresponding term of a series known to converge, it is convergent. If a series has terms that are each larger in magnitude than the corresponding term of a series known to diverge, it is divergent.

2. *The Alternating Series Test.* If a series has terms that alternate in sign, it is convergent if the terms approach zero as you go further and further into the series and if each term is smaller in magnitude than the previous term.

3. The *nth-Term Test*. If the terms of a series approach some limit other than zero or do not approach any limit as you go further into the series, the series diverges.

4. *The Integral Test*. If a formula can be written to deliver the terms of a series

$$a_n = f(n), \tag{6.14}$$

then the series will converge if the improper integral

$$\int_1^\infty f(x)\, dx \tag{6.15}$$

converges and will diverge if the improper integral diverges.

5. *The Ratio Test*. For a series of positive terms or a series of negative terms, we define the limit

$$r = \lim_{n\to\infty} \frac{a_{n+1}}{a_n}. \tag{6.16}$$

If $r < 1$, the series converges. If $r > 1$, the series diverges. If $r = 1$, the test fails, and the series might either converge or diverge. If the ratio does not approach any limit but does not increase without bound, the test also fails.

EXAMPLE 6.4 Apply the ratio test and the integral test to the harmonic series, Eq. (6.13).

SOLUTION ► Apply the ratio test:

$$r = \lim_{n\to\infty} \left[\frac{1/n}{1/(n-1)}\right] = \lim_{n\to\infty} \frac{n-1}{n} = 1.$$

The ratio test fails. Apply the integral test:

$$\int_1^0 \frac{1}{x} dx = \ln(x)\Big|_1^\infty = \lim_{b\to\infty} [\ln(b) - \ln(1)] = \infty.$$

The series diverges by the integral test. ◄

EXAMPLE 6.5 Determine whether the series converges:

$$s = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \cdots = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n}.$$

SOLUTION ► This is an alternating series, so the alternating series test applies. Since every term approaches more closely to zero than the previous term, the series is convergent. ◄

EXAMPLE 6.6 Determine whether the series converges:

$$s = 1 - \frac{1}{2} + \frac{2}{2} - \frac{1}{3} + \frac{2}{3} - \frac{1}{4} + \frac{2}{4} - \frac{1}{5} + \frac{2}{5} - \cdots.$$

SOLUTION ► This is a tricky series, because it is an alternating series, and the nth term approaches zero as n becomes large. However, the series diverges. The alternating series test does not apply, because it requires that each term be closer to zero than the previous term. Half the time as you go from one term to the next in this series, the magnitude increases instead of decreasing. Let us manipulate the series by subtracting each negative term from the following positive term to obtain

$$s = 1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \frac{1}{5} + \cdots .$$

This is the harmonic series, which we already found to diverge. ◄

EXERCISE 6.5 ► Show that the geometric series converges if $r^2 < 1$. ◄

EXERCISE 6.6 ► Test the following series for convergence.

(a) $\sum_{n=0}^{\infty} \left(1/n^2\right)$.

(b) $\sum_{n=0}^{\infty} (1/n!)$.

(c) $\sum_{n=0}^{\infty} \left((-1)^n (n-1)/n^2\right)$.

(d) $\sum_{n=0}^{\infty} \left((-1)^n n/n!\right)$.

◄

Note. $n!$ (n factorial) is defined for positive integral values of n to be $n(n-1)(n-2)\ldots(2)(1)$, and is defined to equal 1 if $n = 0$.

6.2 Functional Series

A *functional series* has terms that are constants times functions. If a single independent variable is called x,

$$s(x) = a_0 g_0(x) + a_1 g_1(x) + a_2 g_2(x) + a_3 g_3(x) + \cdots . \tag{6.17}$$

We call the set of constant quantities a_0, a_1, a_2, and so on, the *coefficients* of the series and the set of functions $g_0, g_1, g_2, g_3, \ldots$ the *basis functions*. Just as with constant series, a functional series such as that of Eq. (6.17) might converge or it might diverge. However, it might converge for some values of x and diverge for others. If there is an interval of values of x such that the series converges for all values of x in that interval, we say that the series is *convergent in that interval*.

There is an important mathematical concept called *uniform convergence*. If a functional series converges in some interval, it is uniformly convergent in that interval if it converges with at least a certain fixed rate of convergence in the entire interval. We do not discuss the details of this concept.[2] If a functional series is uniformly convergent in some interval, it has been shown to have some useful mathematical properties, which we discuss later.

There are two problems to be faced in constructing a series to represent a given function. The first is finding the values of the coefficients so that the function will be correctly represented. The second is finding the interval in which the series is convergent and in which it represents the given function.

[2]David Bressoud, *A Radical Approach to Real Analysis*, pp. 191–194, Math. Assoc. of America, Washington, DC, 1994.

Power Series

A common type of functional series is the *power series*, in which the basis functions are powers of $x - h$, where x is the independent variable and h is a constant (it can equal zero).

$$s(x) = a_0 + a_1(x - h) + a_2(x - h)^2 + a_3(x - h)^3 + \cdots , \tag{6.18}$$

where a_0, a_1, and so on, are constant coefficients. An infinite series of this form is called a *Taylor series*, and if $h = 0$ it is called a *Maclaurin series*. If we represent a function by a power series, we say that we *expand* the function in terms of the power series. Several methods of theoretical chemistry, such as the *perturbation method* in quantum mechanics, use power series.

Maclaurin Series

A Maclaurin series to represent a function $f(x)$ is written

$$f(x) = a_0 + a_1x + a_2x^2 + \cdots = s(x) , \tag{6.19}$$

where $f(x)$ is the function and $s(x)$ is the series. We now show how to determine the a coefficients. In order for the function and the series to be equal at all values of x, they must be equal at $x = 0$, which means that

$$\boxed{f(0) = s(0) = a_0} . \tag{6.20}$$

This determines a_0.

We also require that all derivatives of the function and of the series be equal at $x = 0$. This is sufficient for the series to represent the function in some interval around $x = 0$. Only a function that possesses derivatives of all orders at $x = 0$ can be represented by a Maclaurin series. Such a function is said to be *analytic* at $x = 0$. The nth derivative of the series at $x = 0$ is

$$\left(\frac{d^n s}{dx^n}\right)_{x=0} = n!a_n, \tag{6.21}$$

where $n!$ (n factorial) is defined for $n \geq 1$ by

$$n! = n(n - 1)(n - 2) \cdots (2)(1).$$

This gives us a general formula for the coefficients in a Maclaurin series to represent the function $f(x)$:

$$\boxed{a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_0 \quad (n = 1, 2, 3....)} . \tag{6.22}$$

A power series that is obtained by using Eq. (6.22) to obtain the coefficients faithfully represents the appropriate function in the vicinity of $x = 0$ if it converges and if infinitely many terms are taken. However, we must discuss how far from $x = 0$ we can go and still represent the function by the series.

EXERCISE 6.7 ▶ Show that Eq. (6.22) is correct. ◀

EXAMPLE 6.7 Find all the coefficients for the Maclaurin series representing $\sin(x)$.

SOLUTION ► Since $\sin(\theta) = 0$,

$$\begin{aligned} a_0 &= 0 \\ a_1 &= \left[\frac{d}{dx}\sin(x)\right]_{x=0} = \cos(0) = 1, \end{aligned} \tag{6.23}$$

where the subscript indicates that the derivative is evaluated at $x = 0$. The second partial sum of the series is therefore

$$S_2 = 0 + x = x$$

giving the same approximation as in Eq. (2.26). Figure 6.1 shows the function $\sin(x)$ and the approximation, $S_2 = x$. The derivatives of $\sin(x)$ follow a repeating pattern:

$$\begin{aligned} f(x) &= \sin(x) \\ \frac{df}{dx} &= \cos(x) \\ \frac{d^2f}{dx^2} &= -\sin(x) \\ \frac{d^3f}{dx^3} &= -\cos(x) \\ \frac{d^4f}{dx^4} &= \sin(x), \end{aligned}$$

When these are evaluated at $x = 0$, all of the even-numbered derivatives vanish, and the odd-numbered derivatives are alternately equal to 1 and -1:

$$\boxed{\sin(x) = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \frac{1}{7!}x^7 + \cdots}. \tag{6.24}$$

◄

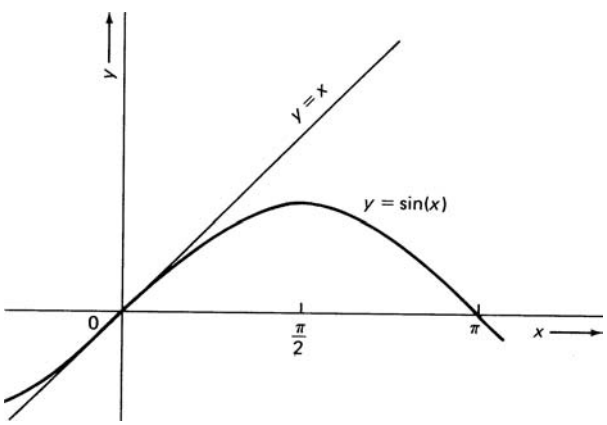

Figure 6.1 ► The function $\sin(x)$ and the approximation $S_2 = x$.

EXERCISE 6.8 ► (a) Show that the Maclaurin series for e^x is

$$\boxed{e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 \cdots} \quad (6.25)$$

(b) Find the Maclaurin series for $\cos(x)$.

◄

Taylor Series

A Taylor series has the form

$$s(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + a_3(x-h)^3 + \cdots,$$

where h is not equal to zero. We say that a Taylor series is *expanded* around $x = h$. There are a number of important functions that are not analytic at $x = 0$, and these cannot be represented by a Maclaurin series, for which $h = 0$. One such function is $\ln(x)$. The first derivative of this function is $1/x$, which becomes infinite as $x \to 0$, as do the other derivatives. Although there is no Maclaurin series for $\ln(x)$, you can find a Taylor series for a positive value of h.

In order to find the coefficients for a Taylor series, we require the function and the series to be equal at $x = h$ and to have the same derivatives of all orders at $x = h$. This gives

$$\boxed{a_0 = f(h); \quad a_n = \frac{1}{n!}\left(\frac{d^n f}{dx^n}\right)_{x=h}}, \quad (6.26)$$

where $f(x)$ is the function to be represented and the subscript h indicates that the derivative is to be evaluated at $x = h$.

EXAMPLE 6.8 Find the Taylor series for $\ln(x)$, expanding about $x = 1$.

SOLUTION ► The first derivative of $\ln(x)$ is $1/x$, which equals 1 at $x = 1$. The second derivative is $-1/x^2$, which equals 1 at $x = 1$. The derivatives follow a regular pattern,

$$\left(\frac{d^n f}{dx^n}\right)_{x=1} = (-1)^{n-1}(n-1)!$$

so that

$$\boxed{\ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 - \frac{1}{4}(x-1)^4 + \cdots} \quad (6.27)$$

◄

EXERCISE 6.9 ► Find the Maclaurin series for $\ln(1+x)$. You can save some work by using the result of Example 6.8. ◄

EXERCISE 6.10 ► Find the Taylor series for $\cos(x)$, expanding about $x = \pi/2$. ◄

The Convergence of Power Series

If a series is to represent a function $f(x)$ in some interval, it must be convergent in the entire interval and must converge to the value of the function for every value of x in the interval. For a fixed value of x, the series $s(x)$ is no different from a constant series, and all the tests for convergence of Section 6.1 can be applied. We can then consider different fixed values of x and determine the *interval of convergence*, that interval in which the series is convergent.

EXAMPLE 6.9 Investigate the convergence of the series for $\ln(x)$ in Eq. (6.27).

SOLUTION ► Let us consider three cases: $x = 1$, $x > 1$, and $x < 1$. If $x = 1$, the entire series vanishes, as does the function, so the series converges to the value of the function for $x = 1$. For $x > 1$, the series is an alternating series, and we can apply the alternating series test. The nth term of the series is

$$t_n = a_n (x-1)^n = \frac{(x-1)^n (-1)^{n-1}}{n}.$$

Look at the limit of this as n becomes large:

$$\lim_{n\to\infty} t_n = \begin{cases} 0 & \text{if } |x-1| \le 1 \text{ or } 0 \le x \le 2 \\ \infty & \text{if } |x-1| > 1 \text{ or } x > 2. \end{cases}$$

The interval of convergence for $x > 1$ extends up to and including $x = 2$. For $x < 1$, the series is not alternating. We apply the ratio test.

$$r = \lim_{n\to\infty} \frac{t_n}{t_{n-1}} = \lim_{n\to\infty} \left[-\frac{(x-1)^n / n}{(x-1)^{n-1} / (n-1)} \right] = -(x-1) = 1 - x.$$

This will be less than unity if x lies between 0 and 1, but if $x = 0$, the text fails. However, if $x = 0$, the series is the same as the harmonic series except for the sign, and thus diverges. The interval of convergence is $0 < x \le 2$. ◄

We summarize the behavior of the Taylor series representation of the previous example: There is a point at which the logarithm function is not analytic, at $x = 0$. The function is analytic to the right of this point, and the series equals the function for positive values arbitrarily close to $x = 0$. Beyond $x = 2$, the series diverges. The interval of convergence is centered on the point about which the function is expanded, which is $x = 1$ in this case. That is, the distance from $x = 1$ to the left end of the interval of convergence is 1 unit, and the distance from $x = 1$ to the right end of the interval of convergence is also 1 unit. This distance is called the *radius of convergence*. Even though the function is defined for values of x beyond $x = 2$, the series does not converge and cannot represent the function for values of x beyond $x = 2$. Another Taylor series expanded about a value of x larger than $x = 1$ can represent the logarithm function beyond $x = 2$.

EXERCISE 6.11 ► Find the Taylor series for $\ln(x)$, expanding about $x = 2$, and show that the radius of convergence for this series is equal to 2, so that the series can represent the function up to and including $x = 4$. ◄

The behavior of the Taylor series representation of the logarithm function is typical. In general, the interval of convergence is centered on the point about which we are expanding. The radius of convergence is the distance from the point about which we are expanding to the closest point at which the function is not analytic, and the interval of convergence extends by this distance in either direction. If a

function is defined on both sides of a point at which the function is not analytic, it is represented on the two sides by different series.

EXAMPLE 6.10 Find the interval of convergence for the series representing the exponential function in Eq. (6.25).

SOLUTION ► We apply the ratio test,

$$r = \lim_{n\to\infty} \frac{t_n}{t_{n-1}} = \lim_{n\to\infty} \frac{x^n/n!}{x^{n-1}/(n-1)!} = \lim_{n\to\infty} \frac{x}{n}.$$

This limit vanishes for any real finite value of x, so the series converges for any real finite value of x, and the radius of convergence is infinite. ◄

EXERCISE 6.12 ► Find the series for $1/(1-x)$, expanding about $x = 0$. What is the interval of convergence?

◄

EXERCISE 6.13 ► Find the interval of convergence for the series for $\sin(x)$ and for $\cos(x)$.

◄

Unfortunately, the situation is not always so simple as in the examples we have been discussing. A power series can represent a function for complex values of the independent variable, and points in the complex plane at which the function is not analytic can determine the radius of convergence. A Taylor series converges to the function in a circle in the complex plane with radius equal to the radius of convergence. The radius of convergence is the distance from the point about which we expand to the closest point in the complex plane at which the function is not analytic.

For example, if we wanted to construct a Maclaurin series for the function

$$f(x) = \frac{1}{1+x^2}$$

the radius of convergence would be determined by discontinuities at $x = i$ and $x = -i$ even though there are no discontinuities for real values of x. The radius of convergence equals unity, the distance from the origin to $x = \pm i$ in the Argand plane. We do not discuss the behavior of power series in the complex plane, but you can read more about this topic in the book by Kreyszig listed at the end of the book.

In physical chemistry there are a number of applications of power series, but in most applications, a partial sum is actually used to approximate the series. For example, the behavior of a nonideal gas is often described by use of the *virial series* or *virial equation of state*,

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \frac{B_4}{V_m^3} + \cdots, \tag{6.28}$$

where P is the pressure, V_m is the molar volume of the gas, T is the Kelvin temperature, and R is the ideal gas constant. The coefficients B_2, B_3, and so on, are called *virial coefficients* and are functions of T but not functions of V_m. If all the

virial coefficients were known for a particular gas, the virial series would represent exactly the volumetric behavior of that gas at all values of $1/V_m$. However, only the first few virial coefficients can be determined experimentally or theoretically, so a partial sum must be used. For many purposes, the two-term truncated equation is adequate:

$$\frac{PV_m}{RT} \approx 1 + \frac{B_2}{V_m}. \tag{6.29}$$

There is another commonly used series equation of state, sometimes called the *pressure virial equation of state*:

$$PV_m = RT + A_2P + A_3P^2 + A_4P^3 + \cdots, \tag{6.30}$$

This is a Maclaurin series in P. It is also truncated for practical use.

EXAMPLE 6.11 Show that the coefficient A_2 in Eq. (6.30) is equal to the coefficient B_2 in Eq. (6.28).

SOLUTION ► We multiply Eq. (6.28) on both sides by RT/V_m to obtain

$$P = \frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \frac{RTB_3}{V_m^3} + \cdots, \tag{6.31}$$

This must be equal to

$$P = \frac{RT}{V_m} + \frac{A_2P}{V_m} + \frac{A_3P^2}{V_m} + \cdots. \tag{6.32}$$

We convert the second series into a series in $1/V_m$ by substituting the first series into the right-hand side wherever a P occurs. When the entire series on the right-hand side of Eq. (6.31) is squared, every term will have a least a V_m^2 in the denominator [see Eq. (11) of Appendix C for the square of a series]. Therefore, Eq. (6.32) becomes

$$P = \frac{RT}{V_m} + \frac{A_2}{V_m}\left(\frac{RT}{V_m} + \frac{RTB_2}{V_m^2} + \cdots\right) + O\left(\frac{1}{V_m}\right)^3, \tag{6.33}$$

where the symbol $O(1/V_m)^3$ stands for terms of degree $1/V_m^3$ or higher (containing no powers of $1/V_m$ lower than the third power).

Equation (6.33) is thus

$$P = \frac{RT}{V_m} + \frac{RTA_2}{V_m^2} + 0\left(\frac{1}{V_m}\right)^3. \tag{6.34}$$

We now use a fact about series [Eq. (9) of Appendix C]: *If two power series in the same independent variable are equal to each other for all values of the independent variable, then any coefficient in one series is equal to the corresponding coefficient of the other series.*

Comparison of Eq. (6.34) with Eq. (6.31) shows that

$$B_2 = A_2.$$

◄

Another application of a power series in physical chemistry is in the discussion of *colligative properties* (freezing-point depression, boiling-point elevation, and osmotic pressure). If X_1 is the mole fraction of solvent, $\Delta_{vap}H_m$ is the molar heat of vaporization of the solvent, T_0 is the pure solvent's boiling temperature, and T is the solution's boiling temperature, it is shown in physical chemistry textbooks that

$$-\ln(X_1) = \frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right). \tag{6.35}$$

If there is only one *solute* (component other than the solvent), then its mole fraction, X_2, is given by

$$X_2 = 1 - X_1. \tag{6.36}$$

The logarithm on the left-hand side of Eq. (6.35) is represented by the power series

$$-\ln(X_1) = -\ln(1 - X_2) = X_2 + \frac{1}{2}X_2^2 + \cdots . \tag{6.37}$$

If X_2 is not too large, we can truncate this series after one term and write

$$X_2 \approx \frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right). \tag{6.38}$$

EXERCISE 6.14 ▶ Determine how large X_2 can be before the truncation of Eq. (6.37) that was used in Eq. (6.38) is inaccurate by more than 1%. ◀

6.3 Fourier Series

If we want to produce a series that will converge rapidly, so that we can approximate it fairly well with a partial sum containing only a few terms, it is good to choose basis functions that have as much as possible in common with the function to be represented. The basis functions in *Fourier series*[3] are sine and cosine functions, which are periodic functions. Fourier series are used to represent periodic functions. A Fourier series that represents a periodic function of period $2L$ is

$$f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right). \tag{6.39}$$

EXERCISE 6.15 ▶ Using trigonometric identities show that the basis functions in the series in Eq. (6.39) are periodic with period $2L$. That is, show for arbitrary n that

$$\sin\left[\frac{n\pi(x + 2L)}{L}\right] = \sin\left(\frac{n\pi x}{L}\right)$$

and

$$\cos\left[\frac{n\pi(x + 2L)}{L}\right] = \cos\left(\frac{n\pi x}{L}\right).$$

◀

Fourier series occur in various physical theories involving waves, because waves often behave sinusoidally. For example, Fourier series can represent the constructive and destructive *interference* of standing waves in a vibrating string.[4] This fact provides a useful way of thinking about Fourier series. A periodic function of arbitrary shape is represented by adding up sine and cosine functions with

[3] The Fourier series is named for its inventor, Jean Baptiste Joseph Fourier, 1768–1730, famous French mathematician and physicist.

[4] Robert G. Mortimer, *Physical Chemistry*, 2nd ed., pp. 338–340, Academic Press, San Diego, 2000.

shorter and shorter wavelengths, having different amplitudes adjusted to represent the function correctly. This is analogous to the constructive and destructive interference of waves resulting from the addition of their displacements.

There are some important mathematical questions about Fourier series, including the convergence of a Fourier series and the completeness of the basis functions. A set of basis functions is said to be *complete* for representation of a set of functions if a series in these functions can accurately represent any function from the set. We do not discuss the mathematics, but state the facts that were proved by Fourier: (1) any Fourier series in x is uniformly convergent for all real values of x; (2) the set of sine and cosine basis functions in Eq. (6.39) is a complete set for the representation of periodic functions of period $2L$. In many cases of functional series, the completeness of the set of basis functions has not been proved, but most people assume completeness and proceed.

Finding the Coefficients of a Fourier Series—Orthogonality

In a power series, we found the coefficients by demanding that the function and the series have equal derivatives at the point about which we were expanding. In a Fourier series, we use a different procedure, utilizing a property of the basis functions that is called *orthogonality*. This property is expressed by the three equations:

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx = L\delta_{mn} = \begin{cases} L & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{6.40}$$

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = 0 \tag{6.41}$$

$$\int_{-L}^{L} \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = L\delta_{mn}. \tag{6.42}$$

The quantity δ_{mn} is called the *Kronecker delta*. It is equal to unity if its two indices are equal and is equal to zero otherwise. Equations (6.40) and (6.42) do not apply if m and n are both equal to zero. The integral in Eq. (6.40) is equal to $2L$ if $m = n = 0$, and the integral in Eq. (6.42) is equal to zero if $m = n = 0$.

Two different functions that yield zero when multiplied together and integrated are said to be *orthogonal to each other*. Equations (6.40), (6.41), and (6.42) indicate that all the basis functions for the Fourier series of period $2L$ are *orthogonal* to each other. An integral of the product of two functions is sometimes called a *scalar product* of the two functions. This terminology is analogous to that used with vectors. If two vectors are at right angles to each other, they are said to be orthogonal to each other, and their scalar product is zero (see Chapter 2). Since each of the basis functions is orthogonal to the others, its scalar product with a different basis function vanishes, just as the scalar product of any two of the unit vectors $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ vanishes.

To find a_m, where $m \neq 0$ we multiply both sides of Eq. (6.39) by $\cos(m\pi x/L)$ and integrate from $-L$ to L.

$$\int_{-L}^{L} f(x)\cos\left(\frac{m\pi x}{L}\right)dx = \sum_{n=0}^{\infty} a_n \int_{-L}^{L} \cos\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right)dx \quad (6.43)$$

$$+\sum_{n=0}^{\infty} b_n \int_{-L}^{L} \sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right)dx \quad (6.44)$$

We have incorporated the a_0 term into the first sum, using the fact that $\cos(0) = 1$. We have also used the fact that the integral of a sum is equal to the sum of the integrals of the terms if the series is uniformly convergent.

We now apply the orthogonality facts, Eqs. (6.40)–(6.42), to find that all of the integrals on the right-hand side of Eq. (6.43) vanish except for the term with two cosines in which $n = m$. The result is

$$\int_{-L}^{L} f(x)\cos\left(\frac{m\pi x}{L}\right)dx = a_m L. \quad (6.45)$$

This is a formula for finding all of the a coefficients except for a_0. To find a_0, we use the fact that

$$\int_{-L}^{L} \cos(0)\cos(0)\,dx = \int_{-L}^{L} dx = 2L \quad (6.46)$$

which leads to our working equations for the a coefficients:

$$\boxed{a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)dx} \quad (6.47)$$

$$\boxed{a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)dx} \quad (6.48)$$

A similar procedure consisting of multiplication by $\sin(m\pi x/L)$ and integration from $-L$ to L yields

$$\boxed{b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)dx}. \quad (6.49)$$

EXERCISE 6.16 ▶ Show that Eq. (6.49) is correct. ◀

A function does not have to be analytic, or even continuous, in order to be represented by a Fourier series. It is only necessary that the function be integrable. As mentioned in Chapter 5, an integrable function can have step discontinuities, as long as the step in the function is finite. At a step discontinuity, a Fourier series will converge to a value halfway between the value just to the right of the discontinuity and the value just to the left of the discontinuity.

We can represent a function that is not necessarily periodic by a Fourier series if we are only interested in representing the function in the interval $-L < x < L$. The Fourier series will be periodic with period $2L$, and the series will be equal to

the function inside the interval, but not necessarily equal to the function outside the interval.

If the function $f(x)$ is an even function, all of the b_n coefficients will vanish, and only the cosine terms will appear in the series. Such a series is called a *Fourier cosine series*. If $f(x)$ is an odd function, only the sine terms will appear, and the series is called a *Fourier sine series*. If we want to represent a function only in the interval $0 < x < L$ we can regard it as the right half of an odd function or the right half of an even function, and can therefore represent it either with a sine series or a cosine series. These two series would have the same value in the interval $0 < x < L$ but would be the negatives of each other in the interval $-L < x < 0$.

EXAMPLE 6.12 Find the Fourier series to represent the function $f(x) = x$ for the interval $-L < x < L$.

SOLUTION ► The function is odd in the interval $(-L, L)$, so the series will be a sine series. Although our function is defined only for the interval $(-L, L)$, the series will be periodic, and will be the "sawtooth" function that is shown in Fig. 6.2.

The coefficients are obtained from Eq. (6.49). Since the integrand is the product of two odd functions, it is an even function and the integral is equal to twice the integral from 0 to L:

$$b_n = \frac{2}{L} x \sin\left(\frac{n\pi x}{L}\right) dx = \frac{2}{L}\left(\frac{L}{n\pi}\right)^2 \int_0^{n\pi} y \sin(y) dy = \frac{2L}{n\pi}(-1)^{n-1}.$$

The series is

$$f(x) = \sum_{n-1}^{\infty} \frac{2L}{n\pi}(-1)^{n-1} \sin\left(\frac{n\pi x}{L}\right).$$

◄

EXERCISE 6.17 ►

(a) Show that the a_n coefficients for the series representing the function in Example 6.12 all vanish.

(b) Show that the series equals zero at $x = -L$, $x = L$, $x = 3L$, etc., rather than equaling the function at this point.

◄

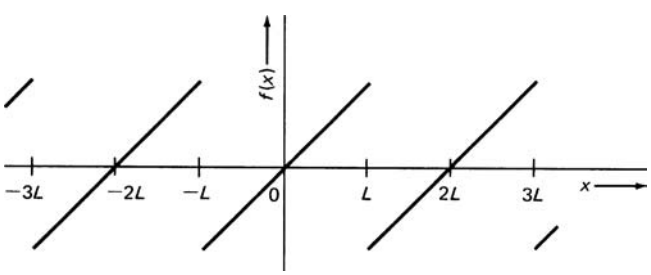

Figure 6.2 ► The sawtooth function of Example 6.12.

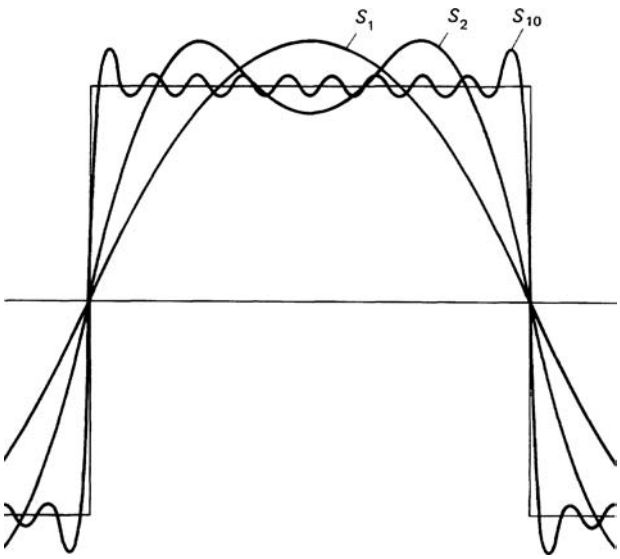

Figure 6.3 ► The square wave function approximated by S_1, S_2, and S_{10}.

EXERCISE 6.18 ► Find the Fourier cosine series for the even function

$$f(x) = |x| \quad \text{for} - L < x < L.$$

Draw a graph of the periodic function represented by the series.

◄

It is a necessary condition for the convergence of Fourier series that the coefficients become smaller and smaller and approach zero as n becomes larger and larger. If a Fourier series is convergent, it will be uniformly convergent for all values of x. If convergence is fairly rapid, it might be possible to approximate a Fourier series by one of its partial sums. Figure 6.3 shows three different partial sums of the series that represents the "square-wave" function

$$f(x) = \begin{array}{l} +1 \text{ for } 0 < x < L \\ -1 \text{ for } -L < x < 0. \end{array}$$

Only the right half of one period is shown. The first partial sum only vaguely resembles the function, but S_{10} is a better approximation. Notice the little spike or overshoot near the discontinuity. This is a typical behavior and is known as the *Gibbs phenomenon*.[5] The partial sum S_{100} fits the function more closely away from the discontinuity, but it has a spike near the discontinuity that is just as high as that of S_{10}, although much narrower.

[5]Named for Josiah Willard Gibbs, 1839–1903, a prominent American physicist who made important contributions to mathematics and chemistry as well as to physics.

Fourier Series with Complex Exponential Basis Functions

The sine and cosine basis functions are closely related to complex exponential functions, as shown in Eqs. (2.105) and (2.106). One can write

$$b_n \sin\left(\frac{n\pi x}{L}\right) + a_n \cos\left(\frac{n\pi x}{L}\right) = \frac{1}{2}(a_n - ib_n)\, e^{in\pi x/L} + \frac{1}{2}(a_n + ib_n)\, e^{in\pi x/L}. \tag{6.50}$$

It is therefore possible to rewrite Eq. (6.39) as an exponential Fourier series:

$$\boxed{f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/L}.} \tag{6.51}$$

We have incorporated the terms with negative exponents into the same sum with the other terms by allowing the summation index to take on negative as well as positive values. The function being represented by a Fourier series does not have to be a real function. If it is a real function, the coefficients a_n and b_n will be real and the coefficients c_n will be complex.

Other Functional Series with Orthogonal Basis Sets

Fourier series are just one example of series using orthogonal sets of basis functions. For example, in quantum mechanics it is found that the eigenfunctions of quantum mechanical operators form orthogonal sets of functions, and these can be used as basis functions for series. It is generally assumed that such a set of functions is complete for representation of functions that obey the same boundary conditions as the basis functions. Boundary conditions are discussed in Chapter 8 in connection with differential equations.

Assume that we have a complete set of orthogonal functions, called ψ_1, ψ_2, ψ_3, and so on, and that these functions have been *normalized* and that they are *orthogonal* to each other. This means that the functions have been multiplied by appropriate constants so that the scalar product of any one of the functions with itself is unity and that the scalar product of two of the functions vanishes:

$$\int \psi_n^* \psi_m dx = \delta_{nm} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{if } n \neq m \end{cases} \tag{6.52}$$

In case the basis functions are complex, the scalar product is defined as the integral of the complex conjugate of the first function times the second function, as in Eq. (6.52).

Since the set of functions is assumed to be complete, we can expand an arbitrary function, f, in terms of the ψ functions so long as f obeys the same boundary conditions as the ψ functions.

$$f = \sum_n c_n \psi_n \tag{6.53}$$

The sum in this equation will include one term for each function in the complete set and can have infinitely many terms.

In order to find the coefficients c_1, c_2, c_3, and so on, we multiply by the complex conjugate of ψ_m and integrate. With Eq. (6.52), our result is

$$\boxed{\int \psi_m^* f\, dx = \textstyle\sum_n c_n \int \psi_m^* \psi_n dx = \sum_n c_n \delta_{nm} = c_m} \tag{6.54}$$

When the final sum over n is carried, only the $n = m$ term survives because of the Kronecker delta. Equations (6.47), (6.48), and (6.49) are special cases of this equation.

EXAMPLE 6.13 The normalized quantum-mechanical wave functions for the particle in a one-dimensional box of length a are

$$\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin(n\pi x/a)$$

These functions are a complete set for expansion of functions that are defined only in the region $0 < x < a$ and vanish at $x = 0$ and at $x = a$. That is, a linear combination of these functions can be an exact representation of the function in the region $0 < x < a$. Find the coefficient c_1 if $f = x^2 - ax$.

SOLUTION ►

$$\begin{aligned} c_1 &= \left(\frac{2}{a}\right)^{1/2} \left(\int_0^a x^2 \sin(\pi x/a)dx + a \int_0^a x \sin(\pi x/a)dx \right) \\ &= \left(\frac{2}{a}\right)^{1/2} (\frac{a}{\pi})^3 \int_0^\pi y^2 \sin(y)dy - a \left(\frac{2}{a}\right)^{1/2} (\frac{a}{\pi})^2 \int_0^\pi y \sin(y)dy \qquad (6.55) \\ &= \left(\frac{2}{a}\right)^{1/2} (\frac{a}{\pi})^3 \left[2y \sin(y) - (y^2 - 2)\cos(y)\right]\Big|_0^\pi \\ &\quad - a \left(\frac{2}{a}\right)^{1/2} (\frac{a}{\pi})^2 \left[\sin(y) - y\cos(y)\right]|_0^\pi \qquad (6.56) \\ &= \left(\frac{2}{a}\right)^{1/2} (\frac{a}{\pi})^3 [(\pi^2 - 2) - 2] - a \left(\frac{2}{a}\right)^{1/2} (\frac{a}{\pi})^2 [\pi^2] \\ &= -\frac{4\sqrt{2}a^{5/2}}{\pi^3} = -0.182442a^{5/2} \qquad (6.57) \end{aligned}$$

◄

EXERCISE 6.19 ► Using Excel, construct a graph of the function f from the previous example in the region $0 < x < a$ and another graph of $c_1\psi_1$. Compare the graphs and comment on how well the partial sum with one term approximates the function. Let $a = 1$ for your graphs. ◄

EXERCISE 6.20 ► Write the formula for finding the coefficients for an exponential Fourier series. Is there any difference in the formulas for odd functions, even functions, or functions that are neither odd nor even? What conditions must the function obey to be represented by an exponential Fourier series? ◄

6.4 Mathematical Operations on Series

Carrying out mathematical operations such as integration or differentiation on a functional series with a finite number of terms is straightforward, since no questions of convergence arise. However, carrying out such operations on an infinite

series presents a few difficulties. The question arises whether differentiating each term and then summing the result gives the same result as first summing the series and then differentiating. Although we do not prove it, the principal fact is: *If a series is uniformly convergent the result of operating on the series is the same as the result of operating on the individual terms and then summing the resulting series*. For example, if

$$f(x) = \sum_{n=0}^{\infty} a_n g_n(x) \tag{6.58}$$

and if the series is uniformly convergent, then

$$\frac{df}{dx} = \frac{d}{dx}\left[\sum_{n=0}^{\infty} a_n g_n(x)\right] = \sum_{n=0}^{\infty} a_n \frac{dg_n}{dx}. \tag{6.59}$$

This amounts to interchange of the operations of summing and differentiating. Similarly, for a uniformly convergent series,

$$\int_a^b f(x)dx = \int_a^b \left[\sum_{n=0}^{\infty} a_n g_n(x)\right] dx = \sum_{n=0}^{\infty} a_n \int_a^b g_n(x)\, dx. \tag{6.60}$$

This amounts to interchange of the operations of summing and integrating.

We have already used Eq. (6.60) in the previous section in deriving the formula for the coefficients in the Fourier series, without commenting on the fact that the series must be uniformly convergent to justify this procedure.

EXAMPLE 6.14 Find the Maclaurin series for $\cos(x)$ from the Maclaurin series for $\sin(x)$, using the fact that $d[\sin(x)]/dx = \cos(x)$.

SOLUTION ► The series happens to be uniformly convergent for all values of x. From Eq. (6.29), we have

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$

so that

$$\frac{d[\sin(x)]}{dx} = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots.$$

◄

EXERCISE 6.21 ► From the Taylor series for $\ln(x)$ expanded about $x = 1$ given in Eq. (6.27), find the Taylor series for $1/x$ about $x = 1$, using the fact that

$$\frac{d[\ln(x)]}{dx} = \frac{1}{x}$$

and the fact that the series is uniformly convergent for all $x > 0$. Comment on the range of values of x for which your series is valid. ◄

6.5 Integral Transforms

Integral transforms are closely related to functional series. However, instead of a sum with each term consisting of a coefficient multiplying a basis function, we have an integral in which the summation index is replaced by an integration variable. The basis functions are multiplied by a function of this integration variable, and integration over this variable yields a representation of the function. This function of the integration variable is called the *integral transform* of the given function. The transform is a function of the integration variable, in the same way as the coefficients in a functional series depend on the value of the summation index. You can think of a transform as encoding the same information as in the original representation of the function, but with a different independent variable. There are several kinds of integral transforms, including Mellin transforms, Hankel transforms, and so forth,[6] but the principal kinds of transforms encountered by physical chemists are Fourier transforms and Laplace transforms.

Fourier Transforms (Fourier Integrals)

Although Fourier transforms were once important only to mathematicians and some theoretical scientists, they are now widely used in spectroscopy, because instruments have been designed that produce a superposition of wave-like signals such that the spectrum is the Fourier transform of the detected signal.[7] Let us see how Fourier transforms compare with Fourier series, which are designed to represent periodic functions with period $2L$. If we allow L to become larger and larger without bound, the values of $n\pi x/L$ become closer and closer together. We let

$$k = \frac{n\pi}{L}. \tag{6.61}$$

As the limit $L \to \infty$ is taken, k becomes a continuously variable quantity. In this limit, an exponential Fourier series becomes an integral, which is called a *Fourier integral* or a *Fourier transform*,

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} dk, \tag{6.62}$$

where the coefficient c_n in Eq. (6.51) is replaced by a function of k, denoted by $F(k)$.

The equation for determining $F(k)$ is analogous to Eq. (6.47), (6.48), and (6.49)

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx. \tag{6.63}$$

We have introduced a factor of $1/\sqrt{2\pi}$ in front of the integral in Eq. (6.62) in order to have the same factor in front of this integral and the integral in Eq. (6.63).

The function $F(k)$ is called the *Fourier transform* of $f(x)$ and the function $f(x)$ is also called the *Fourier transform* of $F(k)$. The function $f(x)$ is no longer

[6] A. Erdelyi Ed., *Tables of Integral Transforms*, Vols. I and II, McGraw–Hill, New York, 1954; A. G. Marshall. Ed., *Fourier, Hadamard, and Hilbert Transforms in Chemistry*, Plenum, New York, 1982.

[7] L. Glasser, *J. Chem. Educ.* **64**, $A_2$28(1987); *J. Chem. Educ.* **64**, A260(1987); and *J. Chem. Educ.* **64**, A306(1987).

required to be periodic, because the period $2L$ has been allowed to become infinite. Since we now have improper integrals, the functions $f(x)$ and $F(k)$ must have properties such that the integrals converge. For the integral of Eq. (6.63) to converge, the following integral must converge:

$$\int_{-\infty}^{\infty} |f(x)|^2 \, dx.$$

We say that the function $f(x)$ must be *square integrable*. The function $f(x)$ must approach zero as $x \to -\infty$ and as $x \to \infty$ to be square integrable. If the Fourier transform $F(k)$ exists, it will also be square integrable.

EXAMPLE 6.15 Find the Fourier transform of the Gaussian function

$$f(x) = e^{-ax^2}.$$

SOLUTION ►

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2} e^{-ikx} dx.$$

From Eq. (2.93),

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2} \cos(kx) dx - \frac{i}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-ax^2} \sin(kx) dx.$$

The second integral in this equation is equal to zero because its integrand is an odd function. The first integral is twice the integral of Eq. (47) of Appendix F,

$$\begin{aligned} F(k) &= \frac{2}{\sqrt{2\pi}} \int_0^{\infty} e^{-ax^2} \cos(kx) dx = \frac{2}{\sqrt{2\pi}} \frac{1}{2} \sqrt{\frac{\pi}{a}} e^{-k^2/4a} \\ &= \frac{1}{\sqrt{2a}} e^{-k^2/4a}. \end{aligned}$$

◄

This example illustrates that interesting fact that the Fourier transform of a Gaussian function of x is another Gaussian function of k.

In the previous example the transform integral was separated into one part containing a cosine function and one containing a sine function. If the function $f(x)$ is an even function, its Fourier transform is a *Fourier cosine transform*:

$$F(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} f(x) \cos(kx) dx = \sqrt{\frac{2}{\pi}} \int_0^{\infty} f(x) \cos(kx) dx \quad (f \text{ even}). \tag{6.64}$$

The second version of the transform is called a *one-sided cosine transform*.

If $f(x)$ is an odd function, its Fourier transform is a *Fourier sine transform*:

$$F(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} f(x) \sin(kx) dx = \sqrt{\frac{2}{\pi}} \int_0^{\infty} f(x) \sin(kx) dx \quad (f \text{ odd}). \tag{6.65}$$

There is a useful theorem for the Fourier transform of a product of two functions, called the *convolution theorem* or the *Faltung theorem* (*Faltung* is German for "folding"). The convolution of two functions $f(x)$ and $g(x)$ is defined as the integral

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(y) g(x - y) dy. \tag{6.66}$$

This integral is a function of x, and its Fourier transform is equal to $F(k)G(k)$ where $F(k)$ is the Fourier transform of $f(x)$ and $G(k)$ is the Fourier transform of $g(x)$.[8] Since the Fourier transform is nearly the same going in both directions, the analogous convolution

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(l)G(k-l)dl \tag{6.67}$$

has as its Fourier transform the product $f(x)g(x)$.

EXERCISE 6.22 ▶ Take the two Gaussian functions

$$f(x) = e^{-ax^2} \quad \text{and} \quad g(x) = e^{-bx^2}.$$

Find the Fourier transform of the product of the functions using the convolution theorem. Show that this transform is the same as that obtained by multiplying the functions together and computing the transform in the usual way. ◀

The two principal applications of Fourier transformation for chemists are in infrared spectroscopy and nuclear magnetic resonance spectroscopy. In both cases, the instrument takes raw data as a function of time and a spectrum as a function of frequency is obtained. In a Fourier transform infrared instrument, an *interferometer* varies the intensities of radiation of various frequencies as a function of time, and a detector determines the intensity as a function of time, producing an interferogram, which is the Fourier transform of the desired spectrum. The Fourier transformation is carried out by a computer program for predetermined values of the frequency, so that the spectrum is obtained only for a discrete set of frequencies. Numerical Fourier transformation is usually a fairly slow process, demanding a lot of computer time, but a Fast Fourier Transform (FFT) algorithm has been developed that makes the process practical for routine usage.[9] In a Fourier transform NMR instrument, a signal called the *free induction decay signal* is obtained as a function of time, and the Fourier transform of this signal is the desired NMR spectrum. The FFT algorithm is used to carry out the transformation.

Laplace Transforms

The *Laplace transform* $F(s)$ of the function $f(t)$ is defined by[10]

$$\boxed{F(s) = \int_0^{\infty} f(t)e^{-st}\,dt}. \tag{6.68}$$

We use the same notation as with the Fourier transform, denoting a Laplace transform by a capital letter and the function by a lowercase letter. You will have to tell from the context whether we are discussing a Fourier transform or a Laplace transform. We use the letter t for the independent variable of the function, since Laplace transforms are commonly applied to functions of the time. The letter x could also have been used.

[8] Philip M. Morse and Herman Feshbach, *Methods of Theoretical Physics*, Part 1, pp. 464ff, McGraw-Hill, New York, 1953.

[9] J. W. Cooley and J. W. Tukey, *Math. Computation*, **19**, 297–301 (1965). See the book by James under Additional Reading.

[10] The Laplace transform is named for Pierre Simon Laplace, Marquis de LaPlace, 1749–1827, French astronomer and mathematician.

TABLE 6.1 ► Laplace Transforms

$\mathbf{F}(s)$	$f(t)$
$1/s$	1
$1/s^2$	t
$n!/s^{n+1}$	t^n
$\dfrac{1}{s-a}$	e^{at}
$\dfrac{s}{s^2+k^2}$	$\cos(kt)$
$\dfrac{k}{s^2+k^2}$	$\sin(kt)$

The Laplace transform is similar to a one-sided Fourier transform, except that it has a real exponential instead of the complex exponential of the Fourier transform. If we consider complex values of the variables, the two transforms become different versions of the same transform, and their properties are related.[11] The integral that is carried out to invert the Laplace transform is carried out in the complex plane, and we do not discuss it. Fortunately, it is often possible to apply Laplace transforms without carrying out such an integral.[12] We will discuss the use of Laplace transforms in solving differential equations in Chapter 8.

The Laplace transform and its inverse are often denoted in the following way:

$$F(s) = \mathcal{L}\{f(t)\} \tag{6.69}$$

$$f(t) = \mathcal{L}^{-1}\{F(s)\}. \tag{6.70}$$

Table 6.1 gives a few common Laplace transforms.

EXAMPLE 6.16 Find the Laplace transform of the function $f(t) = t^2$.

SOLUTION ►

$$F(s) = \int_0^\infty t^2 e^{-st} dt = \frac{1}{s^3}\int_0^\infty u^2 e^{-u} du = \frac{2!}{s^3},$$

where we have used Eq. (1) of Appendix F to obtain the value of the definite integral. ◄

EXERCISE 6.23 ► Find the Laplace transform $F(s)$ of the function $f(t) = e^{at}$ where a is a constant. ◄

There are several theorems that are useful in obtaining Laplace transforms of various functions.[13] The first is the *shifting theorem*:

$$\boxed{\mathcal{L}\left\{e^{at} f(t)\right\} = F(s-a)}. \tag{6.71}$$

EXAMPLE 6.17 Use the theorem of Eq. (6.71) to obtain the Laplace transform of the function

$$f(t) = e^{at}\cos(kt).$$

[11] Philip M. Morse and Herman Feshbach, op. cit., pp. 467ff.

[12] Erwin Kreyszig, *Advanced Engineering Mathematics*, 8th ed., Wiley, New York, 1999.

[13] *Ibid*.

SOLUTION ► We transcribe the entry for $\cos(kx)$ from Table 6.1, replacing s by $s - a$, obtaining

$$F(s) = \frac{s-a}{(s-a)^2 + k^2.}$$

◄

EXERCISE 6.24 ► Find the Laplace transform of the function

$$f(t) = t^n e^{at}.$$

◄

The next useful theorem is the *derivative theorem*

$$\boxed{\mathcal{L}\left\{f'\right\} = s\mathcal{L}\{f\} - f(0)}, \tag{6.72}$$

where we use the notation f' for the first derivative of f. This theorem can be applied to the solution of first-order differential equations and can be applied repeatedly to obtain the extended version,

$$\boxed{\mathcal{L}\left\{f^{(n)}\right\} = s^n\mathcal{L}\{f\} - s^{n-1}f(0) - s^{n-2}f''(0) - \cdots - f^{(n-1)}(0)}, \tag{6.73}$$

where we use the notation $f^{(n)}$ for the nth derivative of f, and so on.

EXERCISE 6.25 ► Derive the version of Eq. (6.73) for $n = 2$. ◄

The next theorem is for the Laplace transform of an integral of a given function f,

$$\boxed{\mathcal{L}\left\{\int_0^t f(u)\,du\right\} = \tfrac{1}{s}\mathcal{L}\{f(t)\}}. \tag{6.74}$$

These theorems can be used to construct the Laplace transforms of various functions, and to find inverse transforms without carrying out an integral in the complex plane.

EXAMPLE 6.18 Find the inverse Laplace transform of

$$\frac{1}{s(s-a)}.$$

SOLUTION ► From Table 6.1, we recognize $1/(s-a)$ as the Laplace transform of e^{at}. From the theorem of Eq. (6.74),

$$\mathcal{L}\left\{\int_0^t e^{au}\,du\right\} = \frac{1}{s}\mathcal{L}\left\{e^{at}\right\} = \frac{1}{s}\frac{1}{s-a}.$$

Therefore, the inverse transform is

$$\mathcal{L}^{-1}\left\{\frac{1}{s(s-a)}\right\} = \int_0^t e^{ay}dy = \frac{1}{a}(e^{at} - 1).$$

◄

EXERCISE 6.26 ► Find the inverse Laplace transform of

$$\frac{1}{s(s^2 + k^2)}.$$

◄

SUMMARY

In this chapter we introduced mathematical series and mathematical transforms. A finite series is a sum of a finite number of terms, and an infinite series is a sum of infinitely many terms. A constant series has terms that are constants, and a functional series has terms that are functions. The two important questions to ask about a constant series are whether the series converges and, if so, what value it converges to. We presented several tests that can be used to determine whether a series converges. Unfortunately, there appears to be no general method for finding the value to which a convergent series converges.

A functional series is one way of representing a function. Such a series consists of terms, each one of which is a basis function times a coefficient. A power series uses powers of the independent variable as basis functions and represents a function as a sum of the appropriate linear function, quadratic function, cubic function, etc. We discussed Taylor series, which contain powers of $x - h$, where h is a constant, and also Maclaurin series, which are Taylor series with $h = 0$. Taylor series can represent a function of x only in a region of convergence centered on h and reaching no further than the closest point at which the function is not analytic. We found the general formula for determining the coefficients of a power series.

The other functional series that we discussed was the Fourier series, in which the basis functions are sine and cosine functions. This type of series is best suited for representing periodic functions and represents the function as a sum of the sine and cosine functions with the appropriate coefficients. The method of determining the coefficients to represent any particular function was given.

Integral transforms were discussed, including Fourier and Laplace transforms. Fourier transforms are the result of allowing the period of the function to be represented by a Fourier series to become larger and larger, so that the series approaches an integral in the limit. Fourier transforms are usually written with complex exponential basis functions, but sine and cosine transforms also occur. Laplace transforms are related to Fourier transforms, with real exponential basis functions. We presented several theorems that allow the determination of some kinds of inverse Laplace transforms and that allow later applications to the solution of differential equations.

PROBLEMS

1. By use of the Maclaurin series already obtained in this chapter, prove the identity $e^{ix} = \cos(x) + i \sin(x)$.

2.

a) Show that no Maclaurin series

$$f(x) = a_0 + a_1 x + a_2 x^2 + \cdots$$

can be formed to represent the function $f(x) = \sqrt{x}$. Why is this?

b) Find the first few coefficients for the Maclaurin series for the function

$$f(x) = \sqrt{1 + x}.$$

3. Find the coefficients of the first few terms of the Taylor series

$$\tan(x) = a_0 + a_1 \left(x - \frac{\pi}{4}\right) + a_2 \left(x - \frac{\pi}{4}\right)^2 + \cdots,$$

where x is measured in radians. What is the radius of convergence of the series?

4. Find the coefficients of the first few terms of the Maclaurin series

$$\cosh(x) = a_0 + a_1 x + a_2 x^2 + \cdots,$$

What is the radius of convergence of the series?

5. The sine of $\pi/4$ radians (45°) is $\sqrt{2}/2 = 0.70710678\cdots$. How many terms in the series

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$

must be taken to achieve 1% accuracy at $x = \pi/4$?

6. The cosine of 30° ($\pi/6$ radians) is equal to $\sqrt{3}/2 = 0.866025\cdots$. How many terms in the series

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots.$$

must be taken to achieve 0.1% accuracy $x = \pi/6$?

7. Estimate the largest value of x that allows e^x to be approximated to 1% accuracy by the following partial sum

$$e^x \approx 1 + x.$$

8. Estimate the largest value of x that allows e^x to be approximated to 0.01% accuracy by the following partial sum

$$e^x \approx 1 + x + \frac{x^2}{2!}.$$

9. How many terms in the series

$$e^x \approx 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

must be taken to approximate e^x to 0.01% accuracy for $x = 1$? For $x = 2$?

10. Find two different Taylor series to represent the function

$$f(x) = \frac{1}{x^2}$$

such that one series is

$$f(x) = a_0 + a_1(x-1) + a_2(x-1)^2 + \cdots$$

and the other is

$$f(x) = b_0 + b_1(x-2) + b_3(x-2)^2 + \cdots .$$

Show that $b_n = a_n/2^n$ for any value of n. Find the interval of convergence for each series (the ratio test may be used). Which series must you use in the vicinity of $x = 3$? Why?

11. Find the Taylor series in powers of $(x-10)$ that represents the function $\ln(x)$.

12. Using the Maclaurin series for e^x, show that the derivative of e^x is equal to e^x.

13. Find the Maclaurin series that represents $\tan(x)$. What is its radius of convergence?

14. Find the Maclaurin series that represents $\cosh(x)$. What is its radius of convergence?

15. A certain electronic circuit produces the following sawtooth wave,

$$f(t) = \begin{cases} a(-T-t), & -T < t < -T/2 \\ at, & -T/2 < t < T/2 \\ a(T-t), & -T/2 < t < T, \end{cases}$$

where a and T are constants and t represents the time. Find the Fourier series that represents this function. The definition of the function given is for only an interval of length $2T$, but the Fourier series will be periodic. Make a graph of the function and of the first two partial sums.

16. Find the Fourier series that represents the square wave

$$A(t) = \begin{cases} 0, & -T/2 < t < 0 \\ A_0, & 0 < t < T/2, \end{cases}$$

where A_0 is a constant and T is the period.

17. Find the Fourier series to represent the function

$$A(t) = \begin{cases} e^t, & 0 < t < \pi \\ 0, & \text{elsewhere} \end{cases}$$

Your series will be periodic and will represent the function only in the region $0 < t < \pi$.

a) Use a sine series.

b) Use a cosine series.

18. Find the Fourier transform of the function $a \exp(-(x - x_0)^2/b)$, where a and b are constants.

19. Find the Fourier transform of the function $ae^{-b|x|}$.

20. Find the one-sided Fourier sine transform of the function ae^{-bx}

21.

a) Find the Laplace transform of the function $a/(b^2 + t^2)$, where a and b are constants.

b) Find the Fourier transform of the same function.

22. Show that $\mathcal{L}\{t \cos(kt)\} = (s^2 - k^2)/(s^2 + k^2)^2$.

7

Calculus With Several Independent Variables

Preview

In this chapter, we discuss functions of more than one independent variable. For example, if you have a function of three independent variables, the function will deliver a value of the dependent variable if three values are specified: one value of each of the three independent variables. Differential calculus of such functions begins with the differential of the function, which represents an infinitesimal change in the dependent variable resulting from infinitesimal changes in the independent variables and consists of a sum of terms. Each term consists of a partial derivative with respect to an independent variable multiplied by the differential of that variable (an infinitesimal change in that independent variable). Maximum and minimum values of functions can be found using partial derivatives. There are two principal kinds of integrals that have integrand functions depending on several independent variables: line integrals and multiple integrals.

Principal Facts and Ideas

1. Functions of several independent variables occur frequently in physical chemistry, both in thermodynamics and in quantum mechanics.
2. A derivative of a function of several variables with respect to one independent variable is a partial derivative. The other variables are treated as constants during the differentiation.
3. There are some useful identities allowing manipulations of expressions containing partial derivatives.
4. The differential of a function of several variables (an exact differential) has one term for each variable, consisting of a partial derivative times the differential of the independent variable. This differential form delivers the value of an

infinitesimal change in the function produced by infinitesimal changes in the independent variables.

5. Differential forms exist that are not the differentials of any function. Such a differential form delivers the value of an infinitesimal quantity, but it is not the differential of any function. Such a differential form is called an inexact differential.
6. An integral of a differential with several independent variables is a line integral, carried out on a specified path in the space of the independent variables.
7. The line integral of an exact differential depends only on the endpoints of the path, but the line integral of an inexact differential depends on the path.
8. A multiple integral has as its integrand function a function of several variables, all of which are integrated.
9. The gradient operator is a vector derivative operator that produces a vector when applied to a scalar function.
10. The divergence operator is a vector derivative operator that produces a scalar when applied to a vector function.
11. Relative maxima and minima of a function of several variables are found by solving simultaneously the equations obtained by setting all partial derivatives equal to zero.
12. Constrained maxima and minima of a function of several variables can be found by the method of Lagrange multipliers.

Objectives

After studying this chapter, you should be able to:

1. write formulas for the partial derivatives and for the differential of a function if given a formula for the function and use these in applications such as the calculation of small changes in a dependent variable;
2. perform a change of independent variables and obtain formulas relating different partial derivatives;
3. use identities involving partial derivatives to eliminate undesirable quantities from thermodynamic formulas;
4. identify an exact differential and an integrating factor;
5. perform a line integral with two independent variables;
6. perform a multiple integral;
7. change independent variables in a multiple integral;
8. use vector derivative operators;
9. find constrained and unconstrained maximum and minimum values of functions of several variables.

7.1 Functions of Several Independent Variables

A function of several independent variables is similar to a function of a single independent variable except that you must specify a value for each of the independent

variables in order for the function to provide a value for the dependent variable. For example, the equilibrium thermodynamic properties of a fluid (gas or liquid) system of one substance and one phase are functions of three independent variables. If we choose a set of values for the temperature, T, the volume, V, and n, the amount of the substance in moles, then the other thermodynamic properties, such as pressure, P, and thermodynamic energy, U, are functions of these variables. We can write

$$P = P(T,V,n) \tag{7.1a}$$
$$U = U(T,V,n) \tag{7.1b}$$

We can choose any three of the variables as independent variables so long as at least of them is proportional to the size of the system. For example, we could also write

$$\begin{aligned} V &= V(T,P,n) \\ U &= U(P,V,n) \end{aligned} \tag{7.2}$$

and so on. We assume that the functions that represent the behavior of physical systems are *piecewise continuous* with respect to each variable. That is, if we temporarily keep all but one of the independent variables fixed, the function behaves as a piecewise continuous function of that variable. We also assume that the function is piecewise single-valued.

In physical chemistry, we sometimes work with mathematical formulas that represent various functions. For example, if the temperature of a gas is fairly high and its volume is large enough, the pressure of a gas is given to a good approximation by the ideal gas equation

$$P = P(T, V, n) = \frac{nRT}{V} = \frac{RT}{V_m}, \tag{7.3}$$

where T is the temperature on the Kelvin scale, n is the amount of gas in moles, V is the volume, and R is the ideal gas constant. The molar volume, V_m, is equal to V/n.

In addition to formulas, functions can be represented by graphs, by tables of values, or by infinite series. However, graphs, tables, and series become more complicated when used for a function of several variables than for functions of a single variable.

Figure 7.1 shows the dependence of the pressure of a nearly ideal gas as a function of the molar volume, V_m . With only two axes on our graph, a curve can show the dependence of P on V_m only for a fixed value of T. The figure shows curves for several members of a family of functions of V_m, each for a different value of T.

Figure 7.2 is a perspective view of a three-dimensional graph representing P as a function of V_m and T. The value of P is given by the height from the horizontal plane to a surface, which plays the same role as the curve in a two-dimensional graph. It is fairly easy to read quantitative information from the two-dimensional graph in Figure 7.1, but the perspective view in Figure 7.2 is more difficult to read numbers from. If you have more than two independent variables, a graph cannot be constructed. Sometimes attempts are made to show roughly how functions of three variables depend on their independent variables by drawing a perspective

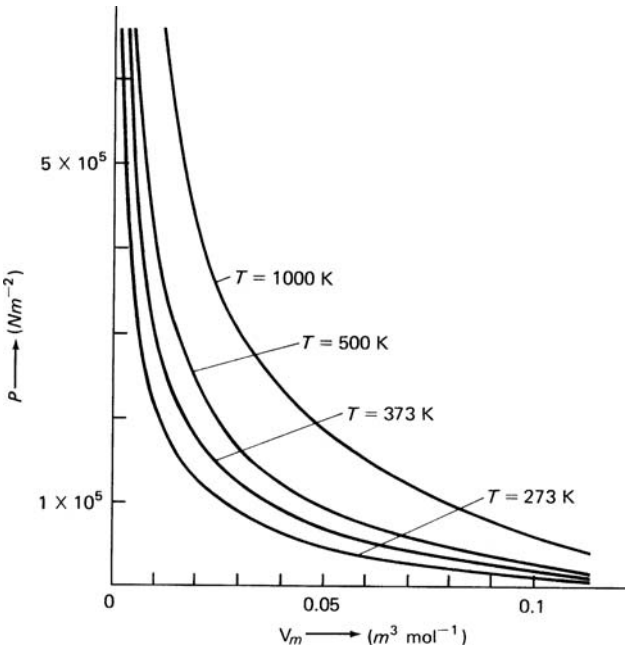

Figure 7.1 ► The pressure of a nearly ideal gas as a function of the molar volume V_m at various fixed temperatures.

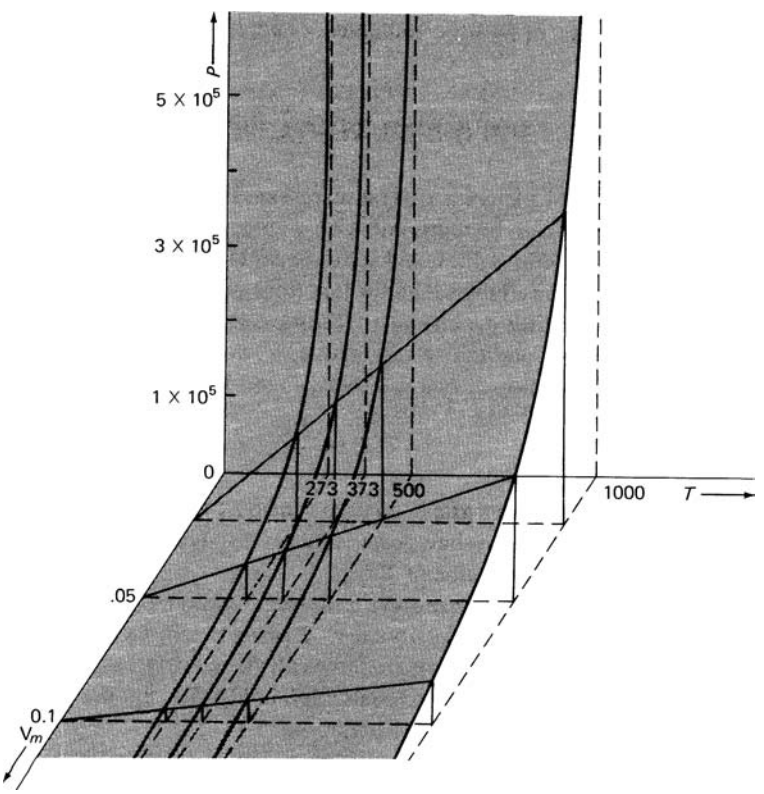

Figure 7.2 ► The pressure of a nearly ideal gas a function of V_m and T.

view of three axes, one for each of the independent variables, and then trying to communicate the approximate value of the dependent variable by a density of dots placed in the diagram.

Tables of values are also cumbersome with two or more independent variables, since a function is now not a set of ordered pairs of numbers but a set of ordered sets of three numbers or four numbers, and so forth. For two independent variables, we need a rectangular array, with values of one independent variable along the top and values of the other along one side, and values of the dependent variable in the body of the array. For a third independent variable, we would need a different sheet of paper for each value of the third variable. The most common way to represent a function of several variables is with a mathematical formula.

Changes in a Function of Several Variables

Many times in physical chemistry we do not have an accurate representation of a function representing some physical variable. Generally we are more interested in changes in a function than in the entire function, and in some cases we can find changes in a function even if we do not know the entire function. We now discuss changes in a function. Consider a gas contained in a cylinder with a movable piston and a valve through which additional gas can be admitted or removed, and let the entire system be immersed in a constant-temperature bath. For the present, we keep the valve closed, so that n is fixed (the system is now a *closed system*). Let us now make an infinitesimal change dV in the volume of the gas, keeping n and T fixed. If n and T are both fixed, P will behave just like a function of the one variable V. The change in P is given in the same way as with a function of one variable:

$$dP = \left(\frac{dP}{dV}\right) dV \quad (n \text{ and } T \text{ fixed}), \tag{7.4}$$

where dP/dV is the derivative of P with respect to V.

Partial Derivatives

We adopt a new notation, replacing the d symbols by symbols that are slightly distorted lowercase Greek deltas and adding subscripts to specify the variables that are being held fixed.

$$dP = \left(\frac{\partial P}{\partial V}\right)_{n,T} dV \quad (n \text{ and } T \text{ fixed}). \tag{7.5}$$

The quantity $(\partial P/\partial V)_{n,T}$ is called the *partial derivative* of P with respect to V at constant n and T. The partial derivative is obtained by the differentiation techniques of Chapter 4, treating n and T like ordinary constants. There are as many partial derivatives of a given function as there are independent variables on which

it depends. For an ideal gas, P is a function of T, V, and n.

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = \left(\frac{\partial}{\partial V}\left[\frac{nRT}{V}\right]\right)_{n,T} = -\frac{nRT}{V^2} \quad (n \text{ and } T \text{ fixed}) \tag{7.6a}$$

$$\left(\frac{\partial P}{\partial T}\right)_{n,V} = \left(\frac{\partial}{\partial T}\left[\frac{nRT}{V}\right]\right)_{n,V} = \frac{nR}{V} \quad (n \text{ and } V \text{ fixed}) \tag{7.6b}$$

$$\left(\frac{\partial P}{\partial n}\right)_{T,V} = \left(\frac{\partial}{\partial n}\left[\frac{nRT}{V}\right]\right)_{T,V} = \frac{RT}{V} \quad (T \text{ and } V \text{ fixed}). \tag{7.6c}$$

Each of these partial derivatives is obtained by the usual differentiation technique, treating the other variables as constants.

Differentials

If we make an infinitesimal change dV in the volume and a change dT in the temperature of the gas while keeping n fixed, the change in P is the sum of two expressions like that in Eq. (7.5).

$$dP = \left(\frac{\partial P}{\partial V}\right)_{n,T} dV + \left(\frac{\partial P}{\partial T}\right)_{n,V} dT \quad (n \text{ fixed}). \tag{7.7}$$

Each term of this equation is the change due to the change in one independent variable, and each partial derivative thus is taken with the other independent variables treated as constants. If we make the changes dV in V, dT in T, and dn in n these changes affect P separately, and we can write for the total infinitesimal change in P,

$$dP = \left(\frac{\partial P}{\partial V}\right)_{n,T} dV + \left(\frac{\partial P}{\partial T}\right)_{n,V} dT + \left(\frac{\partial P}{\partial n}\right)_{T,V} dn. \tag{7.8}$$

The infinitesimal change dP given by this expression is called the *differential* of P, or sometimes the *total differential of* P. It is a sum of terms, one for each independent variable. Each term gives the effect of one variable with the other treated as constants.

If we have a function y that depends on n independent variables, $x_1, x_2, x_3, \ldots, x_n$, its differential is

$$\boxed{dy = \sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i}\right)_{x'} dx_i} \tag{7.9}$$

where the subscript x' stands for keeping all of the variables except for x_i fixed in the differentiation. This equation is sometimes called the *fundamental equation* of differential calculus.

The expression for dP for an ideal gas is

$$dP = -\frac{nRT}{V^2}\,dV + \frac{nR}{V}\,dT + \frac{RT}{V}\,dn \tag{7.10}$$

For small but finite changes, an approximate version of this can be written

$$\Delta P \approx -\frac{nRT}{V^2}\,\Delta V + \frac{nR}{V}\,\Delta T + \frac{RT}{V}\,\Delta n. \tag{7.11}$$

EXAMPLE 7.1 Use Eq. (7.11) to calculate approximately the change in pressure of an ideal gas if the volume is changed from 20.000 l to 19.800 l, the temperature is changed from 298.15 K to 299.00 K, and the amount of gas in moles is changed from 1.0000 mol to 1.0015 mol.

SOLUTION ►

$$\begin{aligned}\Delta P \approx &-\frac{(1.0000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{(0.020000\,\text{m}^3)^2}\left(-0.200\times10^{-3}\,\text{m}^3\right)\\ &+\frac{(1.0000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}{0.020000\,\text{m}^3}(0.85\,\text{K})\\ &+\frac{(8.3144\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{0.020000\,\text{m}^3}(0.0015\,\text{mol})\\ &\approx 1.779\times10^3\,\text{N m}^{-2} = 1.779\times10^3\,\text{Pa},\end{aligned}$$

where we use the fact that $1\,\text{J} = 1\,\text{N m}$. ◄

EXAMPLE 7.2 Compare the result of the previous example with the correct value of the pressure change.

SOLUTION ► We can calculate the actual change as follows. Let the initial values of n, V, and T be called n_1, V_1, and T_1, and the final values be called n_2, V_2, and T_2,

$$\begin{aligned}\Delta P &= P(n_2, V_2, T_2) - P(n_1, V_1, T_1)\\ &= \frac{n_2RT_2}{V_2} - \frac{n_1RT_1}{V_1}.\end{aligned}$$

The result of this calculation is $1.797\times10^3\,\text{N m}^{-2} = 1.797\times10^3\,\text{Pa}$, so that our approximate value is in error by about 1%. ◄

In these examples the exact calculation could be made more easily than the approximation. However, in physical chemistry it is frequently the case that a formula for a function is not known, but values for the partial derivatives are available, so that approximation can be made while the exact calculation cannot. For example, there is usually no simple formula giving the thermodynamic energy as a function of its independent variables. However, the differential of the thermodynamic energy of a system containing only one substance as a function of T, P, and n can be written as

$$dU = \left(\frac{\partial U}{\partial T}\right)_{P,n} dT + \left(\frac{\partial U}{\partial P}\right)_{T,n} dP + \left(\frac{\partial U}{\partial n}\right)_{P,T} dn. \tag{7.12}$$

Experimental values of these partial derivatives are frequently available.

EXERCISE 7.1 ▶ For a sample of 1.000 mol (0.15384 kg) of liquid carbon tetrachloride, CCl_4

$$\left(\frac{\partial U}{\partial T}\right)_{P,n} = 129.4\,\mathrm{J\,K^{-1}}$$
$$\left(\frac{\partial U}{\partial P}\right)_{T,n} = 8.51 \times 10^{-4}\,\mathrm{J\,atm^{-1}}$$

where these values are for a temperature of 20 °C and a pressure of 1.000 atm. Estimate the change in the energy of 1.000 mol of CCl_4 if its temperature is changed from 20.0 °C to 40.0 °C and its pressure from 1.0 atm to 100.0 atm. ◀

EXERCISE 7.2 ▶ The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where r is the radius and h the height. Calculate the percentage error in the volume if the radius and the height are measured and a 1% error is made in each measurement in the same direction. Use the formula for the differential, and also direct substitution into the formula for the volume, and compare the two answers. ◀

7.2 Change of Variables

In thermodynamics there is usually the possibility of choosing between different sets of independent variables. For example, we can consider the thermodynamic energy U of a one-component, one-phase system to be a function of T, V, and n,

$$U = U(T, V, n) \tag{7.13}$$

or a function of T, P, and n,

$$U = U(T, P, n). \tag{7.14}$$

The two choices lead to different expressions for dU,

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial P}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \tag{7.15}$$

and

$$dU = \left(\frac{\partial U}{\partial T}\right)_{P,n} dT + \left(\frac{\partial U}{\partial P}\right)_{T,n} dP + \left(\frac{\partial U}{\partial n}\right)_{T,P} dn. \tag{7.16}$$

There are two different derivatives of U with respect to T: $(\partial U/\partial T)_{V,n}$ and $(\partial U/\partial T)_{P,n}$. These derivatives have different values for most systems. If we did not use the subscripts, there would be no difference between the symbols for the two derivatives, which could lead to confusion.

EXAMPLE 7.3 Express the function $z = x(x, y) = ax^2 + bxy + cy^2$ in terms of x and u, where $u = xy$. Find the two partial derivatives $(\partial z/\partial x)_y$ and $(\partial z/\partial x)_u$.

SOLUTION ►

$$z = z(x, u) = ax^2 + bu + \frac{cu^2}{x^2}$$

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}\left(ax^2 + bxy + y^2\right)\right)_y = 2ax + by$$

$$\left(\frac{\partial z}{\partial x}\right)_u = 2ax - \frac{2cu^2}{x^2} = \left(\frac{\partial z}{\partial x}\right)_y - \frac{bu}{x} - \frac{2cu^2}{x^3}.$$

◄

In this example, there was no difficulty in obtaining an expression for the difference between $(\partial z/\partial x)_y$ and $(\partial z/\partial x)_u$, because we had the formula to represent the mathematical function. In thermodynamics, it is unusual to have a functional form. More commonly we have measured values for partial derivatives and require a separate means for computing the difference between partial derivatives.

We will obtain a formula of the type

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n} + \ ?, \tag{7.17}$$

where the question mark indicates an unknown term. The procedure that we use is not mathematically rigorous, but it does give the correct answer. To construct the partial derivative on the left-hand side of our equation, we begin with an expression for the differential dU that contains the derivative on the right-hand side. This is the same as Eq. (7.16). The first thing we do is to "divide" this differential expression by dT, because the derivative we want on the left-hand side is $(\partial U/\partial T)_{V,n}$. This cannot be done legitimately, because dT is an infinitesimal quantity, but we do it anyway. We get

$$\frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_{P,n}\frac{dT}{dT} + \left(\frac{\partial U}{\partial P}\right)_{T,n}\frac{dP}{dT} + \left(\frac{\partial U}{\partial n}\right)_{P,T}\frac{dn}{dT}. \tag{7.18}$$

This equation contains several things that look like ordinary derivatives. However, we must interpret them as partial derivatives, since we have specified that we want to have V and n constant. We change the symbols to the symbols for partial derivatives and add the appropriate subscripts to indicate the variables that are being held fixed. These variables must be the same in all four of the derivatives to keep a valid equation. We want V and n to be constant, so we write

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial T}\right)_{V,n} + \left(\frac{\partial U}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{V,n} + \left(\frac{\partial U}{\partial n}\right)_{P,T}\left(\frac{\partial n}{\partial T}\right)_{V,n}. \tag{7.19}$$

The partial derivative of T with respect to T is equal to unity, no matter what is held constant, and the partial derivative of n with respect to anything is zero if n is constant, so

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n} + \left(\frac{\partial U}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{V,n}} \tag{7.20}$$

Equation (7.20) is an example of a set of useful equations. If each symbol is consistently replaced by another symbol, we will have a useful equation for other variables besides the thermodynamic energy. We regard this as our first identity for partial derivatives, which we call the *variable-change identity*.

EXAMPLE 7.4 Apply the foregoing method to the function in Example 7.2 and find the relation between $(\partial z/\partial x)_u$, and $(\partial z/\partial x)_y$.

SOLUTION ►

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_u$$

$$\left(\frac{\partial z}{\partial y}\right)_x = bx + 2cy = bx + \frac{2cu}{x}$$

$$\left(\frac{\partial y}{\partial x}\right)_u = \left[\frac{\partial}{\partial x}\left(\frac{u}{x}\right)\right]_u = -\frac{u}{x^2}$$

Thus

$$\left(\frac{\partial z}{\partial x}\right)_u = \left(\frac{\partial z}{\partial x}\right)_y - \frac{bu}{x} - \frac{2cu}{x^3}.$$

This agrees with Example 7.2, as it must. ◄

EXERCISE 7.3 ► Complete the following equations.

(a) $\left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial T}\right)_{V,n} + \ ?$

(b) $\left(\frac{\partial S}{\partial T}\right)_{U,n} = \left(\frac{\partial S}{\partial T}\right)_{U,V} + \ ?$

(c) $\left(\frac{\partial z}{\partial u}\right)_{x,y} = \left(\frac{\partial z}{\partial u}\right)_{x,w} + \ ?$

(d) Apply the equation of part c if $z = \cos(x/u) + e^{-y^2/u^2} + 4y/u$ and $w = y/u$.

◄

7.3 Additional Useful Relations Between Partial Derivatives

It is fairly common in thermodynamics to have measured values for some partial derivative such as $(\partial H/\partial T)_{P,n}$, which is equal to the heat capacity at constant pressure. However, some other partial derivatives are difficult or impossible to measure. It is convenient to be able to express such partial derivatives in terms of measurable quantities. We now obtain some identities that can be used for this purpose.

The next identity is the *reciprocal identity*, which states that a derivative is equal to the reciprocal of the derivative with the roles of dependent and independent variables reversed:

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_{z,u} = \frac{1}{(\partial x/\partial y)_{z,u}}} \tag{7.21}$$

The same variables must be held constant in the two derivatives.

EXAMPLE 7.5 Show that

$$\left(\frac{\partial P}{\partial V}\right)_{n,T} = \frac{1}{(\partial V/\partial P)_{n,T}}$$

for an ideal gas.

SOLUTION ►

$$\begin{aligned}\left(\frac{\partial P}{\partial V}\right)_{n,T} &= -\frac{nRT}{V^2} \\ \frac{1}{(\partial V/\partial P)_{n,T}} &= \frac{1}{-nRT/P^2} = -\frac{P^2}{nRT} \\ &= -\frac{(nRT/V)^2}{nRT} = -\frac{nRT}{V^2}.\end{aligned}$$

◄

EXERCISE 7.4 ► Show that the reciprocal identity is satisfied by $(\partial z/\partial x)$ and $(\partial z/\partial z)_y$ if

$$z = \sin\left(\frac{x}{y}\right) \qquad \text{and} \qquad x = y\sin^{-1}(z)\,.$$

◄

There are two kinds of *second partial derivatives*. If $z = z(x, y)$ we can differentiate twice with respect to x:

$$\left(\frac{\partial^2 z}{\partial x^2}\right) = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right]_y . \tag{7.22}$$

In this case, y is held fixed in both differentiations. In addition, there are *mixed second partial derivatives*, such as the derivative with respect to x and then with respect to y:

$$\boxed{\frac{\partial^2 z}{\partial y \partial x} = \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x} . \tag{7.23}$$

Since both variables are shown in the symbol, the subscripts are usually omitted, as in the symbol on the left. However, if there is a third independent variable, it must be held constant and is listed as a subscript:

$$\left(\frac{\partial^2 U}{\partial V \partial T}\right)_n = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_{V,n}\right]_{T,n} . \tag{7.24}$$

The *Euler reciprocity relation* is an identity relating the mixed second partial derivatives. If $z = z(x, y)$ is a differentiable function, then the two different mixed second partial derivatives must equal each other:

$$\boxed{\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}} . \tag{7.25}$$

EXAMPLE 7.6 Show that $\left(\partial^2 P/\partial V\,\partial T\right)_n = \left(\partial^2 P/\partial T\,\partial V\right)_n$ for an ideal gas.

SOLUTION ►

$$\left(\frac{\partial^2 P}{\partial V\,\partial T}\right)_n = \left[\frac{\partial}{\partial V}\left(\frac{nR}{V}\right)\right]_{T,n} = -\frac{nR}{V^2}$$
$$\left(\frac{\partial^2 P}{\partial T\,\partial V}\right)_n = \left[\frac{\partial}{\partial T}\left(\frac{nRT}{V^2}\right)\right]_{V,n} = -\frac{nR}{V^2}.$$

◄

EXERCISE 7.5 ► Show by differentiation that $(\partial^2 z/\partial y\,\partial x) = (\partial^2 z/\partial x\,\partial y)$ if

$$z = e^{-xy^2}\sin(x)\cos(y).$$

◄

An important set of identities obtained from the Euler reciprocity relation and thermodynamic equations is the set of *Maxwell relations.* These relations allow you to replace a partial derivative that is difficult or impossible to measure with one that can be measured. One of the Maxwell relations is[1]

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

This relation can be used to replace $\left(\frac{\partial S}{\partial V}\right)_{T,n}$ by $\left(\frac{\partial P}{\partial T}\right)_{V,n}$, which is much more easily measured.

Another useful identity is the *cycle rule*

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x = -1}. \tag{7.26}$$

Many people are at first surprised by this identity, thinking at first that the right-hand side should equal $+1$ instead of -1. We will "derive" this in the same nonrigorous way as was used to obtain Eq. (7.20). We write the differential of y as a function of x and z:

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz. \tag{7.27}$$

This equation delivers the value of dy corresponding to arbitrary infinitesimal changes in x and z, so it is still correct if we choose values of dz and dx such that dy vanishes. We now "divide" nonrigorously by dx, and interpret the "quotients" of differentials as partial derivatives, remembering that y is held fixed by our choice that dy vanishes,

$$0 = \left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial x}\right)_y + \left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y. \tag{7.28}$$

[1]Mortimer, *op. cit.*, p. 140.

Since the partial derivative of x with respect to x is equal to unity, this equation becomes identical with Eq. (7.26) when the reciprocal identity is used. Our derivation is indefensible, but the result is correct.

EXAMPLE 7.7 For the particular function $y = z\ln(x)$ show that the cycle rule, Eq. (7.26) is correct.

SOLUTION ► $(\partial y/\partial x)_z = z/x, \quad (\partial x/\partial z)_y = e^{y/z}(-\frac{y}{z^2}), \quad (\partial z/\partial y)_x = 1/\ln(x)$

$$(\partial y/\partial x)_z(\partial x/\partial z)_y(\partial z/\partial y)_x = (z/x)e^{y/z}(-\tfrac{y}{z^2})(1/\ln(x)) = -(\tfrac{1}{x})e^{y/z}(\tfrac{y}{z})(\tfrac{1}{\ln(x)})$$
$$= -(\tfrac{1}{x})e^{y/z} = -\tfrac{x}{x} = -1$$ ◄

EXERCISE 7.6 ► For the particular function $y = x^2/z$, show that Eq. (7.26) is correct. ◄

The final identity that we present in this section is the partial derivative version of the *chain rule*. If $z = z(u, x, y)$ and if x can be expressed as a function of u, v, and y, then

$$\boxed{\left(\frac{\partial z}{\partial y}\right)_{u,v} = \left(\frac{\partial z}{\partial x}\right)_{u,v}\left(\frac{\partial x}{\partial y}\right)_{u,v}}. \tag{7.29}$$

This is very similar to Eq. (4.29). Notice that the same variables must be held fixed in all three derivatives.

EXAMPLE 7.8 Show that if $z = ax^2 + bwx$ and $x = uy$, then Eq. (7.29) is correct.

SOLUTION ►

$$\left(\frac{\partial z}{\partial x}\right)_{u,w}\left(\frac{\partial x}{\partial y}\right)_{u,w} = (2ax + bw)(u) = 2au^2y + buw$$
$$\left(\frac{\partial z}{\partial y}\right)_{u,w} = \left[\frac{\partial}{\partial y}\left(au^2y^2 + bwuy\right)\right]_{u,w} = 2au^2y + buw.$$

◄

The following are commonly measured quantities that are related to partial derivatives:

► heat capacity at constant pressure

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n} = T\left(\frac{\partial S}{\partial T}\right)_{P,n}$$

► heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n} = T\left(\frac{\partial S}{\partial T}\right)_{V,n}$$

► isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}$$

► adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n}$$

► coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

There are a number of useful relationships among these quantities.

EXAMPLE 7.9 Show that $C_P/C_V = \kappa_T/\kappa_S$.

SOLUTION ►

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_{P,n}}{\left(\frac{\partial S}{\partial T}\right)_{V,n}} = \frac{-\left(\frac{\partial S}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{S,n}}{-\left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{S,n}},$$

where we have used the cycle rule twice. We use the reciprocal identity to write

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial S}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial T}\right)_{S,n}}{\left(\frac{\partial S}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{S,n}}.$$

By the chain rule

$$\frac{C_P}{C_V} = \frac{\left(\frac{\partial V}{\partial P}\right)_{T,n}}{\left(\frac{\partial V}{\partial P}\right)_{S,n}} = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n}} = \frac{\kappa_T}{\kappa_S}.$$

◄

7.4 Exact and Inexact Differentials

The differential of a function is called an *exact differential*. There can also be differential forms that are not differentials of any function. A general *differential form* or *pfaffian form* can be written

$$du = M(x, v)\,dx + N(x, v)\,dy. \tag{7.30}$$

If this is the differential of a function, then M and N must be the appropriate derivatives of that function. Pfaffian forms exist in which M and N are not the appropriate partial derivatives of the same function. In this case du is called an *inexact differential*. It is an infinitesimal quantity that can be calculated from specified values of dx and dy, but it is not equal to the change in any function of x and y resulting from these changes.

In order to tell whether some differential form is an exact differential or not, we can use the Euler reciprocity relation. If there exists a function $u = u(x, y)$ such that

$$M(x, y) = \left(\frac{\partial u}{\partial x}\right)_y \qquad \text{and} \qquad N(x, y) = \left(\frac{\partial u}{\partial y}\right)_x,$$

then from the Euler reciprocity relation,

$$\frac{\partial^2 u}{\partial x\, \partial y} = \frac{\partial^2 u}{\partial y\, \partial x},$$

which means that if the differential is exact

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x \qquad \text{(exact differential)}, \tag{7.31}$$

Equation (7.31) represents a necessary and sufficient condition for the differential of Eq. (7.30) to be exact. That is, if the differential is exact, Eq. (7.31) will be obeyed, and if Eq. (7.31) is obeyed, the differential is exact.

EXAMPLE 7.10 Show that the differential

$$du = \left(2xy + \frac{9x^2}{y}\right) dx + \left(x^2 - \frac{3x^2}{y^2}\right) dy$$

is exact.

SOLUTION ►

$$\left[\frac{\partial}{\partial y}\left(2xy + \frac{9x^2}{y}\right)\right]_x = 2x - \frac{9x^2}{y^2}$$

$$\left[\frac{\partial}{\partial x}\left(x^2 - \frac{3x^3}{y^2}\right)\right]_x = 2x - \frac{9x^2}{y^2}.$$

◄

EXERCISE 7.7 ► Determine whether each of the following is an exact differential.

(a) $du = (2ax + by^2)\, dx + (bxy)\, dy$. (b) $du = (x + y)\, dx + (x + y)\, dy$

(c) $du = (x^2 + 2x + 1)\, dx + (y^2 + 25y + 24)\, dy$.

◄

Differential forms with three or more terms can also either be exact or inexact. The Euler reciprocity relation provides a test for such differentials. For example, if

$$du = M(x, v, z)\, dx + N(x, y, z)\, dy + P(x, y, z)\, dz, \tag{7.32}$$

then in order for this to be an exact differential, the three equations must be obeyed:

$$\left(\frac{\partial M}{\partial y}\right)_{x,z} = \left(\frac{\partial N}{\partial x}\right)_{y,z} \tag{7.33}$$

$$\left(\frac{\partial N}{\partial z}\right)_{x,y} = \left(\frac{\partial P}{\partial y}\right)_{x,z} \tag{7.34}$$

$$\left(\frac{\partial M}{\partial z}\right)_{x,y} = \left(\frac{\partial P}{\partial x}\right)_{y,z} \tag{7.35}$$

EXERCISE 7.8 ► Show that the following is not an exact differential $du = (2y)\,dx + (x)\,dy + \cos(z)\;dz$. ◄

There are two important inexact differentials in thermodynamics. If a system undergoes an infinitesimal process (one in which the independent variables specifying the state of the system change infinitesimally), dq denotes the amount of heat transferred to the system and dw denotes the amount of work done on the system. Both of these quantities are inexact differentials. For a fluid system undergoing a reversible process,

$$dw_{rev} = -P\,dV, \tag{7.36}$$

where P is the pressure of the system and V is its volume.

EXAMPLE 7.11 Show that for an ideal gas undergoing a reversible process with n fixed, dw_{rev} is inexact.

SOLUTION ► We choose T and V as our independent variables and write the differential form

$$dw = M\,dT + N\,dV \quad (n \text{ fixed}). \tag{7.37}$$

Comparison with Eq. (7.36) shows that $M = 0$ and $N = P = -nRT/V$. We apply the test for exactness, Eq. (7.31),

$$\left(\frac{\partial M}{\partial V}\right)_{T,n} = 0$$

$$\left(\frac{\partial N}{\partial T}\right)_{V,n} = \left[\frac{\partial}{\partial T}\left(-\frac{nRT}{V}\right)\right]_{V,n} = -\frac{nR}{V} \neq 0.$$

◄

EXERCISE 7.9 ► The thermodynamic energy of a monatomic ideal gas is given approximately by

$$U = \frac{3nRT}{2}. \tag{7.38}$$

Find the partial derivatives and write the expression for dU using T, V, and n as independent variables. Show that the partial derivatives obey the Euler reciprocity relations in Eqs. (7.33–7.35). ◄

In thermodynamics, quantities such as the thermodynamic energy, the volume, the pressure, the temperature, the amount of substances, and so forth, are functions of the variables that can be used to specify the state of the system. They are called *state functions*. The differentials of these quantities are exact differentials. Work and heat are not state functions. There is no such thing as an amount of work or an amount of heat in a system. We have already seen in Example 7.11 that dw_{rev} is not an exact differential, and the same is true of dw for an irreversible process. An infinitesimal amount of heat is also not an exact differential. However, the first law of thermodynamics states that dU, which equals $dq + dw$, is an exact differential.

Integrating Factors

Some inexact differentials become exact differential if the inexact differential is multiplied by a function called an *integrating factor* for that differential.

EXAMPLE 7.12 Show that the differential

$$du = (2ax^2 + bxy)\,dx + (bx^2 + 2cxy)\,dy$$

is inexact, but that $1/x$ is an integrating factor, so that du/x is exact.

SOLUTION ►

$$\left[\frac{\partial}{\partial y}(2ax^2 + bxy)\right]_x = bx$$
$$\left[\frac{\partial}{\partial x}(bx^2 + 2cxy)\right]_y = 2bx + 2cy \neq bx$$

so du is inexact. After we divide by x we obtain the partial derivatives

$$\left[\frac{\partial}{\partial y}(2ax + by)\right]_x = b$$
$$\left[\frac{\partial}{\partial x}(bx + 2cy)\right]_y = b$$

so $(1/x)\,du$ is exact. ◄

EXERCISE 7.10 ► Show that the differential

$$(1 + x)\,dx + \left[\frac{x \ln x}{y} + \frac{x^2}{y}\right] dy$$

is inexact, and that y/x is an integrating factor. ◄

There is no general method for finding an integrating factor, although we will discuss a method that will work for a particular class of differential forms in Chapter 8. However, it is true that if a differential possesses one integrating factor, there are infinitely many integrating factors for that differential.

7.5 Line Integrals

In Chapter 5, we found that a finite increment in a function could be constructed by a definite integration. If x_1 and x_0 are values of the single independent variable x, we can write

$$F(x_1) - F(x_0) = \int_{x_0}^{x_1} f(x)\,dx = \int_{x_0}^{x_1} dF, \tag{7.39}$$

where

$$f(x) = \frac{dF}{dx}. \tag{7.40}$$

We can think of the integral of Eq. (7.39) as being a sum of infinitesimal increments equal to $f(x)\,dx$ and can think of moving along the x axis from x_0 to x_1 as we add up these increments.

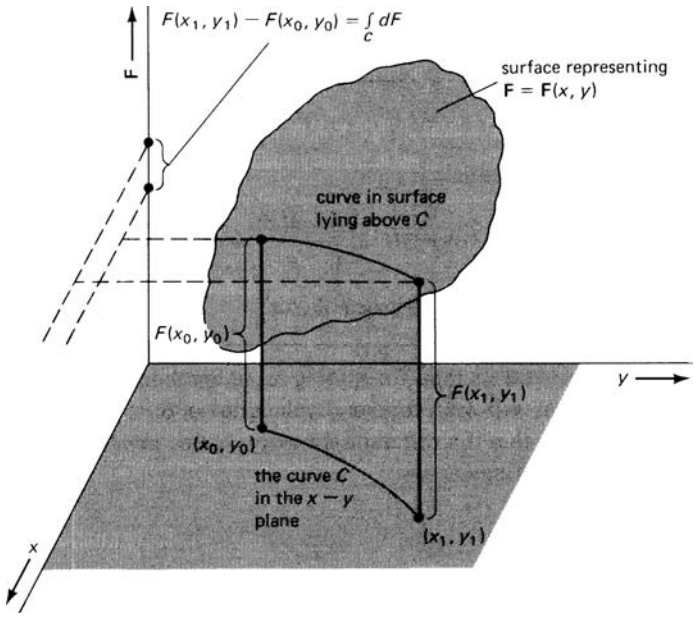

Figure 7.3 ► Diagram illustrating the line integral of an exact differential.

We now consider the analogous process for a differential with two or more independent variables. For two independent variables, x and y, we might try to define

$$\int_{x_0,y_0}^{x_1,y_1} dF = \int_{x_0,y_0}^{x_1,y_1} [M(x, y)\,dx + N(x, y)\,dy]. \tag{7.41}$$

However, this integral is not yet well defined. With a single integration variable, there is only one way to integrate along its axis. With a pair of integration variables the situation is different. This is shown schematically in Fig. 7.3. The pair of values (x_0, y_0) represents one point in the x-y plane, and (x_1, y_1) represents another point in the plane. Many different paths in the plane can join the two points. In order to complete the definition of the integral in Eq. (7.41), we must specify the path in the x-y plane along which we integrate (add up the increments) from the point (x_0, y_0) to the point (x_1, y_1). We introduce the notation

$$\int_C dF = \int_C \left[M(x, y)\,dx + N(x, y)\,dy\right], \tag{7.42}$$

where the letter C stands for the curve joining the two points. The integral is called a *line integral* or a *path integral*.

We can think of Eq. (7.42) as representing a sum of many infinitesimal contributions, each one given by the appropriate infinitesimal value of dF resulting when x is changed by dx and y is changed by dy. However, these changes dx and dy are not independent. They must be related so that we remain on the chosen curve during the integration process. A curve in the x-y plane specifies y as a function of x or x as a function of y. For a given curve, we can write

$$y = y(x) \tag{7.43}$$

$$x = x(y) \tag{7.44}$$

In order to calculate a line integral such as that of Eq. (7.42), we replace y in $M(x, y)$ by the function of x given in Eq. (7.43), and we replace x in $N(x, y)$ by

the function of y given in Eq. (7.44). With this replacement, M is a function of x only, and N is a function of y only, and each term becomes an ordinary one-variable integral:

$$\int_C dF = \int_{x_0}^{x_1} M\left[x, y(x)\right] dx + \int_{y_0}^{y_1} N[y, x(y)]\, dy. \tag{7.45}$$

In these integrals, specification of the curve C determines not only what the beginning point (x_0, y_0) and the final point (x_1, y_1) are, but also what the functions are that replace y in the dx integral and x in the dy integral.

EXAMPLE 7.13 Find the value of the line integral

$$\int_C dF = \int_C \left[(2x + 3y)\, dx + (3x + 4y)\right] dy,$$

where c is the straight-line segment given by $y = 2x + 3$ from $(0, 3)$ to $(2, 7)$.

SOLUTION ► In the first term, y must be replaced by $2x + 3$, and in the second term x must be replaced by $(1/2)(y - 3)$,

$$\begin{aligned}\int_C dF &= \int_0^2 [2x + 3(2x + 3)]\, dx + \int_3^7 \left[\frac{3}{2}(y - 3) + 4y\right] dy \\ &= \left(\frac{8x^2}{2} + 9x\right)\Big|_0^2 + \left(\frac{(11/2)\, y^2}{2} - \frac{9}{2}y\right)\Big|_3^7 = 126.\end{aligned}$$

◄

EXERCISE 7.11 ► Show that the differential in the preceding example is exact. ◄

Line Integrals of Exact Differentials

There is an important theorem, which we now state without proof:

Theorem 1 *If dF is an exact differential, then the line integral $\int_C dF$ depends only on the initial and final points and not on the choice of curve joining these points. Further, the line integral equals the value of the function F at the final point minus the value of the function at the beginning point. We say that the line integral of an exact differential is* path-independent.

For example, if (x_0, y_0) is the initial point of the line integration and (x_1, y_1) is the final point of the line integration, then

$$\begin{aligned}\int_C dF &= \int_C \left[\left(\frac{\partial F}{\partial x}\right) dx + \left(\frac{\partial F}{\partial y}\right) dy\right] \\ &= F(x_1, y_1) - F(x_0, y_0) \quad (dF \text{ exact})\end{aligned} \tag{7.46}$$

We have written M and N as the partial derivatives which they must be equal to in order for dF to be exact (see Section 7.4). If du is not an exact differential, there is no such things as a function u, and the line integral will depend not only on the beginning and ending points, but also on the curve of integration joining these points.

EXAMPLE 7.14 Show that the line integral of Example 7.12 has the same value as the line integral of the same differential on the rectangular path from (0, 3) to (2, 3) and then to (2, 7).

SOLUTION ► The path of this integration is not a single curve but two line segments, so we must carry out the integration separately for each segment. This is actually a simplification, because on the first line segment, y is constant, so $dy = 0$ and the dy integral vanishes. On the second line segment, x is constant, so $dx = 0$ and the dx integral vanishes. Therefore,

$$\int_C dF = \int_0^2 (2x + 9)\, dx + \int_3^7 (6 + 4y)\, dy.$$

This follows from the fact that $y = 3$ on the first line segment, and from the fact that $x = 2$ on the second line segment. Performing the integration yields

$$\int_C dF = \left(\frac{2x^2}{2} + 9x\right)\Bigg|_0^2 + \left(6y + \frac{4y^2}{2}\right)\Bigg|_3^7 = 126.$$

◄

EXERCISE 7.12 ►

(a) (a) Show that the following differential is exact:

$$dz = (ye^{xy})\, dx + (xe^{ey})\, dy$$

(b) Calculate the line integral $\int_c dz$ on the line segment from (0, 0) to (2, 2). On this line segment, $y = x$ and $x = y$.

(c) Calculate the line integral $\int_c dz$ on the path going from (0, 0) to (0, 2) and then to (2, 2) (a rectangular path).

◄

Line Integrals of Inexact Differentials

If a differential is not exact, two line integrals beginning and ending at the same points will not necessarily yield the same result.

EXAMPLE 7.15 Show that the differential

$$du = dx + x\, dy$$

is inexact and carry out the line integral from (0, 0) to (2, 2) by two different paths: path 1, the straight-line segment from (0, 0) to (2, 2); and path 2, the rectangular path from (0, 0) to (2, 0) and then to (2, 2).

SOLUTION ► Test for exactness:

$$\left[\frac{\partial}{\partial y}(1)\right]_x = 0$$
$$\left[\frac{\partial}{\partial x}(x)\right]_y = 1 \neq 0.$$

The differential is not exact.

Path 1:

$$\int_{C_1} du = \int_{C_1} dx + \int_{C_1} x\,dy = \int_0^2 dx + \int_0^2 y\,dy,$$

where we obtained the second integral by using the fact that $y = x$ on the straight-line segment of path 1,

$$\int_{C_1} du = x|_0^2 + \left.\frac{y^2}{2}\right|_0^2 = 4.$$

Path 2,

$$\begin{aligned}\int_{C_2} du &= \int_{C_2} dx + \int_{C_2} x\,dy = \int_0^2 dx + \int_0^2 2\,dy \\ &= x|_0^2 + 2y|_0^2 = 2 + 4 = 6.\end{aligned}$$

The two line integrals have the same beginning point and the same ending point, but are not equal, because the differential is not an exact differential. ◄

EXERCISE 7.13 ►

(a) Carry out the two line integrals of du from Example 7.15 from $(0, 0)$ to (x_1, y_1).

(b) Integrate on the rectangular path from $(0, 0)$ to $(0, y_1)$ and then to (x_1, y_1).

(c) Integrate on the rectangular path from $(0, 0)$ to $(x_1, 0)$ and then to (x_1, y_1).

◄

Line Integrals with Three Integration Variables

There are also line integrals of functions of three independent variables. The line integral of the differential du is

$$\int_C du = \int_C \left[M(x, y, z)\,dx + N(x, y, z)\,dy + P(x, y, z)\,dz\right], \tag{7.47}$$

where C specifies a curve that gives y and z as functions of x, or x and y as functions of z, or x and z as functions of y. If the beginning point of the curve C is (x_0, y_0, z_0) and the ending point is (x_1, y_1, z_1), the line integral is

$$\begin{aligned}\int_C du &= \int_{x_0}^{x_1} M\left[x, y(x), z(x)\right] dx + \int_{y_0}^{y_1} N\left[x(y), y, z(y)\right] dy \\ &\quad + \int_{z_0}^{z_1} P\left[x(z), y(z), z\right] dz.\end{aligned} \tag{7.48}$$

If du is an exact differential, then u is a function, and

$$\boxed{\int_C du = u(x_1, y_1, z_1) - u(x_0, y_0, z_0) \quad \text{(if } du \text{ is an exact differential)}}. \tag{7.49}$$

Line integrals in Thermodynamics

In thermodynamics, the *equilibrium state* of a system is represented by a point in a space whose axes represent the variables specifying the state of the system. A line integral in such a space represents a *reversible process*. A *cyclic process* is one that begins and ends at the same state of a system. A line integral that begins and ends at the same point is denoted by the symbol $\oint du$. Since the beginning and final points are the same, such an integral must vanish if du is an exact differential:

$$\boxed{\oint du = 0 \quad \text{(if } du \text{ is exact)}}. \tag{7.50}$$

If du is inexact, a line integral that begins and ends at the same point will not generally be equal to zero.

EXERCISE 7.14 ▶ Carry out the cyclic line integral of dw_{rev} for 1.000 mol of an ideal gas, using the following reversible cycle: Starting with $T = 500.0\,\text{K}$ and $V = 20.0\,\text{l}$, the system is expanded at constant temperature to a volume of 40.0 l. The system is cooled at constant volume to 300.0 K. The system is then compressed to a volume of 20.0 l at a constant temperature of 300.0 K. It is finally heated at constant volume to 600.0 K. ◀

7.6 Multiple Integrals

While a line integral can be thought of as adding up infinitesimal contributions represented as a differential form, a *multiple integral* can be thought of as adding up contributions given by an integrand function times an infinitesimal element of area or of volume, etc. A *double integral* is the simplest kind of multiple integral. It is written in the form

$$I = \int_{a_1}^{a_2} \int_{b_1}^{b_2} f(x, y)\, dy\, dx, \tag{7.51}$$

where $f(x, y)$ is the integrand function, a_1 and a_2 are the limits of the x integration, and b_1 and b_2 are the limits of the y integration. You should think of the product $dy\ dx$ as an infinitesimal element of area in the x-y plane.

The double integral is carried out as follows: The "inside" integration is done first. This is the integration over the values of the variable whose differential and limits are written closest to the integrand function. During this integration, the other independent variable is treated as a constant if it occurs in the integrand. The result of the first integration is the integrand for the remaining integration. The limits b_1 and b_2 can depend on x, but the limits a_1 and a_2 must be constants.

EXAMPLE 7.16 Evaluate the double integral

$$I = \int_0^a \int_0^b (x^2 + 4xy)\, dy\, dx.$$

SOLUTION ► The integration over y is carried out, treating x as a constant:

$$\int_0^b (x^2 + 4xy)\, dy = \left(x^2 y + \frac{4xy^2}{2}\right)\Bigg|_0^b = bx^2 + 2b^2 x.$$

This becomes the integrand for the second integration, so that

$$\begin{aligned} I &= \int_0^a \left(bx^2 + 2b^2 x\right) dx = \left(\frac{bx^3}{3} + \frac{2b^2 x^2}{2}\right)\Bigg|_0^a \\ &= \frac{ba^3}{3} + b^2 a^2. \end{aligned}$$

◄

EXAMPLE 7.17 Evaluate the double integral

$$\int_0^a \int_0^{3x} (x^2 + 2xy + y^2)\, dy\, dx.$$

SOLUTION ► The result of the inside integration is

$$\begin{aligned} \int_0^{3x} \left(x^2 + 2xy + y^2\right) dy &= \left(x^2 y + \frac{2xy^2}{2} + \frac{y^3}{3}\right)\Bigg|_0^{3x} \\ &= 3x^3 + 9x^3 + 9x^3 = 21x^3. \end{aligned}$$

The x integration gives

$$\int_0^a 21x^3\, dx = \frac{21x^4}{4}\Bigg|_0^a = \frac{21a^4}{4}.$$

◄

EXERCISE 7.15 ► Evaluate the double integral

$$\int_2^4 \int_0^{\pi} x \sin(y)\, dy\, dx.$$

◄

The Double Integral Represented as a Volume

In Section 5.2 we saw that a definite integral with one independent variable is equal to an area in a graph of the integrand function between the axis and the integrand curve. A double integral is equal to a volume in an analogous way. This is illustrated in Fig. 7.4, which is drawn to correspond to Example 7.18. In the x-y plane, we have an infinitesimal element of area $dx\, dy$, drawn in the figure as

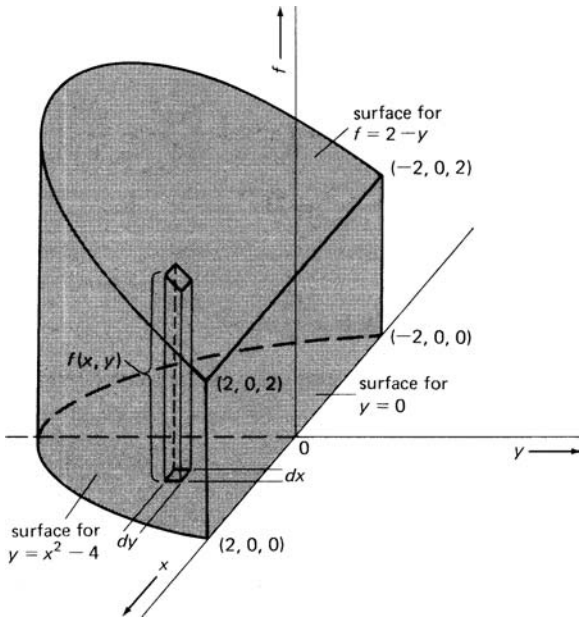

Figure 7.4 ► The diagram for Example 7.18.

though it were finite in size. The vertical distance from the x-y plane to the surface representing the integrand function f is the value of the integrand function, so that the volume of the small box lying between the element of area and the surface is equal to $f(x)\,dx\,dy$.

The double integral is the sum of the volume of all such infinitesimal boxes, and thus equals the volume of the solid bounded by the x-y plane, the surface representing the integrand function, and surfaces representing the limits of integration. If the integrand function is negative in part of the region of integration, we must take the volume above the x-y plane minus the volume below the plane as equal to the integral.

EXAMPLE 7.18 Calculate the volume of the solid shown in Fig. 7.4. The bottom of the solid is the x-y plane. The flat surface corresponds to $y = 0$, the curved vertical surface corresponds to $y = x^2 - 4$, and the top of the solid corresponds to $f = 2 - y$.

SOLUTION ► We carry out a double integral with $f = 2 - y$ as the integrand:

$$V = \int_{-2}^{2} \int_{x^2-4}^{0} (2 - y)\,dy\,dx.$$

The inside integral is

$$\int_{x^2-4}^{0} (2 - y)\,dy = \left(2y - \frac{y^2}{2}\right)\Bigg|_{x^2-4}^{0} = \frac{x^4}{2} - 6x^2 + 16$$

so that

$$V = \int_{-2}^{2} \left(\frac{x^4}{2} - 6x^2 + 16\right) dx = \left(\frac{x^5}{10} - 2x^3 + 16x\right)\Bigg|_{-2}^{2} = 38.4.$$

◄

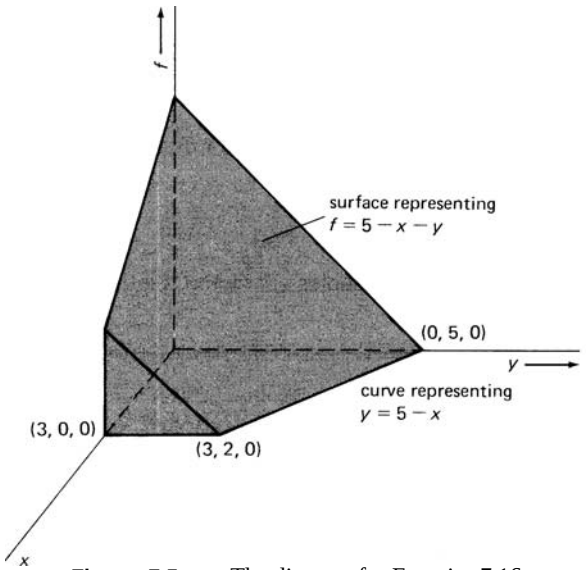

Figure 7.5 ► The diagram for Exercise 7.16.

EXERCISE 7.16 ► Find the volume of the solid object shown in Fig. 7.5. The top of the object corresponds to $f = 5 - x - y$, the bottom of the object is the x-y plane, the trapezoidal face is the x-f plane, and the large triangular face is the y-f plane. The small triangular face corresponds to $x = 3$. ◄

Multiple Integrals in Quantum Mechanics

In quantum mechanics, the square of a wave function is the probability density for finding a particle or particles. Since ordinary space has three dimensions, multiple integrals with three independent variables (*triple integrals*) represent probabilities of finding a particle in the region of integration.. For example, if the integrand function f depends on x, y, and z, we could have the triple integral

$$I = \int_{a_1}^{a_2} \int_{b_1}^{b_2} \int_{c_1}^{c_2} f(x, y, z)\, dz\, dy\, dx. \tag{7.52}$$

To evaluate the integral, we first integrate z from c_1 to c_2 and take the result as the integrand for the double integral over y and x. Then we integrate y from b_1 to b_2, and take the result as the integrand for the integral over x from a_1 to a_2. The limits c_1 and c_2 can depend on y and x, and the limits b_1 and b_2 can depend on x, but a_1 and a_2 must be constants. If the limits are all constants, and if the integrand function can be factored, the entire integral can be factored, as in the following example.

EXAMPLE 7.19 Find the triple integral

$$I = A^2 \int_0^a \int_0^b \int_0^c \sin^2\left(\frac{n\pi x}{a}\right) \sin^2\left(\frac{m\pi y}{b}\right) \sin^2\left(\frac{k\pi z}{c}\right) dz\, dy\, dx.$$

This is a *normalization integral* from quantum mechanics, equal to the total probability for finding a particle in a three-dimensional box. The integrand is the square of the wave function for one of the states of a particle in a three-dimensional box. The quantities m, n, and k are integral quantum numbers specifying the state of the particle. The integral is equal to the total probability of finding a particle in the box. It is customary to choose the value of the constant A so that the total probability equals unity, in which case the wave function is said to be *normalized*.

SOLUTION ► The integrand function is a product of three factors, each of which depends on only one variable, and the limits of integration are constants. The entire integral can therefore be written in factored form:

$$I = A^2 \left[\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx\right] \left[\int_0^b \sin^2\left(\frac{m\pi y}{b}\right) dy\right] \left[\int_0^c \sin^2\left(\frac{k\pi z}{c}\right) dz\right].$$

We first carry out the z integration, using the substitution $u = k\pi z/c$,

$$\int_0^c \sin^2\left(\frac{k\pi z}{c}\right) dz = \frac{c}{k\pi} \int_0^{k\pi} \sin^2(u)\, du.$$

The integrand is a periodic function with period π, so that the integral from 0 to $k\pi$ is just k times the integral from 0 to π, which is given as Eq. (8) of Appendix F:

$$\int_0^c \sin^2\left(\frac{k\pi z}{c}\right) dz = \frac{c}{k\pi} k \frac{\pi}{2} = \frac{c}{2}.$$

The other integrals are similar, except for having a or b instead of c, so that

$$I = A^2 \frac{abc}{8}.$$

Many triple integrals in quantum mechanics are factored in the same way as in this example. ◄

EXERCISE 7.17 ► Find the value of the constant A so that the following integral equals unity.

$$A \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-x^2-y^2} dy\, dx.$$

◄

Changing Variables in Multiple Integrals

Sometimes it is convenient to take a multiple integral over an area or over a volume using polar coordinates or spherical polar coordinates, and so on, instead of Cartesian coordinates. Figure 7.6 shows how this is done in polar coordinates. We require an infinitesimal element of area given in terms of the coordinates ρ and ϕ. One dimension of the element of area is $d\rho$ and the other dimension is $\rho\, d\phi$, from the fact that an arc length is the radius of the circle times the angle subtended by the arc, measured in radians. The element of area is $\rho\, d\phi\, d\rho$. If the element of area

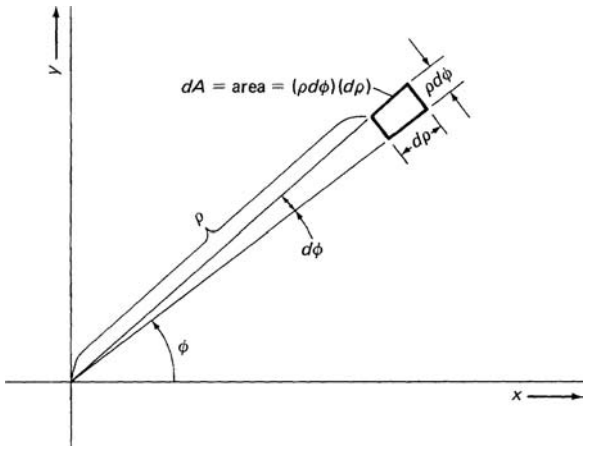

Figure 7.6 ► An infinitesimal element of area in plane polar coordinates.

were finite, it would not quite be rectangular, and this formula would not be exact, but it is valid for an infinitesimal element of area.

We can think of the plane as being covered completely by infinitely many such elements of area, and a double integral over some region of the plane is just the sum of the value of the integrand function at each element of area in the region times the area of the element.

EXAMPLE 7.20 In Cartesian coordinates, the wave function for the ground state of a two dimensional harmonic oscillator is

$$\psi = B \exp\left[-a(x^2 + y^2)\right].$$

Transform this to plane polar coordinates and find the value of B such that the integral of ψ^2 over the entire x–y plane is equal to unity.

SOLUTION ►

$$\psi = Be^{-a\rho^2}.$$

The integral that is to equal unity is

$$B^2 \int_0^\infty \int_0^{2\pi} e^{-2a\rho^2} \rho \, d\phi \, d\rho.$$

The integral can be factored,

$$I = B^2 \int_0^\infty e^{-2a\rho^2} \rho \, d\rho \int_0^{2\pi} d\phi = 2\pi B^2 \int_0^\infty e^{-2a\rho^2} \rho \, d\rho.$$

The ρ integral is done by the method of substitution, letting $u = 2a\rho^2$ and $du = 4a\rho \, d\rho$. We obtain

$$I = 2\pi B^2 \left(\frac{1}{4a}\right) \int_0^\infty e^{-u} \, du = \frac{B^2 \pi}{2a}$$

$$B = \sqrt{\frac{2a}{\pi}}.$$

◄

EXERCISE 7.18 ► Use a double integral to find the volume of a cone of height h and radius a at the base. If the cone is standing with its point upward and with its base centered at the origin, the equation giving the surface of the cone is

$$f = h\left(1 - \frac{\rho}{a}\right).$$

◄

In transforming from Cartesian to plane polar coordinates, the factor ρ, which is used with the product of the differentials $d\phi\, d\rho$ is called a *Jacobian*. The symbol $\partial(x, y)/\partial(\rho, \phi)$ is used for this Jacobian:

$$\iint f(x, y)\, dx\, dy = \iint f(\rho, \phi)\, d\phi\, d\rho = \iint f(\rho, \phi)\, \frac{\partial(x, y)}{\partial(\rho, \phi)}\, d\rho\, d\phi. \tag{7.53}$$

We will not discuss the mathematical theory, but this Jacobian is given by the following determinant (determinants are discussed in Chapter 9):

$$\frac{\partial(x, y)}{\partial(\rho, \phi)} = \begin{vmatrix} \partial x/\partial\rho & \partial x/\partial\phi \\ \partial y/\partial\rho & \partial y/\partial\phi \end{vmatrix}. \tag{7.54}$$

Equation (9.59) gives the formula for a 2 by 2 determinant:

$$\begin{vmatrix} \partial x/\partial\rho & \partial x/\partial\phi \\ \partial y/\partial\rho & \partial y/\partial\phi \end{vmatrix} = \begin{vmatrix} \cos(\phi) & -\rho\sin(\phi) \\ \cos(\phi) & \rho\cos(\phi) \end{vmatrix} = \rho\cos^2(\phi) + \rho\sin^2(\phi) = \rho. \tag{7.55}$$

where we have also used Eq. (7) of Appendix B. This equation gives us the same result as we had before,

$$dA = \text{element of area} = \rho\, d\phi\, d\rho. \tag{7.56}$$

The Jacobian for transformation of coordinates in three dimensions is quite similar. If u, v, and w are some set of coordinates such that

$$\begin{aligned} x &= x(u, v, w) \\ y &= y(u, v, w) \\ z &= z(u, v, w), \end{aligned}$$

then the Jacobian for the transformation of a multiple integral from Cartesian coordinates to the coordinates u, v, and w is given by the determinant

$$\boxed{\frac{\partial(x, y, z)}{\partial(u, v, w)} = \begin{vmatrix} \partial x/\partial u & \partial x/\partial v & \partial x/\partial w \\ \partial y/\partial u & \partial y/\partial v & \partial y/\partial w \\ \partial z/\partial u & \partial z/\partial v & \partial z/\partial w \end{vmatrix}}. \tag{7.57}$$

The rule for expanding a 3 by 3 determinant is discussed in Chapter 9.

EXAMPLE 7.21 Obtain the Jacobian for the transformation from Cartesian coordinates to spherical polar coordinates.

SOLUTION ► The equations relating the coordinates are Eqs. (2.62)–(2.64):

$$\frac{\partial(x,\,y,\,z)}{\partial(r,\,\theta,\,\phi)} = \begin{vmatrix} \sin(\theta)\cos(\theta) & r\cos(\theta)\cos(\phi) & -r\sin(\theta)\sin(\phi) \\ \sin(\theta)\sin(\phi) & r\cos(\theta)\sin(\phi) & r\sin(\theta)\cos(\phi) \\ \cos(\phi) & -r\sin(\theta) & 0 \end{vmatrix}$$

From the expansion of a 3 by 3 determinant illustrated in Example 9.12,

$$\begin{aligned} \frac{\partial(x,\,y,\,z)}{\partial(r,\,\theta,\,\phi)} &= \cos(\theta)\left[r^2\cos(\theta)\sin(\theta)\cos^2(\phi) + r^2\sin(\theta)\cos(\theta)\sin^2(\theta)\right] \qquad (7.58) \\ &\quad + r\sin(\theta)\left[r\sin^2(\theta)\cos^2(\phi) + r^2\sin^2(\theta)\sin^2(\phi)\right] \\ &= r^2\sin(\theta)\cos^2(\theta) + r^2\sin^3(\theta) = r^2\sin(\theta)\,, \qquad (7.59) \end{aligned}$$

where we have used Eq. (7) of Appendix B several times. ◄

EXERCISE 7.19 ► Find the Jacobian for the transformation from Cartesian to cylindrical polar coordinates. ◄

A triple integral in Cartesian coordinates is transformed into a triple integral in spherical polar coordinates by

$$\iiint (x,\,y,\,z)\,dxdydz = \iiint f(r,\theta,\phi)r^2\sin(\theta)\;d\phi\,d\theta\,dr. \qquad (7.60)$$

An element of volume is given by

$$\boxed{dV = dx\,dy\,dz = r^2\sin(\theta)\;d\phi\,d\theta\,dr}.$$

To complete the transformation, the limits on r, θ, and ϕ must be found so that they correspond to the limits on x, y, and z. Sometimes the purpose of transforming to spherical polar coordinates is to avoid the task of finding the limits in Cartesian coordinates when they can be expressed easily in spherical polar coordinates. For example, if the integration is over the interior of a sphere of radius a centered at the origin, ϕ ranges from 0 to 2π, θ ranges from 0 to π, and r ranges from 0 to a. If all of space is to be integrated over, ϕ ranges from 0 to 2π, θ ranges from 0 to π, and r ranges from 0 to ∞.

7.7 Vector Derivative Operators

An *operator* is a symbol for carrying out a mathematical operation (see Chapter 9). There are several *vector derivative operators*. We first define them in Cartesian coordinates.

Vector Derivatives in Cartesian Coordinates

The *gradient* operator is defined in Cartesian coordinates by

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \qquad (7.61)$$

where **i**, **j**, and **k** are the unit vectors in the directions of the x, y, and z axes defined in Chapter 2. The gradient of a scalar function is a vector. The symbol ∇, which is

an upside-down capital Greek delta, is called "*del*." If f is some scalar function of x, y, and z, the gradient of f is given in Cartesian coordinates by

$$\nabla f = \mathbf{i}\frac{\partial f}{\partial x} + \mathbf{j}\frac{\partial f}{\partial y} + \mathbf{k}\frac{\partial f}{\partial z}. \tag{7.62}$$

The gradient of f is sometimes denoted by grad f instead of ∇f. The direction of the gradient of a scalar function is the direction in which the function is increasing most rapidly, and its magnitude is the rate of change of the function in that direction.

EXAMPLE 7.22 Find the gradient of the function

$$f = x^2 + 3xy + z^2 \sin\left(\frac{x}{y}\right).$$

SOLUTION ►

$$\begin{aligned}\nabla f &= \mathbf{i}\left(\frac{\partial f}{\partial y}\right) + \mathbf{j}\left(\frac{\partial f}{\partial y}\right) + \mathbf{k}\left(\frac{\partial f}{\partial z}\right) \\ &= \mathbf{i}\left[2x + 3y + \frac{z^2}{y}\cos\left(\frac{x}{y}\right)\right] + \mathbf{j}\left[3x - \frac{xz^2}{y^2}\cos\left(\frac{x}{y}\right)\right] + \mathbf{k}2z\sin\left(\frac{x}{y}\right)\end{aligned}$$

◄

EXERCISE 7.20 ► Find the gradient of the function

$$g = ax^3 + ye^{bz},$$

where a and b are constants. ◄

A common example of a gradient is found in mechanics. In a conservative system, the force on a particle is given by

$$\boxed{\mathbf{F} = -\nabla \mathcal{V}} \tag{7.63}$$

where $\mathcal{V}$ is the potential energy of the entire system. The gradient is taken with respect to the coordinates of the particle being considered, and the coordinates of any other particles are treated as constants in the differentiations.

EXAMPLE 7.23 The potential energy of an object of mass m near the surface of the earth is

$$\mathcal{V} = mgz,$$

where g is the acceleration due to gravity. Find the gravitational force on the object.

SOLUTION ►

$$\mathbf{F} = -\mathbf{k}mg.$$

◄

EXERCISE 7.21 ► Neglecting the attractions of all other celestial bodies, the gravitational potential energy of the earth and the sun is given by

$$\mathcal{V} = -\frac{Gm_s m_e}{r},$$

where G is the universal gravitational constant, equal to $6.673 \times 10^{-11}\,\mathrm{m^3\,s^{-2}\,kg^{-1}}$, m_s the mass of the sun, m_e the mass of the earth, and r the distance from the center of the sun to the center of the earth,

$$r = \left(x^2 + y^2 + z^2\right)^{1/2}$$

Find the force on the earth in Cartesian coordinates. That is, find the force in terms of the unit vectors **i**, **j**, and **k** with the components expressed in terms of x, y, and z. Find the magnitude of the force. ◄

The operator ∇ can operate on vector functions as well as on scalar functions. An example of a vector function is the velocity of a compressible flowing fluid

$$\mathbf{v} = \mathbf{v}(x, y, z) \tag{7.64}$$

In terms of Cartesian components

$$\mathbf{v} = \mathbf{i}v_x(x, y, z) + \mathbf{j}v_y(x, y, z) + \mathbf{k}v_z(x, y, z). \tag{7.65}$$

There are two principal vector derivatives of vector functions. The *divergence* of **F** is defined in Cartesian coordinates by

$$\boxed{\nabla \cdot \mathbf{F} = \left(\frac{\partial F_x}{\partial x}\right) + \left(\frac{\partial F_y}{\partial y}\right) + \left(\frac{\partial F_z}{\partial z}\right)}, \tag{7.66}$$

where **F** is a vector function with Cartesian components F_x, F_y, and F_z. The divergence of a vector function **F** is a scalar and is somewhat analogous to a scalar product (dot product) of two vectors. The divergence of **F** is sometimes denoted by div**F**.

One way to visualize the divergence of a function is to consider the divergence of the velocity of a compressible fluid. Curves that are followed by small portions of the fluid are called *stream lines*. In a region where the stream lines diverge (become farther from each other) as the flow is followed, the fluid will become less dense, and in such a region the divergence of the velocity is positive. The divergence thus provides a measure of the spreading of the stream lines. The *equation of continuity* of a compressible fluid expresses the effect this spreading has on the density of the fluid,

$$\nabla \cdot (\rho \mathbf{v}) = -\frac{\partial \rho}{\partial t}, \tag{7.67}$$

where ρ is the density of the fluid, **v** is its velocity, and t is the time.

EXAMPLE 7.24 Find $\nabla \cdot \mathbf{F}$ if

$$\mathbf{F} = \mathbf{i}x^2 + \mathbf{j}yz + \mathbf{k}\frac{xz^2}{y}$$

SOLUTION ►

$$\nabla \cdot \mathbf{F} = 2x + z + \frac{2xz}{y}.$$

◄

EXERCISE 7.22 ► Find $\nabla \cdot \mathbf{r}$ if

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$

◄

The *curl* of the vector function $\mathbf{F}$ is defined in Cartesian coordinates by

$$\nabla \times \mathbf{F} = \mathbf{i}\left(\frac{\partial F_z}{\partial y} - \frac{\partial F_y}{\partial z}\right) + \mathbf{j}\left(\frac{\partial F_x}{\partial z} - \frac{\partial F_z}{\partial x}\right) + \mathbf{k}\left(\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y}\right). \quad (7.68)$$

The curl is a vector and is somewhat analogous to the vector product (cross product) of two vectors. To remember which vector derivative is which, remember that "dot" and "divergence" both begin with the letter "d" and that "cross" and "curl" both begin with the letter "c." The symbol curl$\mathbf{F}$ is sometimes used for the curl of $\mathbf{F}$.

The curl of a vector function is more difficult to visualize than is the divergence. In fluid flow, the curl of the velocity gives the *vorticity* of the flow, or the rate of turning of the velocity vector. Because of this, the symbol rot$\mathbf{F}$ is also sometimes used for the curl of $\mathbf{F}$.

EXAMPLE 7.25 Find $\nabla \times \mathbf{F}$ if

$$\mathbf{F} = \mathbf{i}y + \mathbf{j}z + \mathbf{k}x.$$

SOLUTION ►

$$\nabla \times \mathbf{F} = \mathbf{i}(0-1) + \mathbf{j}(0-1) + \mathbf{k}(0-1) = -\mathbf{i} - \mathbf{j} - \mathbf{k}.$$

◄

EXERCISE 7.23 ► Find $\nabla \times \mathbf{r}$ if

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z.$$

◄

We can define derivatives corresponding to successive application of the del operator. The first such operator is the divergence of the gradient. If f is a scalar function, the divergence of the gradient of f is given in Cartesian coordinates by

$$\boxed{\nabla \cdot \nabla f = \nabla^2 f = \left(\frac{\partial^2 f}{\partial x^2}\right) + \left(\frac{\partial^2 f}{\partial y^2}\right) + \left(\frac{\partial^2 f}{\partial z^2}\right)} \quad (7.69)$$

The operator $\nabla \cdot \nabla$ occurs so commonly that it has its own name, the *Laplacian operator*,[2] and its own symbol, ∇^2, sometimes called "del squared." It is an operator that occurs in the Schrödinger equation of quantum mechanics and in electrostatics.

[2] After Pierre Simon, Marquis de Laplace, 1749–1827, a famous French mathematician and astronomer.

EXAMPLE 7.26 Find the Laplacian of the function

$$f(x, y, z) = A \sin(ax) \sin(by) \sin(cz) .$$

SOLUTION ►

$$\begin{aligned} \nabla^2 f &= -Aa^2 \sin(ax) \sin(by) \sin(cz) - Ab^2 \sin(ax) \sin(by) \sin(cz) \\ &= -Ac^2 \sin(ax) \sin(by) \sin(cz) \\ &= -\left(a^2 + b^2 + c^2\right) f. \end{aligned}$$

◄

EXERCISE 7.24 ► Find $\nabla^2 f$ if $f = \exp(x^2 + y^2 + z^2) = e^{x^2} e^{y^2} e^{z^2}$. ◄

Two other possibilities for successive operation of the del operator are the *curl of the gradient* and the *gradient of the divergence*. The curl of the gradient of any differentiable scalar function always vanishes.

EXERCISE 7.25 ►

(a) Show that $\nabla \times \nabla f = 0$ if f is a differentiable scalar function.

(b) Write the expression for $\nabla(\nabla \times \mathbf{F})$, the gradient of the divergence of a vector function $\mathbf{F}$, in Cartesian coordinates.

◄

Vector Derivatives in Other Coordinate Systems

It is sometimes convenient to work in coordinate systems other than Cartesian coordinates. For example, in the Schrödinger equation for the quantum mechanical motion of the electron in a hydrogen atom, the potential energy is a simple function of r, the distance of the electron from the nucleus, but it is a more complicated function of x, y, and z. This Schrödinger equation can be solved only if spherical polar coordinates are used. The complications produced by expressing the Laplacian in spherical polar coordinates are more than outweighed by the simplifications produced by having a simple expression for the potential energy.

Coordinate systems such as spherical polar or cylindrical polar coordinates are called *orthogonal coordinates*, because an infinitesimal displacement produced by changing only one of the coordinates is perpendicular (orthogonal) to a displacement produced by an infinitesimal change in any one of the other coordinates.

1. Figure 7.7 shows displacements, drawn as though they were finite, produced by infinitesimal changes in r, θ, and ϕ. These displacements are lengths

$$\begin{aligned} ds_r &= \text{displacement in } r \text{ direction} = dr \\ ds_\theta &= \text{displacement in } \theta \text{ direction} = r\, d\theta \\ ds_\phi &= \text{displacement in } \phi \text{ direction} = r \sin(\phi)\, d\theta. \end{aligned}$$

We define three vectors of unit length, whose directions are those of the infinitesimal displacements in Fig. 7.7, called $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\phi$.

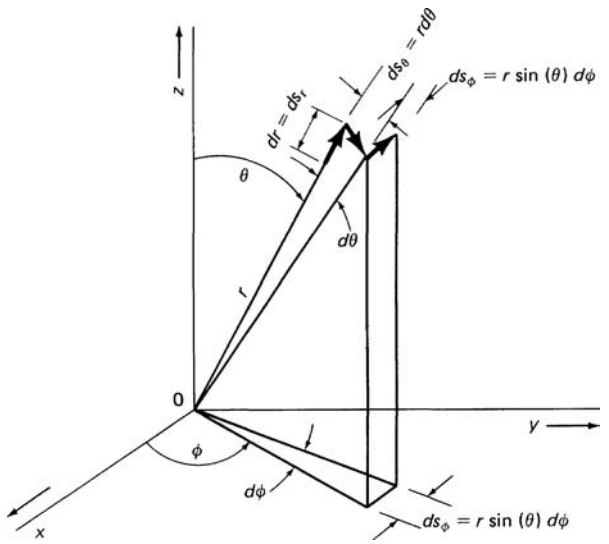

Figure 7.7 ► Infinitesimal displacements ds_r, ds_θ, and ds_ϕ produced by infinitesimal increments dr, $d\theta$, and $d\phi$.

An infinitesimal vector displacement is the sum of displacements in the three orthogonal directions. In Cartesian coordinates,

$$d\mathbf{r} = \mathbf{i}dx + \mathbf{j}dy + \mathbf{k}dz. \tag{7.70}$$

In spherical polar coordinates,

$$d\mathbf{r} = \mathbf{e}_r dr + \mathbf{e}_\theta r\, d\theta + \mathbf{e}_\phi r \sin(\theta)\; d\theta. \tag{7.71}$$

We can write an expression for an infinitesimal vector displacement $d\mathbf{r}$ in a form that will hold for any set of orthogonal coordinates. Let the three coordinates of an orthogonal system in three dimensions be called q_1, q_2, and q_3. Let the displacements due to the infinitesimal increments he called ds_1, ds_2, and ds_3. Let the unit vectors in the directions of the displacements be called $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$. The equation analogous to Eq. (7.71) is

$$d\mathbf{r} = \mathbf{e}_1 ds_1 + \mathbf{e}_2 ds_2 + \mathbf{e}_3 ds_3 = \mathbf{e}_1 h_1 dq_1 + \mathbf{e}_2 h_2 dq_2 + \mathbf{e}_3 h_3 dq_3,$$

where the h's are the factors needed to give the correct expression for each displacement. For Cartesian coordinates, all three of the h factors are equal to unity. For spherical polar coordinates, $h_r = 1$, $h_\theta = r$, and $h_\phi = r \sin(\theta)$. For other systems, you can figure out what the h's are geometrically so that $ds = hdq$ for each coordinate.

Gradients in Orthogonal Coordinates

The gradient of a scalar function f is written in terms of components in the direction of ds_1, ds_2, and ds_3 as

$$\nabla f = \mathbf{e}_1 \frac{\partial f}{\partial s_1} + \mathbf{e}_2 \frac{\partial f}{\partial s_2} + \mathbf{e}_3 \frac{\partial f}{\partial s_3}$$

or

$$\boxed{\nabla f = \mathbf{e}_1 \frac{1}{h_1}\frac{\partial f}{\partial q_1} + \mathbf{e}_2 \frac{1}{h_2}\frac{\partial f}{\partial q_2} + \mathbf{e}_3 \frac{1}{h_3}\frac{\partial f}{\partial q_3}}. \tag{7.72}$$

EXAMPLE 7.27 Find the expression for the gradient of a function of spherical polar coordinates $f = f(r, \theta, \phi)$.

SOLUTION ►

$$\nabla f = \mathbf{e}_r \frac{\partial f}{\partial r} + \mathbf{e}_\theta \frac{1}{r}\frac{\partial f}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r \sin(\theta)}\frac{\partial f}{\partial \phi}.$$

◄

EXERCISE 7.26 ►

(a) Find the h factors for cylindrical polar coordinates.

(b) Find the expression for the gradient of a function of cylindrical polar coordinates, $f = f(\rho, \phi, z)$. Find the gradient of the function

$$f = e^{-(\rho^2+z^2)/a^2} \sin(\phi).$$

◄

The *divergence of a vector function* can similarly be expressed in orthogonal coordinates. If $\mathbf{F}$ is a vector function, it must be expressed in terms of the unit vectors of the coordinate system in which we are to differentiate,

$$\mathbf{F} = \mathbf{e}_1 F_1 + \mathbf{e}_2 F_2 + \mathbf{e}_3 F_3. \tag{7.73}$$

The components F_1, F_2, and F_3 are the components in the directions of $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$, not necessarily the Cartesian components.

The divergence of the vector function $\mathbf{F}$ is given by

$$\boxed{\nabla \cdot \mathbf{F} = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial q_1}(F_1 h_2 h_3) + \frac{\partial}{\partial q_2}(F_2 h_1 h_3) + \frac{\partial}{\partial q_3}(F_3 h_1 h_2)\right]}. \tag{7.74}$$

EXAMPLE 7.28 (a) Write the expression for the divergence of a vector function $\mathbf{F}$ expressed in terms of spherical polar coordinates.

(b) Find the divergence of the position vector, which in spherical polar coordinates is

$$\mathbf{r} = \mathbf{e}_r r.$$

SOLUTION ► (a)

$$\begin{aligned}\nabla \cdot \mathbf{F} &= \frac{1}{r^2 \sin(\theta)}\left[\frac{\partial}{\partial r}\left[F_r r^2 \sin(\theta)\right] + \frac{\partial}{\partial \theta}\left[F_\theta r \sin(\theta)\right] + \frac{\partial}{\partial \phi}(F_\phi r)\right] \\ &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 F_r\right) + \frac{1}{r \sin(\theta)}\frac{\partial}{\partial \theta}\left[\sin(\theta)\, F_\theta\right] \\ &\quad + \frac{1}{r \sin(\theta)}\frac{\partial F_\phi}{\partial \phi}. \end{aligned} \tag{7.75}$$

(b) The divergence of $\mathbf{r}$ is

$$\nabla \cdot \mathbf{r} = \frac{1}{r^2} 3r^2 + 0 + 0 = 3.$$

◄

EXERCISE 7.27 ► Write the formula for the divergence of a function in cylindrical polar coordinates. ◄

The *curl* of a vector function $\mathbf{F}$ is

$$\begin{aligned}\nabla \times \mathbf{F} &= \mathbf{e}_1 \frac{1}{h_2 h_3}\left[\frac{\partial}{\partial q_2}(h_3 F_3) - \frac{\partial}{\partial q_3}(h_2 F_2)\right] \\ &\quad + \mathbf{e}_2 \frac{1}{h_1 h_3}\left[\frac{\partial}{\partial q_3}(h_1 F_1) - \frac{\partial}{\partial q_1}(h_3 F_3)\right] \\ &\quad + \mathbf{e}_3 \frac{1}{h_1 h_2}\left[\frac{\partial}{\partial q_1}(h_2 F_2) - \frac{\partial}{\partial q_2}(h_1 F_1)\right]. \end{aligned} \tag{7.76}$$

The expression for the Laplacian of a scalar function, f, is

$$\boxed{\nabla^2 f = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial q_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial f}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{h_1 h_2}{h_3}\frac{\partial f}{\partial q_3}\right)\right]}. \tag{7.77}$$

EXAMPLE 7.29 Write the expression for the Laplacian in spherical polar coordinates.

SOLUTION ►

$$\boxed{\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial f}{\partial r}\right) + \frac{1}{r^2 \sin(\theta)}\frac{\partial}{\partial \theta}\left[\sin(\theta)\frac{\partial f}{\partial \theta}\right] + \frac{1}{r^2 \sin^2(\theta)}\frac{\partial f}{\partial \phi^2}}. \tag{7.78}$$

EXERCISE 7.28 ► Write the expression for the Laplacian in cylindrical polar coordinates ◄

◄

7.8 Maximum and Minimum Values of Functions of Several Variables

A point at which either a maximum or a minimum value in a function occurs is sometimes called an *extremum*. For example, Fig. 7.8 shows a perspective view of

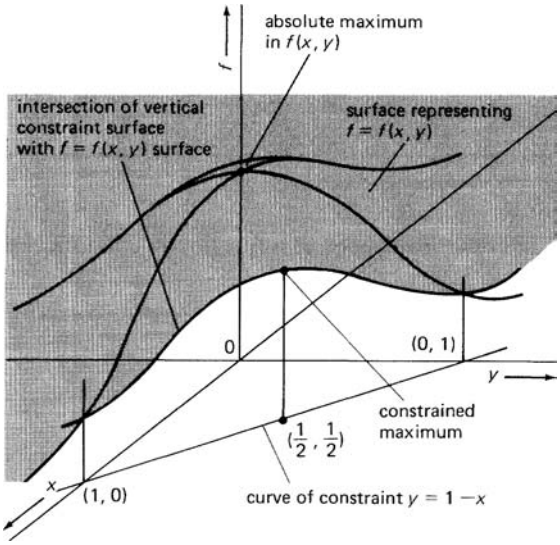

Figure 7.8 ► The surface representing a function of x and y with the absolute maximum and a constrained maximum shown.

a graph of the function $f = e^{-x^2-y^2}$. The surface representing the function has a "peak" at the origin,where the function attains its maximum value. Shown also in the figure is a curve at which the surface intersects with a plane representing the equation $y = 1 - x$. On this curve there is also a maximum, which has a smaller value than the maximum at the peak. We call this value the maximum subject to the constraint that $y = 1 - x$. We discuss the constrained maximum later.

A maximum at a peak such as the maximum at the origin in Fig. 7.8 is called a *local maximum* or a *relative maximum*. The value of the function at such a peak is larger than at any other point in the immediate vicinity. However, a complicated function can have more than one local maximum. Also, if we consider a finite region, the function might have a larger value somewhere on the boundary of the region that is larger than the value at a local maximum. To find the absolute maximum of the function for a given region, we must consider all local maxima and any points on the boundary of the region that might have greater values. The peak at the origin is the absolute maximum of this function. Points of minimum value are completely analogous to points of maximum value. *Local minima* are located at the bottom of depressions or valleys in the surface representing the function. To find an absolute minimum for a given region, you must consider all local minima and any points on the boundary of the region that might have smaller values.

To find a local maximum or minimum, we use the fact that the plane that is tangent to the surface will be horizontal at any local maximum or minimum. Therefore, the curve representing the intersection of any vertical plane with the surface will have a local maximum or a minimum at the same place. The partial derivative with respect to one independent variable gives the slope of the curve in the plane corresponding to a constant value of the other independent variable, so we can find a local maximum or minimum by finding the places where all the partial derivatives of the function vanish simultaneously.

Our method for a differentiable function of two variables is therefore:

1. Solve the simultaneous equations

$$\left(\frac{\partial f}{\partial x}\right)_y = 0 \tag{7.79}$$

$$\left(\frac{\partial f}{\partial y}\right)_x = 0 \tag{7.80}$$

2. Calculate the value of the function at all points satisfying these equations, and also at the boundaries of the region being considered. The maximum or minimum value in the region being considered must be in this set of values.

3. If there are points at which the function is not differentiable, such as discontinuities or cusps, these points must also be included in the set of possible locations of the maximum or minimum.

EXAMPLE 7.30 Find the maximum value of the function shown in Fig. 7.8, $f = e^{-x^2-y^2}$.

SOLUTION ► At a local maximum or minimum

$$\left(\frac{\partial f}{\partial x}\right)_y = e^{-x^2-y^2}(-2x) = 0$$

$$\left(\frac{\partial f}{\partial y}\right)_x = e^{-x^2-y^2}(-2y) = 0.$$

The only solution for finite values of x and y is $x = 0$, $y = 0$. Since no restricted region was specified, we consider all values of x and y. For very large magnitudes of x or y, the function vanishes, so we have found the desired absolute maximum, at which $f = 1$. ◄

In the case of one independent variable, a local maximum could be distinguished from a local minimum or an inflection point by determining the sign of the second derivative. With more than one variable, the situation is more complicated. In addition to inflection points, we can have points corresponding to a maximum with respect to one variable and a minimum with respect to another. Such a point is called a *saddle point*, and at such a point, the surface representing the function resembles a mountain pass or the surface of a saddle. Such points are important in the *transition-state theory* of chemical reaction rates.

For two independent variables, the following quantity is calculated:

$$D = \left(\frac{\partial^2 f}{\partial x^2}\right)\left(\frac{\partial^2 f}{\partial y^2}\right) - \left(\frac{\partial^2 f}{\partial x\,\partial y}\right)^2. \tag{7.81}$$

The different cases are as follows:

1. If $D > 0$ and $(\partial^2 f/\partial x^2) > 0$, then we have a local minimum.

2. If $D > 0$ and $(\partial^2 f/\partial x^2) < 0$, then we have a local maximum.

3. If $D < 0$, then we have neither a local maximum nor a local minimum.

4. If $D = 0$, the test fails, and we cannot tell what we have.

EXERCISE 7.29 ► Evaluate D at the point $(0, 0)$ for the function of Example 7.30 and establish that the point is a local maximum. ◄

For more than two independent variables, the method is similar, except that there is one equation for each independent variable.

Constrained Maximum/Minimum Problems

Sometimes we must find a maximum or a minimum value of a function subject to some condition, which is called a *constraint*. Such an extremum is called a *constrained maximum* or a *constrained minimum*. Generally, a constrained maximum is smaller than the unconstrained maximum of the function, and a constrained minimum is larger than the unconstrained minimum of the function. Consider the following example:

EXAMPLE 7.31 Find the maximum value of the function in Example 7.30 subject to the constraint $x + y = 1$.

SOLUTION ► The situation is shown in Fig. 7.8. The constraint corresponds to the specification of y as a function of x by

$$y = 1 - x. \tag{7.82}$$

This function is given by the line in the x-y plane of the figure. We are now looking for the place along this curve at which the function has a larger value than at any other place on the curve. Unless the curve happens to pass through the unconstrained maximum, the constrained maximum will be smaller than the unconstrained maximum.

Since y is no longer an independent variable on the curve of the constraint, the direct way to proceed is to replace y by use of Eq. (7.82):

$$f = (x, 1 - x) = f(x) = e^{-x^2-(1-x)^2} = e^{-2x^2+2x-1}. \tag{7.83}$$

The local maximum is now at the point where df/dx vanishes:

$$\frac{df}{dx} = e^{-2x^2-(1-x)^2}(-4x + 2) = 0. \tag{7.84}$$

This equation is satisfied by $x = \frac{1}{2}$ and by $|x| \to \infty$. The constrained maximum corresponds to $x = \frac{1}{2}$ and the minimum corresponds to $|x| \to \infty$. At the constrained maximum $y = 1 - \frac{1}{2} = \frac{1}{2}$ and

$$f\left(\frac{1}{2}, \frac{1}{2}\right) \exp\left[-\left(\frac{1}{2}^2\right) - \left(\frac{1}{2}\right)^2\right] = e^{-1/2} = 0.6065\cdots.$$

As expected, this value is smaller than the unconstrained maximum, at which $f = 1$. ◄

EXERCISE 7.30 ► (a) Find the minimum in the function

$$f(x, y) = x^2 + y^2 + 2x.$$

(b) Find the constrained minimum subject to the constraint

$$x + y = 0.$$

◄

Lagrange's Method of Undetermined Multipliers[3]

If we have a constrained maximum or minimum problem with more than two variables, the direct method of substituting the constraint relation into the function is usually not practical. Lagrange's method finds a constrained maximum or minimum without substituting the constraint relation into the function. If the constraint is written in the form $g(x, y) = 0$, the method for finding the constrained maximum or minimum in $f(x, y)$ is as follows:

1. Form the new function

$$u(x, y) = f(x, y) + \lambda g(x, y), \tag{7.85}$$

where λ is a constant called an *undetermined multiplier*. Its value is unknown at this point of the analysis.

2. Form the partial derivatives of u, and set them equal to zero,

$$\left(\frac{\partial u}{\partial x}\right)_y = \left(\frac{\partial f}{\partial x}\right)_y + \lambda \left(\frac{\partial g}{\partial x}\right)_y = 0 \tag{7.86}$$

$$\left(\frac{\partial u}{\partial x}\right)_x = \left(\frac{\partial f}{\partial x}\right)_x + \lambda \left(\frac{\partial g}{\partial x}\right)_x = 0. \tag{7.87}$$

3. Solve the set of equations consisting of $g = 0$ and the two equations of Eqs. (7.86) and (7.87) as a set of simultaneous equations for the value of x, the value of y, and the value of λ that correspond to the local maximum or minimum.

We will not present a proof of the validity of this method, but you can find a proof in calculus textbooks.

EXAMPLE 7.32 Find the constrained maximum of Example 7.31 by the method of Lagrange.

SOLUTION ► The constraining equation is written

$$g(x, y) = x + y - 1 = 0. \tag{7.88}$$

The function u is

$$u(x, y) = e^{-x^2-y^2} + \lambda(x + y - 1)$$

so that the equations to be solved are Eq. (7.88) and

$$\left(\frac{\partial u}{\partial x}\right)_y = (-2x)\, e^{-x^2-y^2} + \lambda = 0 \tag{7.89}$$

$$\left(\frac{\partial u}{\partial y}\right)_x = (-2y)\, e^{-x^2-y^2} + \lambda = 0. \tag{7.90}$$

Let us begin by solving for λ in terms of x and y. Multiply Eq. (7.89) and Eq. (7.90) by x and add the two equations. The result can be solved to give

$$\lambda = \frac{4xy}{x + y} e^{-x^2-y^2}. \tag{7.91}$$

Substitute this into Eq. (7.89) to obtain

[3]Named for Joseph Louis Lagrange (born Guisepps Lodovico Lagrangia), 1736–1813, French-Italian physicist and mathematician.

$$(-2x)\,e^{-x^2-y^2} + \frac{4xy}{x+y}e^{-x^2-y^2} = 0. \tag{7.92}$$

The exponential factor is not zero for any finite values of x and y, so

$$-2x + \frac{4xy}{x+y} = 0. \tag{7.93}$$

When Eq. (7.91) is substituted into Eq. (7.90) in the same way, the result is

$$-2y + \frac{4xy}{x+y} = 0. \tag{7.94}$$

When Eq. (7.94) is subtracted from Eq. (7.94), the result is

$$-2x + 2y = 0$$

which is solved for y in terms of x to obtain

$$y = x.$$

This is substituted into Eq. (7.88) to obtain

$$x + x - 1 = 0$$

which gives

$$x + \frac{1}{2}, \quad y = \frac{1}{2}.$$

This is the same result as in Example 7.31. In this case, the method of Lagrange was more work than the direct method. In more complicated problems, the method of Lagrange will usually be easier. ◄

The method of Lagrange also works if there is more than one constraint. If we desire the local maximum or minimum of the function

$$f = f(x, y, z)$$

subject to the two constraints

$$g_1(x, y, z) = 0 \tag{7.95}$$

and

$$g_2(x, y, z) = 0 \tag{7.96}$$

the procedure is similar, except that two undetermined multipliers are used. One forms the function

$$u = u(x, y, z) = f(x, y, z) + \lambda_1 g_1(x, y, z) + \lambda_2 g_2(x, y, z) \tag{7.97}$$

and solves the set of simultaneous equations consisting of Eqs. (7.95), (7.96), and

$$\left(\frac{\partial u}{\partial x}\right)_{y,z} = 0 \tag{7.98}$$

$$\left(\frac{\partial u}{\partial y}\right)_{x,z} = 0 \tag{7.99}$$

$$\left(\frac{\partial u}{\partial z}\right)_{x,y} = 0 \tag{7.100}$$

The result is a value for λ_1, a value for λ_2, and values for x, y, and z which locate the constrained local maximum or minimum.

EXERCISE 7.31 ► Find the constrained minimum of Exercise 7.30 using the method of Lagrange. ◄

SUMMARY

The calculus of functions of several independent variables is a natural extension of the calculus of functions of one independent variable. The partial derivative is the first important quantity. For example, a function of three independent variables has three partial derivatives. Each one is obtained by the same techniques as with ordinary derivatives, treating other independent variables temporarily as constants. The differential of a function of x_1, x_2, and x_3 is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_{x_3,x_3} dx_1 + \left(\frac{\partial f}{\partial x_2}\right)_{x_1,x_3} dx_2 + \left(\frac{\partial f}{\partial x_3}\right)_{x_1,x_2} dx_3,$$

where df is an infinitesimal change in the function f produced by the changes dx_1, dx_2, and dx_3 imposed on the independent variables and where the coefficients are partial derivatives. This is called an *exact differential*, identifying df as in increment in a function. A similar expression such as

$$dw = Mdx_1 + Ndx_2 + Pdx_3$$

is an inexact differential if the coefficients M, N, and P are not the appropriate derivatives of the same function. If not, they do not obey the Euler reciprocity relation, which is one of several relations that partial derivatives obey.

One application of partial derivatives is in the search for minimum and maximum values of a function. An extremum (minimum or maximum) of a function in a region is found either at a boundary of the region or at a point where all of the partial derivatives vanish. A constrained maximum or minimum is found by the method of Lagrange, in which a particular augmented function is maximized or minimized.

A line integral is denoted by

$$\int_c dw = \int_c (Mdx_1 + Ndx_2 + Pdx_3)\,.$$

In this integral, the variables x_2 and x_3 in M must be replaced by functions of x_1 corresponding to the curve on which the integral is performed, with similar replacements in N and P. The line integral of the differential of a function depends only on the end points of the curve, which the line integral of an inexact differential depends on the path of the curve as well as on the end points.

A multiple integral is an integral of the form

$$\iiint f(x, y, z)\, dz\, dy\, dx$$

in which the integrations are carried out one after another. As each integration is carried out, those integration variables not yet integrated are treated as constants.

PROBLEMS

1. A certain nonideal gas has an equation of state

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m},$$

where T is the temperature on the Kelvin scale, V_m is the molar volume (volume of 1 mol), P is the pressure, and R is the gas constant. The *second virial coefficient* B_2 is given as a function of T by

$$B_2 = \left[-1.00 \times 10^{-4} - \left(2.148 \times 10^{-6}\right) e^{(1956\,\mathrm{K})/T}\right] \mathrm{m}^3\,\mathrm{mol}^{-1},$$

Find $(\partial P/\partial V_m)_T$ and $(\partial P/\partial T)_{V_m}$ and an expression for dP.

2. For a certain system, the thermodynamic energy U is given as a function of S, V,and n by

$$U = U(S, V, n) = Kn^{5/3}V^{-2/3}e^{2S/3nR},$$

where S is the entropy, V is the volume, n is the number of moles, K is a constant, and R is the ideal gas constant.

a) Find dU in terms of dS, dV, and dn.

b) Find an expression for $(\partial U/\partial S)_{V,n}$.

c) Find an expression for $(\partial U/\partial V)_{S,n}$.

d) Find an expression for $(\partial U/\partial n)_{S,V}$.

3. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

a) $f = axy\ln(y) + bx\cos(x + y)$

b) $f = ae^{-b(x^2+y^2)} + c\sin\left(x^2y\right)$

c) $f = a(x + by)/(c + xy)$

4. Find $(\partial f/\partial x)_y$, and $(\partial f/\partial y)_x$ for each of the following functions, where a, b, and c are constants.

a) $f = a(bx + cy)^{-3}$.

b) $f = a\cos^2(bx) - b\sin^3(y)$

c) $f = a\exp\left(-b(x^2 - y^2)\right)$

5. Find $(\partial^2 f/\partial x^2)_y$, $(\partial^2 f/\partial x\partial y)$, $(\partial^2 f/\partial y\partial x)$, and $\left(\partial^2 f/\partial y^2\right)$, for each of the following functions, where a, b, and c are constants.

a) $f = (x + y)^{-1}$

b) $f = \cos(x/y)$

c) $f = e^{(ax^2+by^2)}$.

6. Find $(\partial^2 f/\partial x^2)_y$, $(\partial^2 f/\partial x\partial y)$, $(\partial^2 f/\partial y\partial x)$, and $\left(\partial^2 f/\partial y^2\right)$, for each of the following functions, where a, b, and c are constants.

a) $f = a\ln(bx^2 + cy^2)$

b) $f = a(x^2 + y^2)^{-2}$

c) $f = a\cos(\sin(x))$

7.

a) Find the area of the semicircle of radius a given by

$$y = +(a^2 - x^2)^{1/2}$$

by doing the double integral

$$\int_{-a}^{a} \int_{0}^{(a^2-x^2)^{1/2}} 1 \, dy \, dx.$$

b) Change to polar coordinates and repeat the calculation.

8. Test each of the following differentials for exactness.

a) $du = by \cos(bx)\ dx + \sin(bx)\ dy$

b) $du = ay \sin(xy)\ dx + ax \sin(xy)\ dy$

c) $du = (y/(1 + x^2))\, dx - \tan^{-1}(x)\, dy$

9. Test each of the following differentials for exactness.

a) $du = x\, dy + y\, dx$

b) $du = y \ln(x)\, dx + x \ln(y)\, dy$

c) $du = 2xe^{axy}\, dx + 2ye^{axy}\, dy.$

10. If $G = -RT \ln(aT^{3/2}V/n)$ find dG in terms of dT, dV, and dn, where R and a are constants.

11.

a) Perform the line integral

$$\int_C du = \int_C (x^2 y\, dx + xy^2 dy),$$

where c represents the line segment from $(0, 0)$ to $(2, 2)$. Would another path with the same end points yield the same result?

b) Perform the line integral on the path from $(0, 0)$ to $(2, 0)$ and then from $(2, 0)$ to $(2, 2)$.

12.

a) Perform the line integral

$$\int_C du = \int_C (xy^2\, dx + x^2 y dy),$$

where c represents the line segment from $(0, 0)$ to $(2, 2)$. Would another path with the same end points yield the same result?

b) Perform the line integral on the path from $(0, 0)$ to $(2, 0)$ and then from $(2, 0)$ to $(2, 2)$.

13. Find the function $f(x, y)$ whose differential is

$$df = (x + y)^{-1}\, dx + (x + y)^{-1} dy$$

and which has the value $f(1, 1) = 0$. Do this by performing a line integral on a rectangular path from $(1, 1)$ to (x_1, y_1) where $x_1 > 0$ and $y_1 > 0$.

14. A wheel of radius R has a distribution of mass given by

$$m(\rho) = a\rho^2 + b,$$

whereρ is the distance from the center, a and b are constants, and $m(\rho)$ is the mass per unit area as a function of ρ. Assume that m depends only on ρ. Find the *moment of inertia*, defined by

$$I = \iint m(\rho)\rho^2\, dA = \int_0^{\infty} \int_0^{2\pi} m(\rho)\rho^2 \rho d\phi d\rho,$$

where dA represents the element of area and the integral is a double integral over the entire wheel. Transform to Cartesian coordinates and carry out the integral again. In order to simplify the limits of integration in Cartesian coordinate, integrate over half of the wheel and double your result.

15. Complete the formula

$$\left(\frac{\partial S}{\partial V}\right)_{P,n} = \left(\frac{\partial S}{\partial V}\right)_{T,n} + ?$$

16. Find the location of the minimum in the function

$$f = f(x, y) = x^2 - 6x + 8y + y^2$$

considering all real values of x and y. What is the value of the function at the minimum?

17. Find the minimum in the function of the previous problem subject to the constraint $x + y = 2$. Do this by substitution and by the method of undetermined multipliers.

18. Find the location of the maximum in the function

$$f = f(x, y) = x^2 - 6x + 8y + y^2$$

considering the region $0 < x < 2$ and $0 < y < 2$. What is the value of the function at the maximum?

19. Find the maximum in the function of the previous problem subject to the constraint $x + y = 2$. Do this by substitution and by Lagrange's method of undetermined multipliers.

8

Differential Equations

Preview

A differential equation contains one or more derivatives of an unknown function, and solving a differential equation means finding what that function is. One important class of differential equations consists of classical equations of motion, which come from Newton's second law of motion. We will discuss the solution of several kinds of differential equations, including linear differential equations, in which the unknown function and its derivatives enter only to the first power, and exact differential equations, which can be solved by a line integration. We will also introduce partial differential equations, in which partial derivatives occur and in which there are two or more independent variables. We will also discuss the solution of differential equations by use of Laplace transformations. Some differential equations can be solved either symbolically or numerically using Mathematica.

Principal Facts and Ideas

1. The solution of a differential equation is a function whose derivative or derivatives satisfy the differential equation.

2. An equation of motion is a differential equation obtained from Newton's second law of motion, $\mathbf{F} = m\mathbf{a}$.

3. In principle, an equation of motion can be solved to give the position and velocity as a function of time for every particle in a system governed by Newton's laws of motion.

4. A homogeneous linear differential equation with constant coefficients can be solved by use of an exponential trial solution.

5. An inhomogeneous linear differential equation can be solved if a particular solution can be found.

6. An exact differential equation can be solved by a line integration.

7. Some inexact differential equations can be converted to exact differential equations by multiplication by an integrating factor.

8. Some partial differential equations can be solved by separation of variables.
9. A differential equation can be transformed into an algebraic equation by a Laplace transformation. Solution of this equation followed by inverse transformation provides a solution to the differential equation.
10. Differential equations can be solved numerically by a variety of methods, including the use of Mathematica.

Objectives

After studying this chapter, you should be able to:

1. construct an equation of motion for a particle from Newton's second law;
2. solve a linear homogeneous differential equation with constant coefficients;
3. solve a differential equation whose variables can be separated;
4. solve an exact differential equation;
5. use an integrating factor to solve an inexact differential equation;
6. solve a simple partial differential equation by separation of variables;
7. solve a differential equation by use of Laplace transforms;
8. use Mathematica to solve differential equations symbolically and numerically.

8.1 Differential Equations and Newton's Laws of Motion

A *differential equation* is an equation that contains one or more derivations of an unknown function. The solution of a differential equation is the unknown function, not a set of constant values of an unknown variable as is the case with an algebraic equation. Our first examples of differential equations are *equations of motion*, obtained from *Newton's second law of motion*. These equations are used to determine the time dependence of the position and velocity of particles. The position of a particle is given by the position vector $\mathbf{r}$ with Cartesian components x, y, and z. The velocity $\mathbf{v}$ of a particle is the rate of change of its position vector,

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \mathbf{i}\frac{dx}{dt} + \mathbf{j}\frac{dy}{dt} + \mathbf{k}\frac{dz}{dt} = \mathbf{i}v_x + \mathbf{j}v_y + \mathbf{k}v_z, \tag{8.1}$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the unit vectors defined in Chapter 2. The acceleration $\mathbf{a}$ is the rate of change of the velocity:

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{r}}{dt^2} = \mathbf{i}\frac{d^2x}{dt^2} + \mathbf{j}\frac{d^2y}{dt^2} + \mathbf{k}\frac{d^2z}{dt^2} = \mathbf{i}a_x + \mathbf{j}a_y + \mathbf{k}a_z. \tag{8.2}$$

Consider a particle that moves in the z direction only, so that v_x, v_y, a_x, and a_y vanish. If a_z is known as a function of time,

$$a_z = a_z(t) \tag{8.3}$$

we can write an equation by equating the time derivative of the velocity to this known function:

$$\frac{dv_z}{dt} = a_z(t). \tag{8.4}$$

This is a differential equation for the velocity, since it contains the derivative of the velocity. Solving this equation means finding a function to represent the velocity as a function of time.

To solve Eq. (8.4), we multiply both sides by dt and perform a definite integration from $t = 0$ to $t = t_1$.

$$v_z(t_1) - v_z(0) = \int_0^{t_1} \left(\frac{dv_z}{dt}\right) dt = \int_0^{t_1} a_z(t)dt. \tag{8.5}$$

The result of this integration gives v_z as a function of time, so that the position obeys a second differential equation

$$\frac{dz}{dt} = v_z(t). \tag{8.6}$$

A second integration gives the position as a function of time:

$$z_z(t_2) - z(0) = \int_0^{t_2} \left(\frac{dz}{dt_1}\right) dt_1 = \int_0^{t_2} v_z(t_1)dt_1. \tag{8.7}$$

There are inertial navigation systems used on submarines and space vehicles that determine the acceleration as a function of time and perform two numerical integrations in order to determine the position of the vehicle.

EXAMPLE 8.1 At time $t = 0$, a certain particle has $z(0) = 0$ and $v_z(0) = 0$. Its acceleration is given as a function of time by

$$a_z(t) = a_0 e^{-t/b},$$

where a_0 and b are constants.

(a) Find v_z as a function of time.

(b) Find z as a function of time.

(c) Find the speed and the position of the particle at $t = 30.0\,\text{s}$ if $a_0 = 10.0\,\text{m s}^{-2}$ and if $b = 20.0\,\text{s}$.

(d) Find the limiting value of the speed as $t \to \infty$.

SOLUTION ► (a) The antiderivative of the given acceleration function plus a constant v_0 is the velocity:

$$v_z(t) = -a_0 b e^{-t/b} + v_0 = -a_0 b e^{-t/b} + a_0 b = a_0 b(1 - e^{-t/b})$$

since it was specified that $v_z(0) = 0$, the constant $v_0 = a_0 b$.

(b) The antiderivative of the velocity plus a constant z_0 is the position:

$$z(t) = a_0 b^2 e^{-t/b} + a_0 bt + z_0 = a_0 b^2 e^{-t/b} + a_0 bt - a_0 b^2$$

Since it was specified that $z(0) = 0$, the constant $z_0 = -a_0 b^2$.

(c) At $t = 30.0\,\mathrm{s}$

$$\begin{aligned} v_z(30.0\,\mathrm{s}) &= (10.0\,\mathrm{m\,s^{-2}})(20.0\,\mathrm{s})(1 - e^{-1.50}) = 155\,\mathrm{m\,s^{-1}} \\ z(30.0\,\mathrm{s}) &= (10.0\,\mathrm{m\,s^{-2}})(20.0\,\mathrm{s})^2 e^{-1.50} + (200.0\,\mathrm{m\,s^{-1}})(30.0\,\mathrm{s}) \\ &\quad - (10.0\,\mathrm{m\,s^{-2}})(20.0\,\mathrm{s})^2 = 2890\,\mathrm{m} \end{aligned}$$

(d) As $t \to \infty$, the speed approaches

$$\lim_{t\to\infty} v_z(t) = a_0 b = 200.\,\mathrm{m\,s^{-1}}$$

◀

Unfortunately, the acceleration is very seldom known as a function of time, so integration as in the previous example cannot usually be used to find how a particle moves. Instead, we must obtain the acceleration of the particle from knowledge of the force on it, using Newton's second law.

Newton's Laws of Motion

These laws were deduced by Isaac Newton[1] from his analysis of observations of the motions of actual objects, including apples and celestial bodies. The laws can be stated:

1. A body on which no forces act does not accelerate.
2. A body acted on by a force $\mathbf{F}$ accelerates according to

$$\mathbf{F} = m\mathbf{a}, \tag{8.8}$$

   where m is the mass of the object and $\mathbf{a}$ is its acceleration.
3. Two bodies exert forces of equal magnitude and opposite direction on each other.

Classical mechanics is primarily the study of the consequences of these laws. It is sometimes called *Newtonian mechanics*. The first law is just a special case of the second, and the third law is primarily used to obtain forces for the second law, so Newton's second law is the most important equation of classical mechanics.

If the force on a particle can be written as a function of its position alone, we have an *equation of motion*. If the force on a particle depends on the positions of other particles, the equations of motion of the particles are coupled together and must be solved simultaneously. The equations of motion cannot be solved exactly for a system of more than two interacting particles.

The simplest equation of motion is for a single particle that can move in only one direction. From Newton's second law, we can write the following equation for a particle that moves in the z direction:

$$F_z(z) = m\frac{d^2z}{dt^2}. \tag{8.9}$$

A force that depends only on position can be derived from a potential energy function, as in Eq. (7.63). Equation (8.9) becomes

$$-\frac{d\mathcal{V}}{dz} = m\frac{d^{2z}}{dt^2}, \tag{8.10}$$

[1] Isaac Newton, 1642–1727, was a great English physicist and mathematician who discovered the law of gravity and the laws of motion and who helped invent calculus.

where $\mathcal{V}$ is the potential energy function. We now examine these equations for a particular example system.

8.2 The Harmonic Oscillator: Linear Differential Equations with Constant Coefficients

Consider an object of mass m attached to the end of a coil spring whose other end is rigidly fastened. Let the object move only in the z direction, the direction in which the spring is stretched or compressed. Define the z coordinate so that $z = 0$ when the spring has its equilibrium length. To a good approximation, the force on the object due to the spring is given by *Hooke's law*,[2]

$$F_z = -kz, \tag{8.11}$$

where k is a constant called the *spring constant*. The negative sign produces a negative force (downward) when z is positive and vice versa, so that the force pushes the mass toward its equilibrium position. The *harmonic oscillator* is a *model system* that represents the mass on a spring. That is, it is a hypothetical system (existing only in our minds) which has some properties in common with the real system, but it is enough simpler to allow exact mathematical analysis. Our model system is defined by saying that the spring has no mass and that Eq. (8.11) is exactly obeyed, even if z has a large magnitude.

Replacement of F by md^2z/dt^2 according to Newton's second law gives the equation of motion for our harmonic oscillator:

$$\frac{d^2z}{dt^2} + \frac{k}{m}z = 0. \tag{8.12}$$

This differential equation has the properties:

1. It is called an *ordinary differential equation* because it contains only ordinary derivatives as opposed to partial derivatives.
2. It is *linear*, which means that the dependent variable z and its derivatives enter only to the first power.
3. It is *homogeneous*, which means that there are no terms that do not contain z.
4. It is *second order*, which means that the highest order derivative in the equation is a second derivative.
5. It has *constant coefficients*, which means that the quantities which multiply z and its derivatives are constants.

There are two important facts about linear homogeneous differential equations:

1. If $z_1(t)$ and $z_2(t)$ are two functions that satisfy the equation, then the linear combination $z_3(t)$ is also a solution, where

$$z_3(t) = c_1z_1(t) + c_2z_2(t) \tag{8.13}$$

and c_1 and c_2 are constants. A *linear combination* is a sum of functions multiplied by constant coefficients.

[2] After Robert Hooke, 1635–1703, one of Newton's contemporaries and rivals.

2. If $z(t)$ satisfies the equation, then $cz(t)$ is also a solution, where c is a constant.

A linear homogeneous differential equation with constant coefficients can be solved by the following routine method:

1. Assume the trial solution

$$z(t) = e^{\lambda t}, \tag{8.14}$$

where λ is a constant. A *trial solution* is what the name implies. We try it by substituting it into the equation and produce an algebraic equation in λ called the *characteristic equation*.

2. Find the values of λ that satisfy the characteristic equation. For an equation of order n, there will be n values of λ. Call these values $\lambda_1, \lambda_2, \ldots, \lambda_n$. These values produce n versions of the trial solution that satisfy the equation.

3. Use fact (1) to write a solution

$$z(t) = c_1 e^{\lambda_1 t} + c_2 e^{\lambda_2 t} + \cdots + c_n e^{\lambda_n t}. \tag{8.15}$$

EXAMPLE 8.2 Show that the differential equation

$$a_3\left(\frac{d^3y}{dx^3}\right) + a_2\left(\frac{d^2y}{dx^2}\right) + a_1\left(\frac{dy}{dx}\right) + a_0 y = 0 \tag{8.16}$$

can be satisfied by a trial solution $y = e^{\lambda x}$.

SOLUTION ► We substitute the trial solution $y = e^{\lambda x}$ into the differential equation:

$$a_3\lambda^3 e^{\lambda x} + a_2\lambda^2 e^{\lambda x} + a_1\lambda^2 e^{\lambda x} + a_1\lambda e^{\lambda x} + a_0 e^{\lambda x} = 0. \tag{8.17}$$

If x remains finite, we can divide by $e^{\lambda x}$ to obtain the characteristic equation:

$$a_3\lambda^3 + a_2\lambda^2 + a_1\lambda + a_0 = 0. \tag{8.18}$$

If the constants a_o, a_1, a_2,and a_3 are known, this is an equation that can be solved for three values of λ which cause the trial solution to satisfy Eq. (8.16). ◄

EXAMPLE 8.3 Solve the differential equation

$$\frac{d^2y}{dx^2} + \frac{dy}{dx} - 2y = 0. \tag{8.19}$$

SOLUTION ► Substitution of the trial solution $y = e^{\lambda x}$ gives the characteristic equation

$$\lambda^2 + \lambda - 2y = 0.$$

The solutions to this equation are

$$\lambda = 1, \quad \lambda = -2.$$

The solution to the differential equation is thus

$$y(x) = c_1 e^x + c_2 e^{-2x}. \tag{8.20}$$

◄

The solution to this example satisfies the differential equation no matter what values c_1 and c_2 have. It is actually a *family of functions*, one function for each set of values for c_1 and c_2. A solution to a linear differential equation of order n that contains n arbitrary constants is known to be a *general solution*. A general solution is a family of functions which includes almost every solution to the differential equation. The solution of Eq. (8.20) is a general solution, since it contains two arbitrary constants. There is only one general solution to a differential equation. If you find two general solutions for the same differential equation that appear to be different, there must be some mathematical manipulations that will reduce both to the same form. A solution to a differential equation that contains no arbitrary constants is called a *particular solution*. A particular solution is usually one of the members of the general solution, but it might possibly be another function.

We are not finished with a problem when we find a general solution to a differential equation. We usually have additional information that will enable us to pick a particular solution out of the family of solutions. Such information consists of knowledge of boundary conditions and initial conditions. *Boundary conditions* arise from physical requirements on the solution, such as necessary conditions that apply to the boundaries of the region in space where the solution applies, or the requirement that the value of a physically measurable quantity must be a real number. *Initial conditions* arise from knowledge of the state of the system at some initial time.

We now solve the equation of motion for the harmonic oscillator, Eq. (8.12). We begin by finding the characteristic equation.

EXERCISE 8.1 ▶ Show that the characteristic equation for Eq. (8.12) for the harmonic oscillator is

$$\lambda^2 + \frac{k}{m} = 0. \tag{8.21}$$

◀

The solution of the characteristic equation for the harmonic oscillator is

$$\lambda = \pm i \left(\frac{k}{m}\right)^{1/2}, \tag{8.22}$$

where $i = \sqrt{-1}$, the imaginary unit.

The general solution to Eq. (8.12) is therefore

$$z = z(t) = c_1 \exp\left[+i\left(\frac{k}{m}\right)^{1/2} t\right] + c_2 \exp\left[-i\left(\frac{k}{m}\right)^{1/2} t\right], \tag{8.23}$$

where c_1 and c_2 are arbitrary constants.

Our principal boundary condition is that the solution be real, because imaginary and complex numbers cannot represent physically measurable quantities like the position of the oscillator. From the trigonometric identity in Eq. (2.93) we can write

$$z = c_1 \left[\cos(\omega t) + i \sin(\omega t)\right] + c_2 \left[\cos(\omega t) - i \sin(\omega t)\right], \tag{8.24}$$

where we let

$$\omega = \left(\frac{k}{m}\right)^{1/2}.$$

If we let $c_1 + c_2 = b_1$ and $i(c_1 - c_2) = b_2$, then

$$z = b_1 \cos(\omega t) + b_2 \sin(\omega t). \tag{8.25}$$

Although the solutions in Eq. (8.23) and Eq. (8.25) look different, they are equivalent to each other. Since the sine and cosine of a real variable are real we can eliminate complex solutions by requiring that b_1 and b_2 be real.

EXERCISE 8.2 ▶ Show that the function of Eq. (8.25) satisfies Eq. (8.12). ◀

Our new general solution applies to a particular harmonic oscillator if we use that oscillator's values of k and m to calculate the value of ω. We now require some conditions to make it apply to a particular case of motion. These conditions are *initial conditions* that specify the oscillator's position and velocity at some initial time. Say that we have the initial conditions at $t = 0$:

$$z(0) = 0 \tag{8.26a}$$
$$v_z(0) = v_0 \tag{8.26b}$$

where v_0 is a constant.

We require one initial condition to evaluate each arbitrary constant, so these two initial conditions will enable us obtain a particular solution for the case at hand. Knowledge of the position at time $t = 0$ without knowledge of the velocity at that time would not suffice, nor would knowledge of the velocity without knowledge of the position. For our initial conditions, b_1 must vanish:

$$z(0) = b_1 \cos(0) + b_2 \sin(0) = b_1 = 0. \tag{8.27}$$

The position is therefore given by

$$z(t) = b_2 \sin(\omega t). \tag{8.28}$$

The expression for the velocity is obtained by differentiation,

$$v_2(t) = \frac{dz}{dt} = b_2 \omega \cos(\omega t) \tag{8.29}$$

so that

$$v_z(0) = b_2 \omega \cos(0) = b_2 \omega$$

which gives

$$b_2 = \frac{v_0}{\omega} \tag{8.30}$$

and gives us our particular solution

$$z(t) = \left(\frac{v_0}{\omega}\right) \sin(\omega t). \tag{8.31}$$

The motion given by this solution is called *uniform harmonic motion*. It is a sinusoidal oscillation in time with a fixed frequency of oscillation. Figure 8.1 shows the position and the velocity of the suspended mass as a function of time. The motion is *periodic*, repeating itself over and over. During one period, the argument of the sine changes by 2π, so that if τ is the *period* (the length of time required for one cycle of the motion),

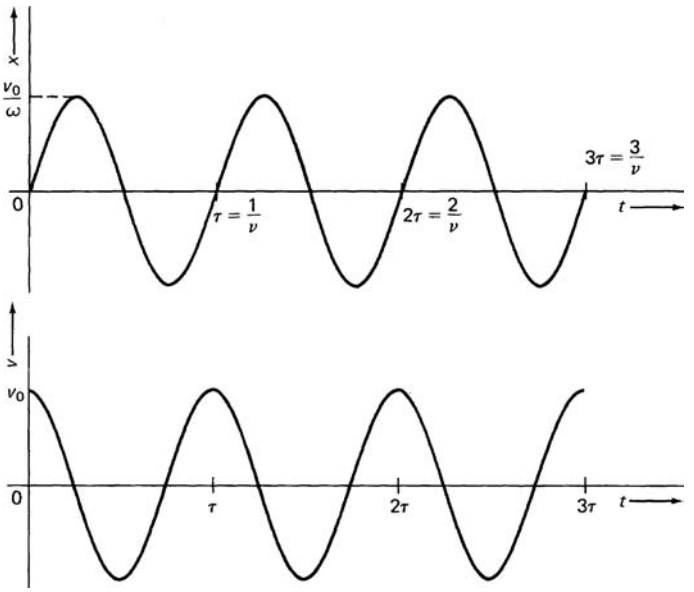

Figure 8.1 ► The position and velocity of a harmonic oscillator as functions of time.

$$2\pi = \omega\tau = \left(\frac{k}{m}\right)^{1/2}\tau. \tag{8.32}$$

Thus,

$$\tau = 2\pi\left(\frac{m}{k}\right)^{1/2}. \tag{8.33}$$

The reciprocal of the period is called the *frequency*, denoted by ν. (This is the Greek letter *nu*. Try not to confuse it with the letter "*vee*").

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{\omega}{2\pi} \tag{8.34}$$

The frequency gives the number of oscillations per second. The quantity ω is called the *circular frequency*. It gives the rate of change of the argument of the sine or cosine function in radians per second.

EXERCISE 8.3 ► The vibration of a diatomic molecule resembles that of a harmonic oscillator. Since both nuclei move, the mass must be replaced by the reduced mass,

$$\mu = \frac{m_1 m_2}{m_1 + m_2},$$

where m_1 is the mass of one nucleus and m_2 the mass of the other nucleus.[a] Calculate the frequency of vibration of a hydrogen chloride molecule. The force constant k is equal to $481\,\mathrm{N\,m^{-1}} = 481\,\mathrm{J\,m^2}$. Be sure to use the mass of the nuclei in kilograms, not the mass of a mole of atoms. ◄

The *kinetic energy* of the harmonic oscillator is

$$\mathcal{K} = \frac{1}{2}mv_z^2. \tag{8.35}$$

[a] See, for example, Robert G. Mortimer, *Physical Chemistry*, 2nd ed., Academic Press, 2000, p. 1030.

In order for the force to be the negative derivative of the potential energy as in Eq. (7.63), the *potential energy* of the harmonic oscillator must be

$$\mathcal{V}(z) = \frac{1}{2}kz^2. \tag{8.36}$$

The total energy is the sum of the kinetic energy and the potential energy

$$\begin{aligned} E &= \mathcal{K} + \mathcal{V} = \frac{1}{2}mv_0^2\cos^2(\omega t) + \frac{1}{2}k\left(\frac{v_0}{\omega}\right)^2\sin^2(\omega t) \\ &= \frac{1}{2}mv_0^2, \end{aligned} \tag{8.37}$$

where we have used the identity of Eq. (7) of Appendix B. As a harmonic oscillator moves, the total energy remains constant. As the kinetic energy rises and falls, the potential energy changes so that the total energy remains constant. When the energy is constant we say that the energy is *conserved*, and that the system is *conservative*. There is an important theorem of classical mechanics: *If the forces on the particles of a system can be obtained from a potential energy function, the system will be conservative.*

The Damped Harmonic Oscillator—A Nonconservative System

We now discuss a *damped harmonic oscillator*, which is a harmonic oscillator that is subject to an additional force that is proportional to the velocity, such as a frictional force due to fairly slow motion of an object through a fluid,

$$\mathbf{F}_f = -\zeta\mathbf{v} = -\zeta\frac{d\mathbf{r}}{dt}, \tag{8.38}$$

where ζ is called the *friction constant*. Since this force cannot be derived from a potential energy, the system is not conservative and its energy will change with time.

The equation of motion is, for motion in the z direction

$$F_z = -\zeta\frac{dz}{dt} - kz = m\left(\frac{d^2z}{dt^2}\right). \tag{8.39}$$

This equation is a linear homogeneous equation with constant coefficients, so a trial solution of the form of Eq. (8.14) will work. The characteristic equation is

$$\lambda^2 + \frac{\zeta\lambda}{m} + \frac{k}{m} = 0. \tag{8.40}$$

From the quadratic equation, the solutions of this equation are

$$\lambda_1 = -\frac{\zeta}{2m} + \frac{\sqrt{(\zeta/m)^2 - 4k/m}}{2} \tag{8.41a}$$

$$\lambda_2 = -\frac{\zeta}{2m} - \frac{\sqrt{(\zeta/m)^2 - 4k/m}}{2} \tag{8.41b}$$

and the general solution to the differential equation is

$$z(t) = c_1e^{\lambda_1 t} + c_2e^{\lambda_2 t}. \tag{8.42}$$

EXERCISE 8.4 ► Show that Eq. (8.40) is the correct characteristic equation, that Eq. (8.41a) gives the correct solutions to the characteristic equation, and that the function of Eq. (8.42) does satisfy Eq. (8.39). ◄

Greater than Critical Damping

There are three cases. In the first case, the quantity inside the square root in Eq. (8.41a) is positive, so that λ_1 and λ_2 are both real. This corresponds to a relatively large value of the friction constant ζ, and the case is called *greater than critical damping*. In this case, the mass at the end of the spring does not oscillate, but returns smoothly to its equilibrium position of $z = 0$ if disturbed from this position.

Figure 8.2 shows the position of a greater than critically damped oscillator as a function of time for a particular set of initial conditions.

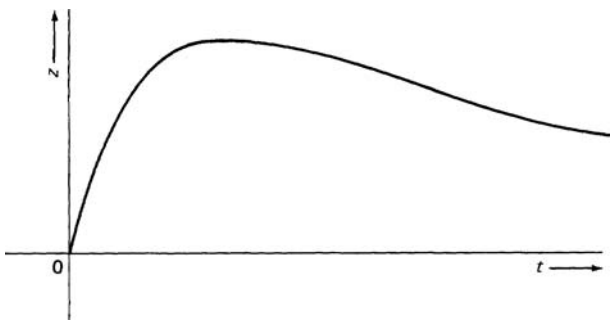

Figure 8.2 ► The position of a greater than critically damped harmonic oscillator as a function of time.

EXERCISE 8.5 ► From the fact that ζ, k, and m are all positive, show that λ_1 and λ_2 are both negative in the case of greater than critical damping, and from this fact, show that

$$\lim_{t\to\infty} z(t) = 0. \tag{8.43}$$

◄

Less than Critical Damping

The next case is that of small values of ζ, or *less than critical damping*. If

$$\left(\frac{\zeta}{m}\right)^2 < \frac{4k}{m},$$

the quantity inside the square root in Eq. (8.41a) is negative, and λ_1 and λ_2 are complex quantities,

$$\lambda_1 = -\frac{\zeta}{2m} + i\omega \tag{8.44}$$

$$\lambda_2 = -\frac{\zeta}{2m} - i\omega, \tag{8.45}$$

where

$$\omega = \sqrt{\frac{k}{m} - \left(\frac{\zeta}{2m}\right)^2}. \tag{8.46}$$

The solution thus becomes

$$z(t) = \left(c_1 e^{i\omega t} + c_2 e^{i\omega t}\right) e^{-\zeta t/2m} \tag{8.47}$$

which can also be written in a form that is similar to Eq. (8.25),

$$z(t) = [b_1 \cos(\omega t) + b_2 \sin(\omega t)]\, e^{-\zeta t/2m}. \tag{8.48}$$

This shows $z(t)$ to be an oscillatory function times an exponentially decreasing function, giving the "ringing" behavior shown in Fig. 8.3.

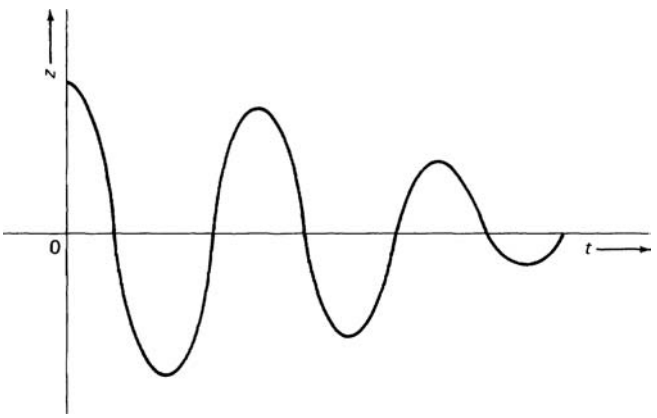

Figure 8.3 ► The position of a less than critically damped oscillator as a function of time for the initial conditions $z(0) = z_0$, $v_z(0) = 0$.

EXERCISE 8.6 ► If the position of the oscillator at time 0 is a particular value $z(0) = z_0$ and if the velocity at time zero is a particular value $v_z(0) = v_0$, express the constants b_1 and b_2 in terms of these values. ◄

Critical Damping

The final case is that of *critical damping*, in which the quantity inside the square root in Eq. (8.41) exactly vanishes. This case is not likely to happen by chance, but it is possible to construct an oscillating object such as a galvanometer mirror or a two-pan balance beam that is critically damped by a magnetic field. The condition for critical damping is

$$\left(\frac{\zeta}{2m}\right)^2 = \frac{k}{m}. \tag{8.49}$$

An interesting thing happens to the solution of Eq. (8.42) in the case of critical damping. The values of λ are equal to each other,

$$\lambda_1 = \lambda_2 = -\frac{\zeta}{2m} \tag{8.50}$$

so that Eq. (8.42) becomes

$$z(t) = (c_1 + c_2)\, e^{\lambda t} = ce^{\lambda t}, \tag{8.51}$$

where c is the sum of the two constant c_1 and c_2 and where we drop the subscript on λ. This is not a general solution, since a general solution for a second order linear equation must contain two arbitrary constants, and a sum of two constants does not constitute two separate constants. This is called *linear dependence*. With two functions, linear dependence means that the functions are proportional to each other, so that they are not distinct solutions. If we have several solutions, they are linearly dependent if one or more of the solutions equals a linear combination of the others.

Since we do not have a general solution, there must be another family of solutions that is not included in the solution of Eq. (8.51). One way to find it is by attempting additional trial functions until we find one that works. The one that works is

$$z(t) = te^{\lambda t}. \tag{8.52}$$

EXERCISE 8.7 ► Substitute the trial solution of Eq. (8.52) into Eq. (8.39), using the condition of Eq. (8.49) to restrict the discussion to critical damping, and show that the equation is satisfied. ◄

Our general solution is now

$$z(t) = (c_1 + c_2 t)\, e^{\lambda t}, \tag{8.53}$$

where we drop the subscript on λ. The velocity is given by

$$v_z(t) = \frac{dz}{dt} = c_1\lambda e^{\lambda t} + c_2 e^{\lambda t} + c_2 t\lambda e^{\lambda t}$$

For any particular set of initial conditions, we can find the appropriate values of c_1 and c_2. The behavior of a critically damped oscillator is much the same as that of Fig. 8.2.

EXAMPLE 8.4 Consider a critically damped oscillator with $\lambda = -1.00\,\mathrm{s}^{-1}$. Assume that its initial position is $z(0) = 0.00\,\mathrm{m}$ and that its initial velocity is $1.00\,\mathrm{m\,s}^{-1}$. Find its position and velocity at $t = 1.00\,\mathrm{s}$.

SOLUTION ► In order for $z\,(0)$ to equal $0.00\,\mathrm{m}$, we must require that $c_1 = 0.00\,\mathrm{m}$. The velocity is given by

$$v_z(t) = c_2 e^{\lambda t} + c_2 t\lambda e^{\lambda t}$$

The velocity at $t = 0$ is

$$v_z(0) = c_2$$

so that

$$c_2 = 1.00\,\mathrm{m\,s}^{-1}$$

The position at $t = 1.00\,\mathrm{s}$ is

$$z(1.00\,\mathrm{s}) = c_2 t e^{\lambda t} = (1.00\,\mathrm{m\,s}^{-1})(1.00\,\mathrm{s})e^{-1.00} = 0.368\,\mathrm{m}$$

◄

EXERCISE 8.8 ▶ (a) Construct an accurate graph of the position of the critically damped oscillator of the previous example.
(b) Locate the time at which z attains its maximum value and find the maximum value. ◀

EXERCISE 8.9 ▶ Find a formula for the position of the critically damped oscillator of the previous example if the initial position is $z(0) = 0.500\,\text{m}$ and $v_z(0) = 0.00\,\text{s}$. Find the velocity and the position of the oscillator at $t = 1.00\,\text{s}$. ◀

The Forced Harmonic Oscillator: Inhomogeneous Linear Differential Equations

An *inhomogeneous differential equation* contains a term that is not proportional to the unknown function or to any of its derivatives. An example of a linear inhomogeneous equation is

$$f_3(t)\frac{d^3z}{dt^3} + f_2(t)\frac{d^2z}{dt^2} + f_1(t)\frac{dz}{dt} = g(t), \tag{8.54}$$

where f_3 f_2, f_1, and g are some functions of time but do not depend on z. The term $g(t)$ is the *inhomogeneous term.* If an external force exerted on a harmonic oscillator depends only on the time, the equation of motion is an inhomogeneous differential equation:

$$\frac{d^2z}{dt^2} + \frac{k}{m}z = \frac{F(t)}{m}, \tag{8.55}$$

where $F(t)$ is the external time-dependent force and the term $F(t)/m$ is the inhomogeneous term.

A method for solving such an equation is:

Step 1. Solve the equation obtained by deleting the inhomogeneous term. This homogeneous equation is called the *complementary equation,* and the general solution to this equation is called the *complementary function.*

Step 2. Find a particular solution to the inhomogeneous equation by whatever means may be necessary.

Step 3. Take the sum of the complementary function and this particular solution. This is the general solution to the inhomogeneous equation.

EXERCISE 8.10 ▶ If $z_c(t)$ is a general solution to the complementary equation and $z_p(t)$ is a particular solution to the inhomogeneous equation, show that $z_c + z_p$ is a solution to the inhomogeneous equation of Eq. (8.54). ◀

Variation of Parameters Method

There is a method for finding a particular solution to a linear inhomogeneous equation, known as the *variation of parameters*. If the inhomogeneous term is a power of t, an exponential, a sine, a cosine, or a combination of these functions, this method can be used. One proceeds by taking a suitable trial function that contains parameters (constants whose values need to be determined). This is substituted into the inhomogeneous equation and the values of the parameters are found so that the inhomogeneous equation is satisfied. Table 8.1 gives a list of suitable trial functions for various inhomogeneous terms.

EXAMPLE 8.5 Let us assume that the external force on a forced harmonic oscillator is

$$F(t) = F_0 \sin(\alpha t), \tag{8.56}$$

where $F_0$and α are constants. Find the general solution to the equation of motion.

SOLUTION ► Use of Table 8.1 and determination of the parameters gives the particular solution

$$z_p(t) = \frac{F_0}{m(\omega^2 - \alpha^2)} \sin(\alpha t), \tag{8.57}$$

where ω is the circular frequency in the solution of Eq. (8.25), which is the solution to the complementary equation. The general solution is

$$z(t) = b_1 \cos(\omega t) + b_2 \sin(\omega t) + z_p(t), \tag{8.58}$$

where the constants b_1 and b_2 are to be determined by the initial conditions. Let us assume that $z(0) = 0$, so that

$$z(t) = b_2 \sin(\omega t) + \frac{F_0}{m(\omega^2 - \alpha^2)} \sin(\alpha t). \tag{8.59}$$

◄

EXERCISE 8.11 ► Verify Eq. (8.57) and (8.58). ◄

TABLE 8.1 ► Particular Trial Solutions for the Variation of Parameters Method*

Inhomogeneous Term	Trial Solution	Forbidden Characteristic Root†
1	A	0
t^n	$A_0 + A_1 t + A_2 t^2 + \cdots + A_n t^n$	0
$e^{\alpha t}$	$Ae^{\alpha t}$	α
$t^n e^{\alpha t}$	$e^{\alpha t}(A_0 + A_1 t + A_2 t^2 + \cdots + A_n t^n)$	α
$e^{\alpha t} \sin(\beta t)$	$e^{\alpha t}[A \cos(\beta t) + B \sin(\beta t)]$	$\alpha,\ \beta$
$e^{\alpha t} \cos(\beta t)$	$e^{\alpha t}[A \cos(\beta t) + B \sin(\beta t)]$	$\alpha,\ \beta$

* *Source:* M. Morris and O. E. Brown, *Differential Equations,* 3rd ed., Prentice-Hall, Englewood Cliffs, N.J., 1952.

$A,\ B,\ A_0,\ A_1$, etc., are parameters to be determined. α and β are constants in the differential equation to be solved.

† The trial solution given will not work if the characteristic equation for the complementary differential equation has a root equal to the entry in this column. If such a root occurs with multiplicity k, multiply the trial solution by t^k to obtain a trial solution that will work.

The motion of the forced harmonic oscillator shows some interesting features. The solution in the previous example is a linear combination of the natural motion and a motion proportional to the external force. If the frequencies of these are not very different, a motion such as shown in Fig. 8.4, known as *beating*, can result. There is a periodic variation of the amplitude of vibration with a circular frequency equal to $\omega - \alpha$. You can hear this beating when a piano is being tuned. There are two or three string for each note, and they are tuned separately. Each string can excite a "sympathetic vibration" in the other, which acts as an external force. When the frequencies of two strings are slightly different you can hear a pulsation like that in Fig. 8.4.

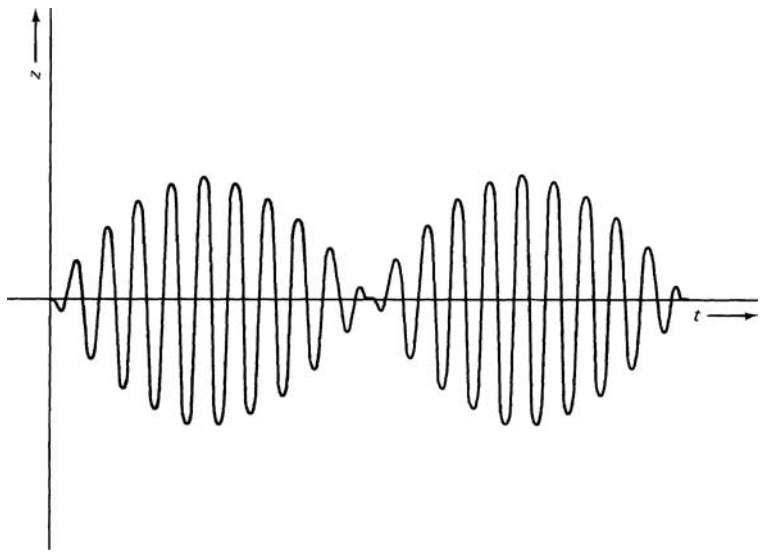

Figure 8.4 ► The position of a forced harmonic oscillator as a function of time for the case $\alpha = 1.1\omega$.

8.3 Differential Equations with Separable Variables

In this section, we discuss equations that can be manipulated algebraically into the form

$$g(y)\frac{dy}{dx} = f(x), \tag{8.60}$$

where $g(y)$ is some integrable function of y and $f(x)$ is some integrable function of x. To solve Eq. (8.60), we multiply both sides of the equation by dx and use Eq. (4.20):

$$\frac{dy}{dx}dx = dy. \tag{8.61}$$

We now have

$$g(y)dy = f(x)dx. \tag{8.62}$$

If we have manipulated the equation into the form of Eq. (8.62), we say that we have *separated the variables*, because we have no x dependence in the left-hand side of the equation and no y dependence in the right-hand side. We can perform

an indefinite integration on both sides of this equation to obtain

$$\int g(y)\,dy = \int f(x)\,dx + C, \tag{8.63}$$

where C is a constant of integration. We can alternatively do a definite integration

$$\int_{y_1}^{y_2} g(y)\,dy = \int_{x_1}^{x_2} f(x)\,dx, \tag{8.64}$$

where

$$\begin{aligned} y_1 &= y(x_1) \\ y_2 &= y(x_2). \end{aligned}$$

EXAMPLE 8.6 In a *first-order chemical reaction* with no back reaction, the concentration of the reactant is governed by

$$-\frac{dc}{dt} = kc, \tag{8.65}$$

where c is the concentration of the single reactant, t is the time, and k is a function of temperature called the *rate constant*. Solve the equation to find c as a function of t.

SOLUTION ► We divide by c and multiply by dt to separate the variables:

$$\frac{1}{c}\frac{dc}{dt}dt = \frac{1}{c}dc = -k dt.$$

We perform an indefinite integration

$$\int \frac{1}{c}dc = \ln(c) = -k\int dt + C = -kt + C, \tag{8.66}$$

where C is a constant of integration. Although each indefinite integration would require a constant of integration, we include only one constant, since the second constant of integration could be moved to the other side of the equation, giving the difference of two constants, which equals a constant.

We take the exponential of each side of Eq. (8.66) to obtain

$$e^{\ln(c)} = c = e^C e^{-kt} = c(0)e^{-kt}. \tag{8.67}$$

In the last step, we recognized that e^C had to equal the concentration at time $t = 0$. A definite integration can be carried out instead of an indefinite integration:

$$\int_{c(0)}^{c(t_1)} \frac{1}{c}dc = \ln\left(\frac{c(t_1)}{c(0)}\right) = -k\int_0^{t_1} dt = -kt_1.$$

This equation is the same as Eq. (8.67) except that the time is now called t_1 instead of t. The limits on the two definite integrations must be done correctly. If the lower limit of the time integration is zero, the lower limit of the concentration integration must be the value of the concentration at zero time. The upper limit is similar. ◄

EXERCISE 8.12 ► In a *second-order chemical reaction* involving one reactant and having no back reaction,

$$-\frac{dc}{dt} = kc^2.$$

Solve this differential equation by separation of variables. Do a definite integration from $t = 0$ to $t = t_1$. ◄

If you are faced with a differential equation and if you think that there is some chance that separation of variables will work, try the method. If it doesn't work you haven't lost very much time since the method is quite rapid.

8.4 Exact Differential Equations

Sometimes you might be faced with an equation that can be manipulated into the *pfaffian form*:

$$M(x, y)dx + N(x, y,)dy = 0. \tag{8.68}$$

Some such differential forms are *exact*, which means that they are differentials of functions. Other differentials are *inexact*, which means that they are not differentials of functions. If the differential is exact, the equation is called an *exact differential equation*.

The test for exactness is based on the *Euler reciprocity relation*, as in Eq. (7.31): If

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y, \tag{8.69}$$

then the differential is exact. If the differential equation is exact, there is a function $f(x, y)$ such that

$$df = M(x, y)dx + N(x, y)dy = 0, \tag{8.70}$$

which implies that

$$f(x, y) = C, \tag{8.71}$$

where C is a constant, because a constant function has a differential that vanishes. This equation can be solved for y in terms of x, providing a solution to the differential equation.

In Chapter 7 we discussed the procedure for finding the function in Eq. (8.71) by using a line integral,

$$f(x_1, y_1) = f(x_0, y_0) + \int_c df, \tag{8.72}$$

where C is a curve beginning at (x_0, y_0) and ending at (x_1, y_1). A convenient curve is the rectangular path from (x_0, y_0) to (x_1, y_0) and then to (x_1, y_1). On the first part of this path, y is constant at y_0, so the dy integral vanishes and y is replaced by y_0 in the dx integral. On the second part of the path, x is constant at x_1, so the dx integral vanishes and x is replaced by x_1 in the dy integral:

$$f(x_1, y_1) = f(x_0, y_0) + \int_{x_0}^{x_1} M(x, y_0)dx + \int_{y_0}^{y_1} N(x_1, y)dy. \tag{8.73}$$

Both integrals are now ordinary integrals, so we have a solution if we can perform the integrals. The solution will contain an arbitrary constant, because different constants can be added to $f(x_1, y_1)$ and $f(x_0, y_0)$ in Eq. (8.73) without changing the equality.

EXAMPLE 8.7 Solve the differential equation

$$2xy\,dx + x^2\,dy = 0.$$

SOLUTION ► The equation is exact, because

$$\frac{\partial}{\partial y}(2xy) = 2x \quad \text{and} \quad \frac{\partial}{\partial x}(x^2) = 2x.$$

We do a line integral from (x_0, y_0) to (x_1, y_0) and then to (x_0, y_1), letting $f(x, y)$ be the function whose differential must vanish:

$$\begin{aligned} 0 &= f(x_1, y_1) - f(x_0, y_0) = \int_{x_0}^{x_1} 2xy_0 dx + \int_{y_0}^{y_1} x_1^2\, dy \\ &= y_0 x_1^2 - y_0 x_0^2 + x_1^2 y_1 - x_1^2 y_0 \\ &= x_1^2 y_1 - x_0^2 y_0. \end{aligned}$$

◄

We regard x_0 and y_0 as constants so that $x_0^2 y_0 = C$, where C is a constant. We drop the subscripts on x_1 and y_1, and write

$$f(x, y) = x^2 y = C.$$

Our general solution is $y = C/x^2$. Some condition would have to be specified to obtain the value of the constant C.

EXERCISE 8.13 ► Show that the solution in the previous example satisfies the equation. ◄

EXERCISE 8.14 ► Solve the equation $(4x + y)\, dx + x\, dy = 0$. ◄

8.5 Solution of Inexact Differential Equations by the Use of Integrating Factors

If we have an *inexact pfaffian differential equation*

$$M(x, y)dx + N(x, y)dy = 0 \tag{8.74}$$

we cannot use the method of the previous section. However, some inexact differentials yield an exact differential when multiplied by a function known as an *integrating factor*. If the function $g(x, y)$ is an integrating factor for the differential in Eq. (8.74),

$$g(x, y)M(x, y)dx + g(x, y)N(x, y)dy = 0 \tag{8.75}$$

is an exact differential equation that can be solved by the method of the previous section. A solution for Eq. (8.75) will also be a solution for Eq. (8.74).

EXAMPLE 8.8 Solve the differential equation

$$\frac{dy}{dx} = \frac{y}{x}.$$

SOLUTION ► We convert the equation to the pfaffian form, $y\,dx - x\,dy = 0$. Test for exactness:

$$\left(\frac{\partial_y}{\partial_y}\right)_x = 1$$
$$\left[\frac{\partial(-x)}{\partial x}\right]_y = -1.$$

The equation is not exact. We show that $1/x^2$ is an integrating factor. Multiplication by this factor gives

$$\left(\frac{y}{x^2}\right)dx - \left(\frac{1}{x}\right)dy = 0. \tag{8.76}$$

This is exact:

$$\left[\frac{\partial(y/x^2)}{\partial y}\right]_x = \frac{1}{x^2}$$
$$\left[\frac{\partial(-1/x)}{\partial x}\right]_y = \frac{1}{x^2}.$$

We can solve Eq. (8.76) by the method of Section 8.4:

$$0 = \int_{x_0}^{x_1}\left(\frac{y_0}{x^2}\right)dx - \int_{y_0}^{y_1}\left(\frac{1}{x_1}\right)dy$$
$$= -y_0\left(\frac{1}{x_1} - \frac{1}{x_0}\right) - \frac{1}{x_1}(y_1 - y_0) = \frac{y_0}{x_0} - \frac{y_1}{x_1}.$$

We regard x_0 and y_0 as constants, so that

$$\frac{y}{x} = \frac{y_0}{x_0} = C,$$

where C is a constant. We solve for y in terms of x to obtain the solution

$$y = Cx.$$

This is a general solution, since the original equation was first order and the solution contains one arbitrary constant. ◄

If an inexact differential has one integrating factor, it has an infinite number of integrating factors. Therefore, there can be other integrating factors for a differential such as the one in the preceding example. Unfortunately, there is no general procedure for finding an integrating factor except by trial and error.

EXERCISE 8.15 ► Show that $1/y^2$ and $1/(x^2 + y^2)$ are integrating factors for the equation in the previous example and show that they lead to the same solution. ◄

8.6 Partial Differential Equations: Waves in a String

Differential equations that contain partial derivatives of several independent variables are called *partial differential equations*. The differential equations that we have been discussing contain ordinary derivatives and are called *ordinary differential equations*. Ordinary differential equations occur that contain more than one dependent variable, but you must have one equation for each dependent variable and must solve them simultaneously. We will not discuss simultaneous differential equations, but you can read about such equations in some of the books listed at the end of the book, and Mathematica is capable of solving simultaneous differential equations.

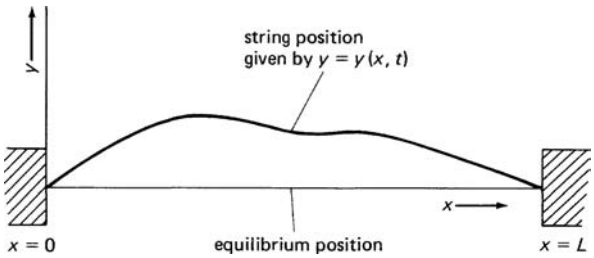

Figure 8.5 ► A flexible string.

We discuss only a rather simple method of solving a partial differential equation, devoting most of this section to an example, the classical equation of motion of a *flexible string* of length L. There are important similarities between this equation and the Schrödinger equation[3] of quantum mechanics. The flexible string that we discuss is a model system that is simpler than a real string. It is defined by the following: (1) It is completely flexible, so that no force is required to bend the string. (2) Its motion is restricted to small vibrations, so that the string is not appreciably stretched. (3) Both ends of the string are fixed in position. Figure 8.5 shows the string. We choose one end of the string as our origin of coordinates and use the equilibrium (straight) position of the string as our x axis. The displacement of the string from its equilibrium position in the y direction is denoted by y and the displacement in the z direction is denoted by z. Since the string moves, y and z are functions of time as well as of x:

$$y = y(x, t) \tag{8.77}$$

$$z = z(x, t). \tag{8.78}$$

The equation of motion of the string is derived by writing Newton's second law for a small segment of the string and taking a mathematical limit as the length of the segment becomes infinitesimal. We do not present the derivation.[4] The result is a partial differential equation

$$\left(\frac{\partial^2 y}{\partial t^2}\right) = \frac{T}{\rho}\left(\frac{\partial^2 y}{\partial x^2}\right) = c^2\left(\frac{\partial^2 y}{\partial x^2}\right) \tag{8.79}$$

and a similar equation for z. In this equation T is the magnitude of the tension force on the string and ρ is the mass of the string per unit length. The quantity c turns out to be the speed of propagation of a wave along the string.

$$c = \sqrt{\frac{T}{\rho}}$$

Since the two equations are independent of each other, we can solve for y and z separately, and the two general solutions will be identical except for the symbol used for the dependent variable.

[3]Named for its discoverer, Erwin Schrödinger, 1887–1961, joint 1933 Nobel Prize winner in physics with P. A. M. Dirac.

[4]Robert G. Mortimer, *Physical Chemistry*, 2nd ed., pp. 1026–1027, Academic Press, San Diego, CA, 2000.

Solution by Separation of Variables

We do not seek a general solution for Eq. (8.79). but seek only a family of solutions that can be written as a product of factors, each of which depends on only one variable:

$$y(x,t) = \psi(x)\theta(t). \tag{8.80}$$

This is called a *solution with the variables separated*. We regard it as a *trial solution* and substitute it into the differential equation to see if it works. This method of separation of variables is slightly different from the previous version, since we are now separating two independent variables instead of one independent variable and one dependent variable.

Since ψ does not depend on t and θ does not depend on x, the result of substituting the trial solution into the Eq. (8.79) is

$$\psi(x)\left(\frac{d^2\theta}{dt^2}\right) = c^2\theta(t)\left(\frac{d^2\psi}{dx^2}\right). \tag{8.81}$$

We write ordinary derivatives since we now have functions of only one variable. We separate the variables by manipulating Eq. (8.81) into a form in which one term contains no x dependence and the other term contains no t dependence, just as we manipulated Eq. (8.59) into a form with only one variable in each term. We divide both sides of Eq. (8.81) by the product $\psi(x)\theta(t)$. We also divide by c^2, but this is not essential.

$$\frac{1}{c^2\theta(t)}\frac{d^2\theta}{dt^2}. = \frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} \tag{8.82}$$

The variables are now separated, since each term contains only one independent variable.

We now use the fact that x and t are both independent variables. If we temporarily keep t fixed at some value, we can still allow x to vary. The function of x on the right-hand side of Eq. (8.82) must be a constant function of x, because it equals a quantity that we can keep fixed while allowing x to range:

$$\frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} = -\kappa^2 = \text{constant}. \tag{8.83}$$

For the same reason, the left-hand side is a constant function of t,

$$\frac{1}{c^2\theta(t)}\frac{d^2\theta}{dt^2} = -\kappa^2. \tag{8.84}$$

We denote the constant by the symbol $-\kappa^2$ because this will make κ real. We now multiply Eq. (8.83) by $\psi(x)$ and multiply Eq. (8.84) by $c^2\theta(t)$. We obtain

$$\frac{d^2\psi}{dx^2} + \kappa^2\psi = 0 \tag{8.85}$$

and

$$\frac{d^2\theta}{dt^2} + \kappa^2 c^2\theta = 0. \tag{8.86}$$

The separation of variables is complete, and we have two ordinary differential equations. Except for the symbols used, both of these equations are the same as

Eq. (8.12). We transcribe the solution to that equation with appropriate changes in symbols:

$$\psi(x) = a_1 \cos(\kappa x) + a_2 \sin(\kappa x) \tag{8.87}$$

$$\theta(t) = b_1 \cos(\kappa c t) + b_2 \sin(\kappa c t). \tag{8.88}$$

These are general solutions to the ordinary differential equations of Eq. (8.85) and (8.86), but we do not necessarily have a general solution to our partial differential equation, because there can be solutions that are not of the form of Eq. (8.80).

We are now ready to consider a specific case. We consider a string of length L with the ends fixed, as in Fig. 8.5. We have the condition that $y = 0$ at $x = 0$ and at $x = L$. These conditions are called *boundary conditions*, and literally arise from a condition at the boundaries of a region. If y must vanish at $x = 0$ and at $x = L$, then ψ must vanish at these points, since the factor θ does not necessarily vanish:

$$\psi(0) = 0 \tag{8.89}$$

and

$$\psi(L) = 0. \tag{8.90}$$

Equation (8.89) requires that

$$a_1 = 0 \tag{8.91}$$

since $\cos(0) = 1$. Equation (8.90) requires that the argument of the sine function in Eq. (8.87) be equal to some integer times π for $x = L$, because

$$\sin(n\pi) = 0 \quad (n = 0, 1, 2, ...). \tag{8.92}$$

Therefore,

$$\kappa = \frac{n\pi}{L} \quad (n = 1, 2, 3, ...). \tag{8.93}$$

We are not interested in the case that $n = 0$, because this corresponds to a stationary string at its equilibrium position.

The coordinate factor ψ in our solution is now

$$\psi(x) = a_2 \sin\left(\frac{n\pi x}{L}\right). \tag{8.94}$$

We return to the time-dependent factor θ. We apply *initial conditions* that make our solution apply to a particular case. Let us consider the case that at $t = 0$, the string is passing through its equilibrium position, which corresponds to $y = 0$ for all x. If so, then $b_1 = 0$ since $\cos(0) = 1$.We now have

$$\theta = b_2 \sin\left(\frac{n\pi ct}{L}\right)$$

and

$$y(x, t) = A \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi ct}{L}\right), \tag{8.95}$$

where we write $A = a_2 b_2$ since the product of two constants is really just one constant. The maximum *amplitude* is A, and another initial condition would be required to specify its value.

We have a set of solutions, one for each value of the integer n. Figure 8.6 shows the function $\psi(x)$ for several values of n. Each curve represents the shape of the

string at an instant when $\theta = 1$. At other times, the string is vibrating between such a position and a position given by $-\psi(x)$. There are fixed points at which the string is stationary. These points are called *nodes*, and the number of nodes other than the two nodes at the ends of the string is $n - 1$. A wave with stationary nodes is called a *standing wave*.

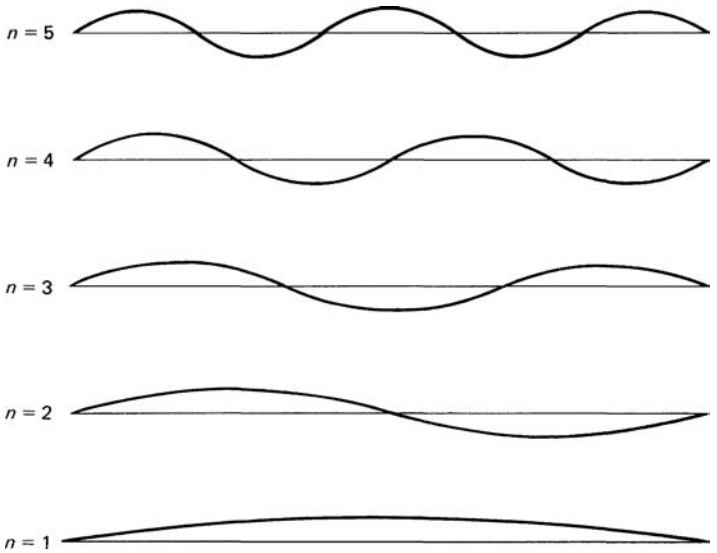

Figure 8.6 ► Standing waves in a flexible string.

If we let λ be the *wavelength*, or the distance for the sine function in ψ to go through a complete period, then

$$n\lambda = 2L. \tag{8.96}$$

The *period* of oscillation is the time required for the sine function in the factor θ to go through a complete oscillation and return the string to its original position and velocity, which requires the argument of the sine function to range through 2π. If τ is the period,

$$\frac{n\pi c\tau}{L} = 2\pi; \quad \tau = \frac{2L}{nc}. \tag{8.97}$$

The *frequency* ν is the reciprocal of the period:

$$\nu = \frac{nc}{2L} = \left(\frac{n}{2L}\right)\left(\frac{T}{\rho}\right)^{1/2}. \tag{8.98}$$

In musical acoustics, the oscillation corresponding to $n = 1$ is called the *fundamental*, that for $n = 2$ is the *first overtone*, etc. The fundamental is also called the *first harmonic*, the first overtone is called the *second harmonic*, and so on.

EXERCISE 8.16 ► A certain violin string has a mass per unit length of $20.00\,\text{mg}\,\text{cm}^{-1}$ and a length of 55 cm. Find the tension force necessary to make it produce a fundamental tone of A above middle C (440 oscillations per second = 440 Hz). ◄

When a string in a musical instrument is struck or bowed, it will usually not vibrate according to a single harmonic. The following Fourier series is a linear

combination that satisfies Eq. (8.79) and can represent any possible motion of the string:

$$y(x,t) = \sum_{n=1}^{\infty} \sin\left(\frac{n\pi x}{L}\right)\left[a_n \cos\left(\frac{n\pi ct}{L}\right) + b_n \sin\left(\frac{n\pi ct}{L}\right)\right]. \tag{8.99}$$

The fact that a linear combination of solutions can be a solution to the equation is an example of the *principle of superposition*. We can regard the linear combination as a physical representation of *constructive* and *destructive interference* of the different harmonics. The strengths of the different harmonics are represented by the values of the coefficients a_n and b_n. Different musical instruments have different relative strengths of different harmonics.

EXERCISE 8.17 ▶ Show that the function in Eq. (8.99) satisfies Eq. (8.79). ◀

EXERCISE 8.18 ▶ For a string of finite length with fixed ends, only standing waves can occur. For an infinitely long string, traveling waves can also occur. The following is a *traveling wave*:

$$y(x,t) = A \sin[k(x - ct)]. \tag{8.100}$$

Show that the function of Eq. (8.100) satisfies Eq. (8.79). ◀

We can show that the function of Eq. (8.100) is a traveling wave by showing that a node in the wave moves along the string. When $t = 0$, there is a node at $x = 0$. At a later time, this node is located at a value of x such that $k(x - ct)$ is still equal to zero. At a time t, $x = ct$ at the node, so that the speed of the wave is equal to c. The traveling wave solution in Eq. (8.100) is not a solution in which the variables are separated. However, using Eq. (14) of Appendix B, we can show that

$$A \sin[k\,(x - ct)] = A\,[\sin(kx)\cos(kct) - \cos(kx)\sin(kct)]. \tag{8.101}$$

This equation exhibits the fact that a traveling wave is equivalent to two standing waves interfering with each other.

EXERCISE 8.19 ▶ Find the speed of propagation of a traveling wave in an infinite string with the same mass per unit length and the same tension force as the violin string in Exercise 8.16. ◀

8.7 Solution of Differential Equations with Laplace Transforms

Some differential equations can be solved by taking the Laplace transform of the equation, applying some of the theorems presented in Section 6.5 to obtain an expression for the Laplace transform of the unknown function, and then finding

the inverse transform. We illustrate this procedure with the differential equation for the damped harmonic oscillator,[5] Eq. (8.39), which can be rewritten

$$\left(\frac{d^2z}{dt^2}\right) + \frac{\zeta}{m}\frac{dz}{dt} + \frac{k}{m}z = z'' + \frac{\zeta}{m}z' + \frac{k}{m}z = 0. \tag{8.102}$$

We introduce the notation z'' for the second derivative d^2z/dt^2 and z' for the first derivative dz/dt. We take the Laplace transform of this equation, applying Eq. (6.72) and the $n = 2$ version of Eq. (6.73), to express the Laplace transforms of the first and second derivatives. We let Z be the Laplace transform of z,

$$s^2Z - sz(0) - z'(0) + \frac{\zeta}{m}(sZ - z(0)) + \frac{k}{m}Z = 0. \tag{8.103}$$

This algebraic equation is solved for Z:

$$Z = \frac{sz(0) + z'(0) + (\zeta/m)z(0)}{s^2 + (\zeta/m)s + k/m}. \tag{8.104}$$

When we find the inverse transform of this function, we will have our answer. We must carry out some algebraic manipulations before we can find the inverse transforms in Table 6.1. In order to match an expression for a transform in Table 6.1, we complete the square in the denominator (that is, we add a term so that we have a perfect square plus another term):

$$Z = \frac{z(0)(s + \zeta/2m) + \zeta/2m + z'(0)}{(s^2 + \zeta/2m)^2 - \zeta^2/4m^2 + k/m}. \tag{8.105}$$

We have also expressed the numerator in terms of the quantity that is squared in the denominator. We now make the substitutions,

$$a = \frac{\zeta}{2m} \quad \text{and} \quad \omega^2 = \frac{k}{m} - \frac{\zeta^2}{4m^2}$$

so that Eq. (8.105) can be written

$$Z = \frac{z(0)(s + a)}{(s^2 + a)^2 + \omega^2} + \frac{z(0)a + z'(0)}{(s^2 + a)^2 + \omega^2}. \tag{8.106}$$

We assume the case of less than critical damping, so that ω^2 is positive.

From Table 6.1, we have the inverse transforms,

$$\mathcal{L}^{-1}\left\{\frac{s}{s^2 + \omega^2}\right\} = \cos(\omega t)$$

$$\mathcal{L}^{-1}\left\{\frac{s}{s^2 + \omega^2}\right\} = \sin(\omega t)$$

and from the theorem of Eq. (6.71)

$$\mathcal{L}^{-1}\left\{e^{-at}f(t)\right\} = F(s + a) \tag{8.107}$$

so that

$$z(t) = \left[z(0)\cos(\omega t) + \frac{z(0)a + z'(0)}{\omega}\sin(\omega t)\right]e^{-at}. \tag{8.108}$$

EXERCISE 8.20 ► Substitute the function of Eq. (8.108) into Eq. (8.102) to show that it satisfies the equation. ◄

[5] Erwin Kreyszig, *Advanced Engineering Mathematics*, 8th ed., Wiley, New York, 1999.

EXERCISE 8.21 ► Obtain the solution of Eq. (8.102) in the case of critical damping, using Laplace transforms. ◄

Our discussion of the Laplace transform method for solving differential equations suffices only to introduce the method. The book by Kreyszig in the list at the end of the book is recommended for further study.

8.8 Numerical Solutions of Differential Equations

Many differential equations occur for which no solution can be obtained with pencil and paper. A lot of these occur in the study of chemical reaction rates. With the use of programmable computers, it is now possible to obtain numerical approximations to the solutions of these equations to any desired degree of accuracy.

Euler's Method

This is a method that is extremely simple to understand and implement. However, it is not very accurate and is not used in actual applications. Consider a differential equation for a variable x as a function of time that can be schematically represented by

$$\frac{dx}{dt} = f(x, t) \tag{8.109}$$

with the initial condition that $x(0) = x_0$, a known value. A *formal solution* can be written

$$x(t') = x_0 + \int_0^{t'} f(x, t)\, dt. \tag{8.110}$$

Like any other formal solution, this cannot be used in practice, since the variable x in the integrand function depends on t in some way that we don't yet know.

Euler's method assumes that if t is small enough, the integrand function in Eq. (8.110) can be replaced by its value at the beginning of the integration. We replace t' by the symbol Δt and write

$$x(\Delta t) \approx x_0 + \int_0^{\Delta t} f(x_0, 0)\, dt = x_0 + \Delta t\ f(x_0, 0). \tag{8.111}$$

A small value of Δt is chosen, and this process is repeated until the desired value of t' is reached. Let x_i be the value of x obtained after carrying out the process i times, and let t_i equal $i\,\Delta t$, the value of t after carrying out the process i times. We write

$$x_{i+1} \approx x_i + \Delta t f(x_i, t_i). \tag{8.112}$$

Euler's method is analogous to approximating an integral by the area under a bar graph, except that the height of each bar is obtained by starting with the approximate height of the previous bar and using the known slope of the tangent line.

EXERCISE 8.22 ► The differential equation for a first-order chemical reaction without back reaction is

$$\frac{dc}{dt} = -kc,$$

where c is the concentration of the single reactant and k is the rate constant.

(a) Set up an Excel spreadsheet to carry out Euler's method for this differential equation.[a]
(b) Carry out the calculation for the initial concentration 1.000 mol l^{-1}, $k = 1.000\,\text{s}^{-1}$ for a time of 2.000 s and for $\Delta t = 0.100$ s.
(c) Compare your result with the correct answer. ◄

[a] If you know how to use Visual Basic for Applications, you can write a Macro and use it in an Excel spreadsheet to carry out the calculation of this exercise.

The Runge–Kutta Method

Since Euler's method is not accurate except for very small values of Δt, more sophisticated methods have been devised. One such widely used method is the *Runge–Kutta method*, which is somewhat analogous to using Simpson's method for a numerical integration, as discussed in Chapter 5.[6]

In the Runge–Kutta method, Eq. (8.112) is replaced by

$$x_{i+1} \approx x_i + \frac{1}{6}(F_1 + 2F_2 + 2F_3 + F_4), \tag{8.113}$$

where

$$F_1 = \Delta t f(x_i, t_i) \tag{8.114}$$

$$F_2 = \Delta t f\left(x_i + \frac{1}{2}F_1, t_i + \frac{\Delta t}{2}\right) \tag{8.115}$$

$$F_3 = \Delta t f\left(x_i + \frac{1}{2}F_2, t_i + \frac{\Delta t}{2}\right) \tag{8.116}$$

$$F_4 = \Delta t f\left(x_i + F_3, t_i + \Delta t\right). \tag{8.117}$$

We do not present the derivation of this method, which is discussed in the book by Burden and Faires listed at the end of the book.

There are also other numerical methods for solving differential equations, which we do not discuss. The numerical methods can be extended to sets of simultaneous differential equations such as occur in the analysis of chemical reaction mechanisms. Many of these sets of equations have a property called *stiffness* that makes them difficult to treat numerically. Techniques have been devised to handle this problem, which is beyond the scope of this book.[7]

[6] See the book by Burden, Faires, and Reynolds and the book by Hornbeck listed at the end of the chapter.
[7] C. J. Aro, *Comput. Phys. Comm.* **97**, 304 (1996).

Solution of Differential Equations with Mathematica

Mathematica can solve differential equations both symbolically and numerically.

Symbolic Solution

The statement DSolve is used to carry out a symbolic solution of a differential equation. We illustrate this with an example.

EXAMPLE 8.9 Use Mathematica to solve the differential equation

$$\frac{dy}{dx} = ay(x)$$

SOLUTION ► We enter the Mathematica statement

```
DSolve[y'[x] == a y[x], y[x], x]
```

and press the "Enter" key. Notice how the statement is written inside the brackets. First comes the equation, with the first derivative denoted by y'. The double equal sign must be used to let Mathematica know that an equation is to be solved. We have used a blank space between the a and the y[x] to indicate multiplication. After a comma comes the specification of the dependent variable, y[x]. Note the use of brackets, not parentheses. The independent variable must be included inside the brackets. After another comma comes the statement of the independent variable. Mathematica returns the output

```
Out1 = {{y[x] → e^(a x) C[1]}}
```

Note the space between the a and the x and the space between the exponential and the constant C[1] in the output. The constant C[1] is to be determined by initial conditions. An initial condition can be included in the original input statement. For example, if $y(0) = 2$, we would enter

```
DSolve[{y'[x] == a y[x], y[0] == 2}, y[x], x]
```

and press the "Enter" key or a "Shift-return." The output would be

```
Out1 = {{y[x] → 2 e^(a x)}}
```

◄

Numerical Solution

Mathematica carries out numerical solutions of differential equation for which no exact solution can be written. The solution is given in terms of an interpolating function, which is a table of values of the unknown function for different values of the independent variable. The program finds a numerical value of the function for a specific value of the independent variable by interpolation in this table. The statement NDSolve is used to solve the differential equation, as in the next example:

EXAMPLE 8.10 Obtain the numerical solution to the differential equation

$$\frac{dy}{dx} = 2\sin(x) \tag{8.118}$$

for the interval $0 < x < \pi$ with the initial condition $y(0) = 1$.

SOLUTION ► We type the input

```
NDSolve[{y'[x]==2 sin[x], y[0]==1}, y, {x, 0, Pi}]
```

and press the "Enter" key. The output appears

```
Out[1]={{y→InterpolatingFunction[{0,3.141593}, <>]}}
```

To obtain the value of the function at some value of x, say $x = 2$, we type the input

```
y[2] /.%1
```

and press the "Enter" key or a "Shift-return." The /. is the *replacement operator* in Mathematica, and is typed as two characters, a forward slash and a period. The %1 means that the output line number 1 is referred to. If the interpolating function had been in line 3, we would have typed %3. The output result now appears

```
Out[2]={3.83229}
```

To obtain a graph of the solution, we enter

```
Plot[Evaluate[y[x] /. %1], {x, 0, Pi}]
```

and press the "Enter" key or a "Shift-Return". The graph appears as the output. ◄

EXERCISE 8.23 ► Obtain the numerical solution to the differential equation

$$\frac{d^2y}{dx^2} = \sin(x) \tag{8.119}$$

for the interval $0 < x < \pi$ and for the initial condition $x = 1$. ◄

SUMMARY

A differential equation contains one or more derivatives, and its solution is a function that satisfies the equation. Classical equations of motion are differential equations based on Newton's laws of motion that when solved give the positions of particles as a function of time. We have presented the solution to several of these. These differential equations are deterministic. That is, given the equation of motion for a given system and the initial conditions (position and velocity of every particle at some initial time), the positions and velocities are determined for all times.

Many homogeneous and inhomogeneous linear differential equations with constant coefficients can be solved by routine methods, which we discussed. An exact differential equation can also be solved in a routine way. Such an equation consists of an exact differential set equal to zero. Since a line integral of an exact differential (the differential of a function) is equal to the value of the function at the end of the integration minus the value of the function at the beginning of the integration, a line integration to a general ending point provides the formula for the function, solving the equation. Some inexact differential equations can be converted into exact equations by use of an integrating factor, and solution of the exact equation provides a solution to the inexact equation.

Many partial differential equations arising in physical problems can be solved by separation of variables. In this procedure, a trial solution consisting of factors depending on one variable each is introduced, and the resulting equation is manipulated until the variables occur only in separate terms. Setting these terms equal to constants gives one ordinary differential equation for each variable.

Some ordinary differential equations can be solved by using some theorems of Laplace transforms which transform a differential equation into an algebraic equation. If this equation can be solved for the transform of the unknown function, and if the inverse transform can be found, the equation is solved.

If a mathematical method for solving a differential equation cannot be found, numerical methods exist for generating numerical solutions to any desired degree of accuracy. Euler's method and the Runge–Kutta method were presented.

PROBLEMS

1. An object moves through a fluid in the x direction. The only force acting on the object is a frictional force that is proportional to the negative of the velocity:

$$F_x = -\zeta v_x = -\zeta \left(\frac{dx}{dt}\right).$$

Write the equation of motion of the object. Find the general solution to this equation, and obtain the particular solution that applies if $x(0) = 0$ and $v_x(0) = v_0 =$ constant. Draw a graph of the position as a function of time.

2. A particle moves along the z axis. It is acted upon by a constant gravitational force equal to $-\mathbf{k}mg$, where $\mathbf{k}$ is the unit vector in the z direction. It is also acted on by a frictional force given by

$$\mathbf{F}_f = -\mathbf{k}\zeta \left(\frac{dz}{dt}\right),$$

where ζ is a constant called a "friction constant." Find the equation of motion and obtain a general solution. Find z as a function of time if $z(0) = 0$ and $v_x(0) = 0$. Draw a graph of z as a function of time.

3. An object sliding on a solid surface experiences a frictional force that is constant and in the opposite direction to the velocity if the particle is moving, and is zero it is not moving. Find the position of the particle as a function of time if it moves only in the x direction and the initial position is $x(0) = 0$ and the initial velocity is $v_x(0) = v_0 =$ constant. Proceed as though the constant force were present at all times and then cut the solution off at the point at which the velocity vanishes. That is, just say that the particle is fixed after this time.

4. A harmonic oscillator has a mass $m = 0.200\,\text{kg}$ and a force constant $k = 98\,\text{N m}^{-1}$.

a) Find the period and the frequency of oscillation.

b) Find the value of the friction constant ζ necessary to produce critical damping with this oscillator. Find the value of the constant λ_1.

c) Construct a graph of the position of the oscillator as a function of t for the initial conditions $z(0) = 0$, $v_z(0) = 0.100\,\mathrm{m\,s^{-1}}$.

5. A less than critically damped harmonic oscillator has a mass $m = 0.200\,\mathrm{kg}$, a force constant $k = 98\,\mathrm{N\,m^{-1}}$ and a friction constant $\zeta = 4.00\,\mathrm{kg\,s^{-1}}$.

a) Find the frequency of oscillation ω and compare it with the frequency that would occur if there were no damping.

b) Find the time required for the real exponential factor in the solution to drop to one-half of its value at $t = 0$.

6. A forced harmonic oscillator with a circular frequency $\omega = 6.283\,\mathrm{s^{-1}}$ (frequency $\nu = 1.000\,\mathrm{s^{-1}}$) is exposed to an external force $F_0 \sin(\alpha t)$ with circular frequency $\alpha = 7.540\,\mathrm{s^{-1}}$ such that in the solution of Eq. (8.59) becomes

$$z(t) = \sin(\omega t) + 0.100 \sin(\alpha t)\,. \tag{8.120}$$

Using Excel or Mathematica, make a graph of $z(t)$ for a time period of at least 20 s.

7. A forced harmonic oscillator with mass $m = 0.200\,\mathrm{kg}$ and a circular frequency $\omega = 6.283\,\mathrm{s^{-1}}$ (frequency $\nu = 1.000\,\mathrm{s^{-1}}$) is exposed to an external force $F_0 \exp(-\beta t) \sin(\alpha t)$ with $\alpha = 7.540\,\mathrm{s^{-1}}$and $\beta = 0.500\,\mathrm{s^{-1}}$. Find the solution to its equation of motion. Construct a graph of the motion for several values of F_0.

8. A tank contains a solution that is rapidly stirred, so that it remains uniform at all times. A solution of the same solute is flowing into the tank at a fixed rate of flow, and an overflow pipe allows solution from the tank to flow out at the same rate. If the solution flowing in has a fixed concentration that is different from the initial concentration in the tank, write and solve the differential equation that governs the number of moles of solute in the tank. The inlet pipe allows A moles per hour to flow in and the overflow pipe allows Bn moles per hour to flow out, where A and B are constants and n is the number of moles of solute in the tank. Find the values of A and B that correspond to a volume in the tank of 100.0 l, an input of $1.000\,\mathrm{l\,h^{-1}}$ of a solution with $1.000\,\mathrm{mol\,l^{-1}}$, and an output of $1.000\,\mathrm{l\,h^{-1}}$ of the solution in the tank. Find the concentration in the tank after 5.00 h, if the initial concentration is zero.

9. An nth-order chemical reaction with one reactant obeys the differential equation

$$\frac{dc}{dt} = -kc^n,$$

where c is the concentration of the reactant and k is a constant. Solve this differential equation by separation of variables. If the initial concentration is c_0 moles per liter, find an expression for the time required for half of the reactant to react.

10. Find the solution to the differential equation

$$\left(\frac{d^3y}{dx^3}\right) - 2\left(\frac{d^2y}{dx^2}\right) - \left(\frac{dy}{dx}\right) + 2y = -xe^x.$$

11. Test the following equations for exactness, and solve the exact equations:

a) $(x^2 + xy + y^2)dx + \left(4x^2 - 2xy + 3y^2\right) dy = 0$

b) $ye^x dx + e^x dy = 0$

c) $\left[2xy - \cos(x)\right] dx + \left(x^2 - 1\right) dy = 0$

12. Use Mathematica to solve the differential equation symbolically

$$\frac{dy}{dx} + y\cos(x) = e^{-\sin(x)}.$$

13. Use Mathematica to obtain a numerical solution to the differential equation in the previous problem for the range $0 < x < 10$ and for the initial condition $y(0) = 1$. Evaluate the interpolating function for several values of x and make a plot of the interpolating function for the range $0 < x < 10$.

14. Find a particular solution of

$$\frac{d^2y}{dx^2} - 4y = 2e^{3x} + \sin(x).$$

15. Radioactive nuclei decay according to the same differential equation that governs first-order chemical reactions, Eq. (8.65). In living matter, the isotope ^{14}C is continually replaced as it decays, but it decays without replacement beginning with the death of the organism. The half-life of the isotope (the time required for half of an initial sample to decay) is 5730 years. If a sample of charcoal from an archaeological specimen exhibits 0.97 disintegrations of ^{14}C per gram of carbon per minute and wood recently taken from a living tree exhibits 15.3 disintegrations of ^{14}C per gram of carbon per minute, estimate the age of the charcoal.

16. A pendulum of length L oscillates in a vertical plane. Assuming that the mass of the pendulum is all concentrated at the end of the pendulum, show that it obeys the differential equation

$$L\left(\frac{d^2\phi}{dt^2}\right) = -g\sin(\phi),$$

where g is the acceleration due to gravity and ϕ the angle between the pendulum and the vertical. This equation cannot be solved exactly. For small oscillations such that

$$\sin(\phi) \approx \phi$$

find the solution to the equation. What is the period of the motion? What is the frequency? Evaluate these quantities if $L = 1.000\,\text{m}$ and if $L = 10.000\ \text{m}$.

17. Use Mathematica to obtain a numerical solution to the pendulum equation in the previous problem without approximation for the case that $L = 1.000\,\text{m}$ with the initial conditions $\phi\,(0) = 0.350\,\text{rad}$ (about $20\,^\circ$) and $d\phi/dt = 0$. Evaluate the solution for $t = 0.500\,\text{s}$, $1.000\,\text{s}$, and $1.500\,\text{s}$. Make a graph of your solution for $0 < t < 4.00\,\text{s}$. Repeat your solution for $\phi\,(0) = 0.050\,\text{rad}$ (about $2.9\,^\circ$) and $d\phi/dt = 0$. Determine the period and the frequency from your graphs. How do they compare with the solution from the previous problem?

18. Obtain the solution for Eq. (8.55) and (8.56) for the forced harmonic oscillator using Laplace transforms.

19. An object of mass m is subjected to an oscillating force in the x direction given by $a\sin(bt)$ where a and b are constants. Find the solution to the equation of motion of the particle.

20. An object of mass m is subjected to a gradually increasing force given by $a(1 - e^{-bt})$ where a and b are constants. Solve the equation of motion of the particle. Find the particular solution for the case that $x(0) = 0$ and $dx/dt = 0$ at $t = 0$.

9

Operators, Matrices, and Group Theory

Preview

A mathematical operator is a symbol standing for carrying out a mathematical operation or a set of operations. Operators are important in quantum mechanics, since each mechanical variable has a mathematical operator corresponding to it. Operator symbols can be manipulated symbolically in a way similar to the algebra of ordinary variables, but according to a different set of rules. An important difference between ordinary algebra and operator algebra is that multiplication of two operators is not necessarily commutative, so that if $\hat{A}$ and $\hat{B}$ are two operators, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$ can occur.

A matrix is a list of quantities, arranged in rows and columns. We will introduce matrix algebra, which is a branch of algebra that has rules that are different from the algebra of ordinary variables, and which has similarities with operator algebra.

A group is a set of elements with defined properties, including a single operation which is not necessarily commutative. The elements of a group can represent symmetry operators, and group theory can provide useful information about quantum-mechanical wave functions for symmetrical molecules, spectroscopic transitions, and so forth.

Principal Facts and Ideas

1. An operator is a symbol that stands for a mathematical operation. If an operator $\hat{A}$ operates on a function f the result is a new function, g: $\hat{A}f = g$.

2. Operator algebra manipulates operator symbols according to rules that are slightly different from those of ordinary algebra.

3. An eigenvalue equation has the form $\hat{A}f = af$ where f is an eigenfunction and a is an eigenvalue.

4. Symmetry operators move points in space relative to a symmetry element. A symmetry operator which belongs to the nuclear framework of a molecule moves each nucleus to the former position of a nucleus of the same kind.

5. Symmetry operators can operate on functions as well as on points and can have eigenfunctions with eigenvalues equal to 1 or to -1. An electronic wave function of a molecule can be an eigenfunction of the symmetry operators which belong to the nuclear framework of a molecule.

6. Matrices can be manipulated according to the rules of matrix algebra. which are similar to the rules of ordinary algebra. One exception is that matrix multiplication is not necessarily commutative: if **A** and **B** are matrices, $\mathbf{AB} \neq \mathbf{BA}$ can occur.

7. The inverse of a matrix obeys $\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{E}$ where **E** is the identity matrix. The inverse of a given matrix can be obtained by the Gauss–Jordan elimination procedure.

8. A group is a set of elements obeying certain conditions, with a single operation combining two elements to give a third element of the group. This operation is called multiplication and is noncommutative.

9. The symmetry operators belonging to a symmetrical object such as the equilibrium nuclear framework of a molecule form a group.

10. A set of matrices obeying the same multiplication table as a group is a representation of the group.

11. Various theorems of group theory make it useful in studying the symmetry properties of molecules in quantum chemistry.

Objectives

After studying this chapter, you should be able to:

1. perform the elementary operations of operator algebra;

2. identify and use symmetry operators associated with a symmetrical molecule;

3. perform the elementary operations of matrix algebra, including matrix multiplication and finding the inverse of a matrix;

4. identify a group of symmetry operators and construct a multiplication table for the group.

9.1 Operators and Operator Algebra

A *mathematical operator* is a symbol that stands for carrying out a mathematical operation on some function. For example, we can use the symbol d/dx or the symbol $\hat{D}_x$ to stand for the operation of differentiating with respect to x. We will usually assign a symbol to an operator that consists of a letter with a caret (^) over it. When an operator operates on a function, the result will generally be

another function. We will discuss three principal types of operators: multiplication operators, derivative operators, and symmetry operators. *Multiplication operators* are operators that stand for multiplying a function either by a constant or by a specified function. *Derivative operators* stand for differentiating a function one or more times with respect to one or more independent variables. An operator can correspond to carrying out more than one operation, such as multiplication by a function followed by a differentiation or taking the sum of the results of operating with two operators. *Symmetry operators* are defined by the way they move a point in space but can also operate on functions.

EXAMPLE 9.1 Let the operator $\hat{A}$ be given by

$$\hat{A} = x + \frac{d}{dx}. \tag{9.1}$$

Find $\hat{A}f$ if $f = a\sin(bx)$, where a and b are constants.

SOLUTION ►

$$\hat{A}a\sin(bx) = xa\sin(bx) + ab\cos(bx). \tag{9.2}$$

◄

If the result of operating on a function with an operator is a function that is proportional to the original function, the function is called an *eigenfunction* of that operator, and the proportionality constant is called an *eigenvalue*.[1] If

$$\boxed{\hat{A}f = af} \tag{9.3}$$

then f is an eigenfunction of $\hat{A}$ and a is the eigenvalue corresponding to that eigenfunction. An equation like Eq. (9.3) is called an *eigenvalue equation*. The time-independent Schrödinger equation of quantum mechanics is an eigenvalue equation, and other eigenvalue equations are important in quantum mechanics.

EXAMPLE 9.2 Find the eigenfunctions and corresponding eigenvalues for the operator d^2/dx^2.

SOLUTION ► We need to find a function $f(x)$ and a constant a such that

$$\frac{d^2f}{dx^2} = af.$$

This is a differential equation that was solved as in Chapter 8. The general solution is

$$f(x) = A\exp\left(\sqrt{a}x\right) + B\exp\left(-\sqrt{a}x\right),$$

where A and B are constants. Since no boundary conditions were stated, the eigenvalue a can take on any value, as can the constants A and B. ◄

EXERCISE 9.1 ► Find the eigenfunctions of the operator $i\dfrac{d}{dx}$, where $i = \sqrt{-1}$. ◄

[1] The word *eigenvalue* is a partial translation of the German *Eigenwert*, sometimes translated as "characteristic value." The word *eigenfunction* is a partial translation of the German *Eigenfunktion*, sometimes translated as "characteristic function."

Operator Algebra

Although a mathematical operator is a symbol that stands for the carrying out of an operation, we can define an operator algebra in which we manipulate these symbols much as we manipulate variables and numbers in ordinary algebra. We define the *sum of two operators* by

$$\left(\hat{A} + \hat{B}\right) f = \hat{A} f + \hat{B} f, \tag{9.4}$$

where $\hat{A}$ and $\hat{B}$ are two operators and where f is some function on which $\hat{A}$ and $\hat{B}$ can operate.

The *product of two operators* is defined as the successive operation of the operators, with the one on the right operating first. If

$$\hat{C} = \hat{A}\hat{B} \tag{9.5}$$

then

$$\hat{C} f = \hat{A}\left(\hat{B} f\right). \tag{9.6}$$

The result of $\hat{B}$ operating on f is in turn operated on by $\hat{A}$ and the result is said to equal the result of operating on f with the product $\hat{A}\hat{B}$. It is important that an operator operates on everything to its right in the same term and that the rightmost operator in an operator product operates first. Equation (9.5) is an *operator equation*. The two sides of the equation are equal in the sense that if each is applied to an arbitrary function the two results are the same.

EXAMPLE 9.3 Find the operator equal to the operator product $\dfrac{d}{dx}\hat{x}$.

SOLUTION ► We take an arbitrary differentiable function $f = f(x)$ and apply the operator product to it,

$$\frac{d}{dx}\hat{x} f = x\frac{df}{dx} + f\frac{dx}{dx} = \left(x\frac{d}{dx} + \hat{E}\right) f,$$

where $\hat{E}$ is the *identity operator*, defined to be the operator for multiplication by unity (same as doing nothing). We can write the operator equation that is equivalent to this equation:

$$\frac{d}{dx}\hat{x} = x\frac{d}{dx} + \hat{E}.$$

◄

EXERCISE 9.2 ► Find the operator equal to the operator product $\frac{d^2}{dx^2}x$. ◄

The *difference of two operators* is given by

$$(\hat{A} - \hat{B}) = \hat{A} + (-\hat{E})\hat{B}. \tag{9.7}$$

We now have an operator algebra in which we carry out the operations of addition and multiplication on the operators themselves. These operations have the following properties: Operator multiplication is *associative*. This means that if $\hat{A}$, $\hat{B}$, and $\hat{C}$ are operators, then

$$\boxed{(\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C}).} \tag{9.8}$$

Operator multiplication and addition are *distributive*. This means that if $\hat{A}$, $\hat{B}$, and $\hat{C}$ are operators.

$$\boxed{\hat{A}(\hat{B}+\hat{C}) = \hat{A}\hat{B} + \hat{A}\hat{C}.} \tag{9.9}$$

Operator multiplication is not necessarily *commutative*. This means that in some cases the same result is not obtained if the sequence of operation of two operators is reversed:

$$\boxed{\hat{A}\hat{B} \neq \hat{B}\hat{A} \quad \text{(possible)}} \tag{9.10}$$

If the operator $\hat{A}\hat{B}$ is equal to the operator $\hat{B}\hat{A}$ then $\hat{A}$ and $\hat{B}$ are said to *commute*. The *commutator* of $\hat{A}$ and $\hat{B}$ is denoted by $\left[\hat{A}, \hat{B}\right]$ and defined by

$$\boxed{\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad \text{(definition of the commutator)}}. \tag{9.11}$$

If $\hat{A}$ and $\hat{B}$ commute, then $\left[\hat{A}, \hat{B}\right] = \hat{0}$, where $\hat{0}$ is the *null operator*, equivalent to multiplying by zero.

EXAMPLE 9.4 Find the commutator $\left[\frac{d}{dx}, x\right]$.

SOLUTION ► We apply the commutator to an arbitrary function $f(x)$:

$$\left[\frac{d}{dx}, x\right] f = \frac{d}{dx}(xf) - x\frac{df}{dx} = x\frac{df}{dx} + f - x\frac{df}{dx} = f. \tag{9.12}$$

Therefore,

$$\left[\frac{d}{dx}, x\right] = \hat{E} = \hat{1}, \tag{9.13}$$

where the symbol $\hat{1}$ stands for multiplication by unity and is the same thing as $\hat{E}$. We will generally omit the caret symbol on multiplication operators. ◄

EXERCISE 9.3 ► Find the commutator $[x^2, d^2/dx^2]$. ◄

Here are a few facts that will predict in almost all cases whether two operators will commute:

1. An operator containing a multiplication by a function of x and one containing d/dx will not generally commute.
2. Two multiplication operators commute. If g and h are functions of the same or different independent variables or are constants, then

$$[\hat{g}, \hat{h}] = 0. \tag{9.14}$$

3. Operators acting on different independent variables commute. For example,

$$\left[x\frac{d}{dx}, \frac{d}{dy}\right] = 0. \tag{9.15}$$

4. An operator for multiplication by a constant commutes with any other operator.

EXERCISE 9.4 ► Show that Eq. (9.15) is correct, and that statement (4) is correct. ◄

Since we have defined the product of two operators, we have a definition for the *powers of an operator*. An operator raised to the nth power is the operator for n successive applications of the original operator:

$$\boxed{\hat{A}^n = \hat{A}\,\hat{A}\,\hat{A}\cdots\hat{A} \quad (n \text{ factors})}. \tag{9.16}$$

EXAMPLE 9.5 If the operator $\hat{A}$ is $x + \frac{d}{dx}$, find $\hat{A}^3$.

SOLUTION ►

$$\begin{aligned}\hat{A}^3 &= \left(x+\frac{d}{dx}\right)\left(x+\frac{d}{dx}\right)\left(x+\frac{d}{dx}\right)\\ &= \left(x+\frac{d}{dx}\right)\left(x^2+\frac{d}{dx}x+x\frac{d}{dx}+\frac{d^2}{dx^2}\right)\\ &= x^3+x\frac{d}{dx}\hat{x}+x^2\frac{d}{dx}+x\frac{d^2}{dx^2}+\frac{d}{dx}x^2+\frac{d^2}{dx^2}x+\frac{d}{dx}x\frac{d}{dx}+\frac{d^3}{dx^3}.\end{aligned}$$

The order of the factors in each term must be maintained because the two terms in the operator do not commute with each other. ◄

EXERCISE 9.5 ►

(a) For the operator $\hat{A} = x + \frac{d}{dx}$, find $\hat{A}^3 f$ if $f(x) = \sin(ax)$.

(b) Find an expression for $\hat{B}^2$ if $\hat{B} = x(d^2/dx^2)$ and find $\hat{B}^2 f$ if $f = bx^4$.

◄

Division by an operator is not defined. However, we define the *inverse of an operator* as that operator which "undoes" what the first operator does. The inverse of $\hat{A}$ is denoted by $\hat{A}^{-1}$, and

$$\boxed{\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{E}} \tag{9.17}$$

$$\boxed{\hat{A}^{-1}\hat{A}f = \hat{E}f = f.} \tag{9.18}$$

The inverse of a nonzero multiplication operator is the operator for multiplication by the reciprocal of the original quantity. Not all operators possess inverses. For example, there is no inverse for $\hat{0}$ (multiplication by zero).

Operator algebra can be used to solve some differential equations.[2] A linear differential equation with constant coefficients can be written in operator notation

[2]See, for example, Max Morris and Orley Brown, *Differential Equations*, 3rd ed. pp. 86–89, Prentice-Hall, Englewood Cliffs, NJ, 1952.

and solved by operator algebra. The equation

$$\frac{d^2y}{dx^2} - 3\frac{dy}{dx} + 2y = 0 \tag{9.19}$$

can be written as

$$(\hat{D}_x^2 - 3\hat{D}_x + 2)y = 0 \tag{9.20}$$

where we introduce the symbol $\hat{D}_x$ as an abbreviation for d/dx. The equation can be written as an operator equation:

$$(\hat{D}_x^2 - 3\hat{D}_x + 2) = 0. \tag{9.21}$$

Using operator algebra, we manipulate this equation as though it were an ordinary equation. We factor it to obtain

$$\left(\hat{D}_x - 2\right)\left(\hat{D}_x - 1\right) = 0. \tag{9.22}$$

The two roots are obtained from

$$\hat{D}_x - 2 = 0 \tag{9.23a}$$
$$\hat{D}_x - 1 = 0. \tag{9.23b}$$

These equations are the same as

$$\frac{dy}{dx} - 2y = 0 \tag{9.24a}$$
$$\frac{dy}{dx} - y = 0. \tag{9.24b}$$

The solutions to these equations are

$$y = e^{2x} \tag{9.25a}$$
$$y = e^{\lambda} \tag{9.25b}$$

Since both of these must be solutions to the original equation, the general solution is

$$y = c_1 e^{2x} + c_2 e^{x}, \tag{9.26}$$

where c_1 and c_2 are arbitrary constants.

EXERCISE 9.6 ▶ Show that the function in Eq. (9.26) satisfies Eq. (9.19). ◀

Operators in Quantum Mechanics

One of the postulates of quantum mechanical theory is that for every mechanical quantity there is a mathematical operator. The theory of quantum mechanics defines how these operators are constructed, and they contain derivative operators and multiplication operators. The eigenfunctions and eigenvalues of these operators play a central role in the theory. For example, the operator that corresponds to the mechanical energy is the Hamiltonian operator, and the time-independent Schrödinger equation is the eigenvalue equation for this operator. For motion in

the x direction of a single particle of mass m with a potential energy given by $\mathcal{V}(x)$, the Hamiltonian operator is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \mathcal{V}(x) \tag{9.27}$$

where $\hbar$ is Planck's constant divided by 2π. The term $\mathcal{V}(x)$ stands for a multiplication operator. You will become familiar with these operators in any physical chemistry class.

9.2 Symmetry Operators

Many common objects are said to be symmetrical. The most symmetrical object is a sphere, which looks just the same no matter which way it is turned. A cube, although less symmetrical than a sphere, has 24 different orientations in which it looks the same. Many biological organisms have approximate *bilateral symmetry*, meaning that the left side looks like a mirror image of the right side. Symmetry properties are related to *symmetry operators*, which can operate on functions like other mathematical operators. We first define symmetry operators in terms of how they act on points in space and will later define how they operate on functions. We will consider only *point symmetry operators*, a class of symmetry operators that do not move a point if it is located at the origin of coordinates.

We denote the position of a point by its Cartesian coordinates, keeping the Cartesian coordinate axes fixed as the point moves. The action of a general symmetry operator denoted by $\hat{O}$ is specified by writing

$$\hat{O}(x_1, y_1, z_1) = (x_2, y_2, z_2), \tag{9.28}$$

where x_1, y_1, z_1 are the coordinates of the original location of a point and x_2, y_2, z_2 are the coordinates of the location to which the operator moves the point.

Specific Symmetry Operators

Our first symmetry operator is the *identity operator*, which leaves any point in its original location. We denote it by $\hat{E}$,the same symbol as for the multiplicative identity operator.

$$\hat{E}(x_1, y_1, z_1) = (x_1, y_1, z_1) \tag{9.29}$$

If $\mathbf{r}_1$ is the vector with components (x_1, y_1, z_1), this equation can be written

$$\hat{E}\mathbf{r}_1 = \mathbf{r}_1. \tag{9.30}$$

The *inversion operator* is denoted by $\hat{\imath}$. It moves a point on a line from its original position through the origin to a location at the same distance from the origin as the original position:

$$\boxed{\hat{\imath}(x_1, y_1, z_1) = (-x_1, -y_1, -z_1)} \tag{9.31}$$

or

$$\boxed{\hat{\imath}\mathbf{r}_1 = -\mathbf{r}_1} \tag{9.32}$$

For each symmetry operator, we define a *symmetry element*, which is a point, line, or plane relative to which the symmetry operation is performed. The symmetry element for a given symmetry operator is sometimes denoted by the same symbol as the operator, but without the caret (^). For example, the symmetry element for the inversion operator is the origin. The symmetry element of any point symmetry operator must include the origin. If a point is located on the symmetry element for a symmetry operator, that symmetry operator will not move that point.

A *reflection operator* moves a point on a line perpendicular to a specified plane, through the plane to a location on the other side of the plane at the same distance from the plane as the original point. This motion is called *reflection through the plane*. The specified plane is the symmetry element and must pass through the origin if the operator is a point symmetry operator. There is a different reflection operator for each of the infinitely many planes passing through the origin. The operator $\hat{\sigma}_h$ corresponds to reflection through the x-y plane (the h subscript stands for "horizontal"). Figure 9.1 shows the action of the $\hat{\sigma}_h$ operator. There is only one horizontal plane passing through the origin, so there is only one $\hat{\sigma}_h$ operator among the point symmetry operators. The action of $\hat{\sigma}_h$ corresponds to

$$\boxed{\hat{\sigma}_h(x_1, y_1, z_1) = (x_1, y_1, -z_1)}. \tag{9.33}$$

A reflection operator whose symmetry element is a vertical plane is denoted by $\hat{\sigma}_v$. You must separately specify which vertical plane is the symmetry element.

EXERCISE 9.7 ► Write an equation similar to Eq. (9.33) for the $\hat{\sigma}_v$ operator whose symmetry element is the x-z plane, and one for the $\hat{\sigma}_v$ operator whose symmetry element is the y-z plane. ◄

Next we have *rotation operators*. An ordinary rotation, in which a point moves as if it were part of a rigid object rotating about an axis, is called a *proper rota-*

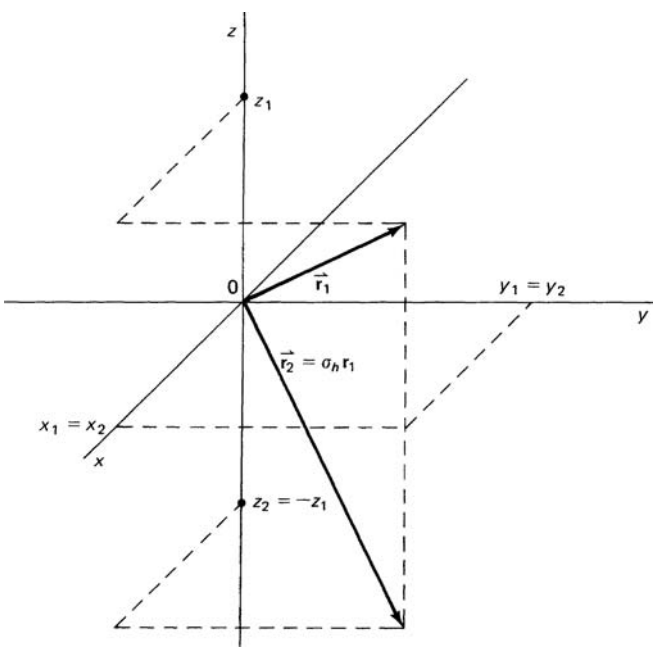

Figure 9.1 ► The action of the reflection operator, $\hat{\sigma}_h$.

tion. The axis of rotation is the symmetry element, and the action of the rotation operator is to move the point along an arc, staying at a fixed perpendicular distance from a fixed point on the axis. The axis of rotation must pass through the origin if the rotation operator is a point symmetry operator. In addition to specifying the axis of rotation, one must specify the direction of rotation and the angle of rotation. By convention, the direction of rotation is taken as counterclockwise when viewed from the end of the axis that is designated as the positive end. We consider only angles of rotation such that n applications of the rotation operator will produce exactly one complete rotation, where n is a positive integer. Such a rotation operator is denoted by $\hat{C}_n$. The axis of rotation must be specified separately. For example, the operator for a rotation of 90^o about the z axis can be called $\hat{C}_4(z)$.

Figure 9.2 shows the action of the $\hat{C}_4(z)$ operator. For this operator,

$$\hat{C}_4(z)(x_1, y_1, z_1) = (-y_1, x_1, z_1) \tag{9.34}$$

so that

$$x_2 = -y_1, \quad y_2 = x_1, \quad z_2 = z_1. \tag{9.35}$$

EXERCISE 9.8 ▶ Find the following:

(a) $\hat{C}_4(z)(1, -4, 6)$ (b) $C_2(x)(1, 2, -3)$.

◀

An *improper rotation* is equivalent to a proper rotation followed by a reflection through a plane that is perpendicular to the rotation axis. For this to be a point symmetry operation, both the rotation axis and the reflection plane must pass through

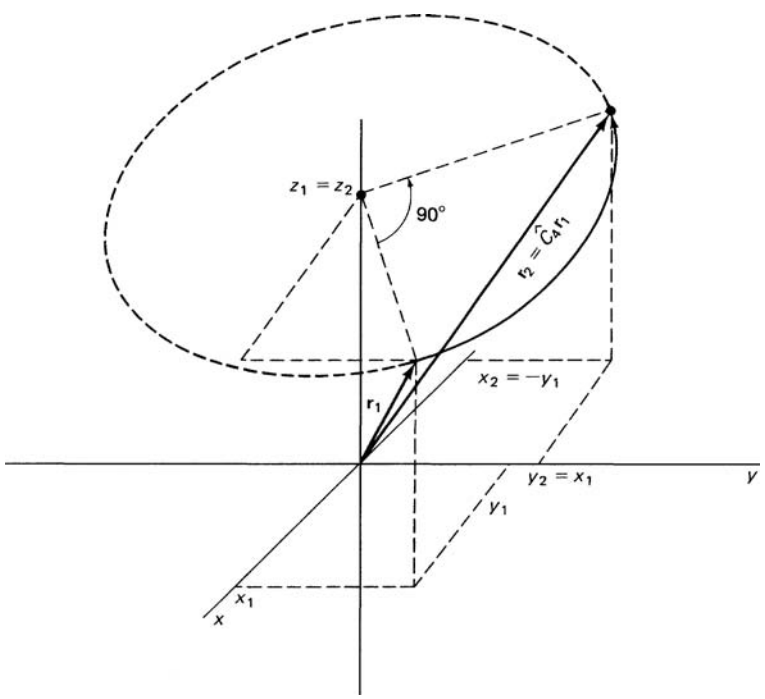

Figure 9.2 ▶ The action of a rotation operator, $\hat{C}_4$.

the origin. The symbol for an improper rotation operator is $\hat{S}_n$, where the subscript n has the same meaning as with a proper rotation. The symmetry element for an improper rotation is the axis of rotation. The action of the operator for an improper rotation of 90° about the z axis is given by

$$\hat{S}_4(z)(x_1, y_1, z_1) = (-y_1, x_1, -z_1). \tag{9.36}$$

An improper rotation operator $\hat{S}_2$ is the same as the inversion operator $\hat{\imath}$, and any $\hat{S}_1$ operator is the same as a reflection operator.

EXERCISE 9.9 ► Find the following:

(a) $\hat{S}_3(z)(1, 2, 3)$ (b) $\hat{S}_2(y)(3, 4, 5)$.

◄

We have defined all of the point symmetry operators. In addition, there are other symmetry operators and symmetry elements, such as translations, glide planes, screw axes, etc., which are useful in describing crystal lattices but which are not useful for molecules. We do not discuss these operators.

Symmetry operators can operate on a set of points as well as on a single point. For example, they can operate simultaneously on all of the particles of a solid object or on all of the nuclei of a molecule, or on all of the electrons of a molecule. For example, a benzene molecule in its equilibrium conformation has the shape of a regular hexagon. If the center of mass is at the origin, the inversion operator moves each of the carbon nuclei to the original location of another carbon nucleus and each of the hydrogen nuclei to the original location of another hydrogen nucleus. If after a symmetry operation all of the particles in an object are in the same conformation as before except for the exchange of identical particles, we say that the symmetry operator *belongs* to the object. Any object has a set of symmetry operators (or symmetry elements) that belong to it. An unsymmetrical object possesses only the identity operator, but a symmetrical object possesses at least one additional symmetry operator. The symmetry properties of the object can be specified by listing all symmetry operators that belong to it or by listing their symmetry elements. It is found that the symmetry operators belonging to any rigid object form a *mathematical group*, which we discuss later in this chapter. The symmetry of the object can also be specified by giving the symbol assigned to the appropriate group.

A uniform spherical object is the most highly symmetrical object. If the center of the sphere is at the origin, every mirror plane, every rotation axis, every improper rotation axis, and the inversion center at the origin are symmetry elements of symmetry operators belonging to the sphere.

EXAMPLE 9.6 List the symmetry elements of a uniform cube centered at the origin with its faces parallel to the coordinate planes.

SOLUTION ► The symmetry elements are:
The inversion center at the origin.
Three C_4 axes coinciding with the coordinate axes.
Four C_3 axes passing through opposite corners of the cube.

Four S_6 axes. coinciding with the C_3 axes.
Six C_2 axes connecting the midpoints of opposite edges.
Three mirror planes in the coordinate planes.
Six mirror planes passing through opposite edges. ◄

EXERCISE 9.10 ►

(a) List the symmetry elements of a right circular cylinder. It is customary to place the highest-order rotation axis on the axis, so we place the axis of the cylinder on the z axis and place its center at the origin. Since even an infinitesimal rotation belongs to the object, the z axis is a C_∞ axis.

(b) List the symmetry elements of a uniform regular tetrahedron. It is possible to arrange the object so that its center is at the origin and the four corners are at alternate corners of a cube oriented as in Example 9.6.

◄

EXAMPLE 9.7 List the symmetry elements of the benzene molecule.

SOLUTION ► Locate the molecule with its nuclei in their equilibrium conformation as shown in Fig. 9.3. The symmetry elements are:
The inversion center at the origin.
The σ_h mirror plane containing the nuclei.
A C_6 axis and an S_6 axis on the z axis.
Six vertical mirror planes, three through carbon nuclei and three that pass halfway between adjacent carbon nuclei.
Six C_2 axes located where the mirror planes intersect the x-y plane. These are also S_2 axes.
Some of the symmetry elements are shown in Fig. 9.3. The symbols on the rotation axes identify them, with a hexagon labeling a sixfold axis, a square labeling a fourfold axis, and so on. ◄

EXERCISE 9.11 ► List the symmetry elements for

(a) H_2O (bent) (b) CH_4 (tetrahedral)

(c) CO_2 (linear).

◄

The Operation of Symmetry Operators on Functions

We have described the action of symmetry operators on points. We now define how they act on functions. When a mathematical operator operates on a function, a new

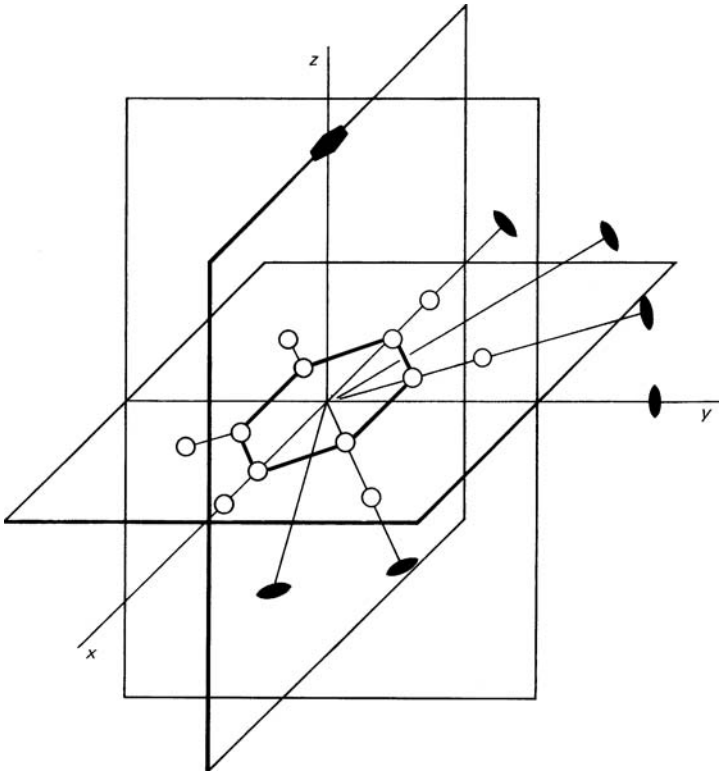

Figure 9.3 ► The benzene molecule with symmetry elements shown.

function is produced. We define this same action for a symmetry operator. If ψ is some function of x, y, and z and $\hat{O}$ is some symmetry operator, then we define

$$\hat{O}\psi = \phi, \tag{9.37}$$

where ϕ is a newly produced function. We now have to define this new function. If $\hat{O}$ is the operator that carries a point from (x_1, y_1, z_1) to (x_2, y_2, z_2), we define ϕ to have the same value at (x_2, y_2, z_2) that ψ has at (x_1, y_1, z_1):

$$\boxed{\phi(x_2, y_2, z_2) = \psi(x_1, y_1, z_1)} \tag{9.38}$$

This definition allows us to treat symmetry operators on an equal footing with other mathematical operators that operate on functions.

EXAMPLE 9.8 The unnormalized $2px$ wave function for the electron in a hydrogen atom is

$$\psi_{2px} = x \exp\left[\frac{-(x^2 + y^2 + z^2)^{1/2}}{2a_0}\right], \tag{9.39}$$

where a_0 is a constant called the *Bohr radius*. Find $\hat{C}_4(z)\psi_{2px}$.

SOLUTION ► The effect of this operator is given by Eq. (9.34)

$$\hat{C}_4(z)(x_1, y_1, z_1) = (x_2, y_2, z_2) = (-y_1, x_1, z_1).$$

The new function is thus

$$\phi(x_2, y_2, z_2) = \psi_{2px}(x_1, y_1, z_1) = y_2 \exp\left[\frac{-(y_2^2 + x_2^2 + z_2^2)^{1/2}}{2a_0}\right].$$

Thus

$$\hat{C}_4(z)\psi_{2px} = \psi_{2py}. \tag{9.40}$$

The original function has a positive region in front of the x-z plane and a negative region behind the x-z plane. The symmetry operator has moved the positive region in the same way that it moves a rigid object, and similarly for the negative region. ◄

Symmetry operators can have *eigenfunctions*, like any other operator. The result of operating on an eigenfunction of the operator is equal to a constant (the *eigenvalue*) times the original function. If a symmetry operator leaves a function unchanged, its eigenvalue is equal to unity. The only other possible eigenvalue for a symmetry operator is -1.

EXERCISE 9.12 ► Find $\hat{\imath}\psi_{2px}$. Show that ψ_{2px} is an eigenfunction of the inversion operator, and find its eigenvalue. ◄

The importance of symmetry operators in the study of electronic wave functions arises from the fact that two commuting operators can have a set of common eigenfunctions. In quantum mechanical theory, there is an operator corresponding to each mechanical variable. The most important quantum mechanical operator is the *Hamiltonian operator*, which corresponds to the energy. In the *Born–Oppenheimer approximation*, the electronic Hamiltonian operator operates on the coordinates of the electrons, but treats the nuclear coordinates as constants. This operator has a term in it that is the operator for multiplication by the potential energy as a function of the positions of the nuclei and electrons. If a symmetry operator leaves the potential energy unchanged when applied to the electrons' positions, it will commute with the Hamiltonian operator, and the eigenfunctions of the Hamiltonian operator can also be eigenfunctions of the symmetry operator.

A symmetry operator leaves the potential energy unchanged if it moves each electron so that after the motion it is the same distance from each nucleus or the same distance from another nucleus of the same charge as it was prior to the motion. If this is the case, the symmetry operator commutes with the Born-Oppenheimer Hamiltonian. There is another way to see if the symmetry operator will commute with the electronic Hamiltonian. Apply it to the nuclei and not to the electrons. If the symmetry operator either leaves a nucleus in the same position or places it in the original position of a nucleus of the same type, it belongs to the nuclear framework. The symmetry operators that belong to the nuclear framework will commute with the electronic Hamiltonian when applied to the electrons.

EXERCISE 9.13 ► The potential energy of two charges Q_1 and Q_2 in a vacuum is

$$\mathcal{V} = \frac{Q_1 Q_2}{4\pi\epsilon_0 r_{12}}$$

where r_{12} is the distance between the charges and ε_0 is a constant called the permittivity of a vacuum. If a hydrogen molecule is placed so that the origin is midway between the two nuclei and the nuclei are on the z axis, show that the inversion operator $\hat{\imath}$ and the reflection operator $\hat{\sigma}_h$ do not change the potential energy if applied to the electrons but not to the nuclei. ◄

Full exploitation of the symmetry properties of electronic wave functions requires the use of group theory, which we briefly introduce in a later section of this chapter. However, we state some facts:

1. If a molecule has a permanent dipole moment, the dipole vector must lie along a proper rotation axis and in a plane of symmetry.
2. A molecule with an improper rotation axis cannot be optically active.
3. A given object, such as a nuclear framework of a molecule, cannot possess a completely arbitrary collection of symmetry elements. Group theory can tell us which ones can belong together.

9.3 Matrix Algebra

A *matrix* is an array or list of numbers arranged in rows, columns, and so forth. Most of the matrices that you will encounter are two-dimensional arrays. That is, they have rows and columns. If the matrix A has m rows and n columns, it is called an m by n matrix and is written

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ \cdots & & & & \\ \cdots & & & & \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{bmatrix}. \tag{9.41}$$

The quantities that are entries in the two-dimensional list are called *matrix elements*. The brackets written on the left and right are included to show where the matrix starts and stops. If $m = n$, we say that the matrix is a *square matrix*. A vector in ordinary space can be represented as a list of three components. We consider a matrix with one row and n columns to be a *row vector*. We consider a matrix with m rows and one column to be a *column vector*. We now refer to ordinary numbers as *scalars*, to distinguish them from vectors and matrices.

Matrices and mathematical operators have some things in common. There is a well-defined matrix algebra in which matrices are operated on and this matrix algebra is similar to operator algebra. Two matrices are equal to each other if and only if both have the same number of rows and the same number of columns and if every element of one is equal to the corresponding element of the other. The *sum of two matrices* is defined by

$$\mathbf{C} = \mathbf{A} + \mathbf{B} \quad \text{if and only if } c_{ij} = a_{ij} + b_{ij} \text{ for every } i \text{ and } j. \tag{9.42}$$

Two matrices can be added only if they have the same number of rows and the same number of columns. The *product of a scalar and a matrix* is defined by

$$\mathbf{B} = c\mathbf{A} \quad \text{if and only if } b_{ij} = ca_{ij} \text{ for every } i \text{ and } j, \tag{9.43}$$

where c is a scalar and $\mathbf{A}$ is a matrix. The *product of two matrices* is similar to the scalar product of two vectors. If we rename the components of two vectors F_1, F_2, F_3, G_1, G_2, and G_3 instead of Fx, F_y, F_z, G_x, G_y, and G_z, we can write the scalar product of two vectors in Eq. (2.70) in the form

$$\mathbf{F} \cdot \mathbf{G} = F_1G_1 + F_2G_2 + F_3G_3 = \sum_{k=1}^{3} F_kG_k. \tag{9.44}$$

We define matrix multiplication in a way that is similar to this. If $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$ are matrices such that $\mathbf{C}$ is the matrix product $\mathbf{AB}$, we define

$$c_{ij} = \sum_{k=1}^{n} a_{ik}b_{kj}. \tag{9.45}$$

In this equation, n is the number of columns in $\mathbf{A}$, which must equal the number of rows in the matrix $\mathbf{B}$. The matrix $\mathbf{C}$ will have as many rows as $\mathbf{A}$ and as many columns as $\mathbf{B}$.

We can think of the vector $\mathbf{F}$ in Eq. (9.44) as a row vector with one row and three columns and the vector $\mathbf{G}$ as being a column vector with three rows and one column. Equation (9.44) is then a special case of Eq. (9.45):

$$\mathbf{F} \cdot \mathbf{G} = [F_1 \; F_2 \; F_3] \begin{bmatrix} G_1 \\ G_2 \\ G_3 \end{bmatrix}.$$

Row and column vectors can have a number of elements other than three, just as a matrix can have a number of rows and columns other than three.

The scalar product $\mathbf{F} \cdot \mathbf{G}$ is a scalar, which is equivalent to a matrix with one row and one column. If $\mathbf{A}$ is a 2 by 3 matrix and $\mathbf{B}$ is a 3 by 3 matrix, we can write their matrix product as

$$\mathbf{AB} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \end{bmatrix} = \mathbf{C}. \tag{9.46}$$

Each element in $\mathbf{C}$ is obtained in the same way as taking a scalar product of a row from $\mathbf{A}$ and a column from $\mathbf{B}$. For a particular element in $\mathbf{C}$, we take the row in $\mathbf{A}$ which is in the same position as the row in $\mathbf{C}$ containing the desired element, and the column in $\mathbf{B}$ which is in the same position as the column in $\mathbf{C}$ containing the desired element and sum the products of the respective elements.

EXAMPLE 9.9 Find the matrix product

$$\begin{bmatrix} 1 & 0 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 0 & 2 \\ 3 & 0 & 1 \\ 1 & 1 & -1 \end{bmatrix}.$$

SOLUTION ►
$$\begin{bmatrix} 1 & 0 & 2 \\ 0 & -1 & 1 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 0 & 0 & 2 \\ 3 & 0 & 1 \\ 1 & 1 & -1 \end{bmatrix} = \begin{bmatrix} 2 & 2 & 0 \\ -2 & 1 & -2 \\ 1 & 1 & -1 \end{bmatrix}.$$ ◄

EXERCISE 9.14 ► Find the two matrix products

$$\begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix}\begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & 1 & -1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 1 & 3 & 2 \\ 2 & 2 & -1 \\ -2 & -1 & -1 \end{bmatrix}\begin{bmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \\ 1 & -1 & 2 \end{bmatrix}.$$

The left factor in one product is equal to the right factor in the other product, and vice versa. Are the two products equal? ◄

As you can see, matrix multiplication with fairly large matrices can involve a lot of computation. Computer programs can be written to carry out the process, and such programs are built into Mathematica and also into computer languages such as BASIC so that a matrix multiplication can be carried out with a single statement.

Two square matrices can be multiplied together in either order. However, the multiplication is not always *commutative*. It is possible that

$$\boxed{\mathbf{AB} \neq \mathbf{BA} \text{ (in some cases)}}. \tag{9.47}$$

However, matrix multiplication is *associative*,

$$\boxed{\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C}} \tag{9.48}$$

Matrix multiplication and addition are *distributive*,

$$\boxed{\mathbf{A}(\mathbf{B}+\mathbf{C}) = \mathbf{AB}+\mathbf{AC}}. \tag{9.49}$$

Show that the properties of Eqs. (9.48) and (9.49) are obeyed by the particular matrices

$$\mathbf{A} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} 0 & 2 & 2 \\ -3 & 1 & 2 \\ 1 & -2 & -3 \end{bmatrix} \quad \mathbf{C} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 3 & -2 \\ 2 & 7 & -7 \end{bmatrix}.$$

Matrix multiplication is similar to operator multiplication. Both are associative and distributive but not necessarily commutative. In Section 8.1 we defined an identity operator, and we now define an identity matrix **E**. We require

$$\boxed{\mathbf{EA} = \mathbf{AE} = \mathbf{A}.}$$

The fact that we require **E** to be the identity matrix when multiplied on either side of **A** requires both **A** and **E** to be square matrices. In fact, only with square matrices will we get a strict similarity between operator algebra and matrix algebra.

An identity matrix can have any number of rows and columns. It has the form

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix}. \tag{9.50}$$

The *diagonal elements* of any square matrix are those with both indices equal. The diagonal elements of **E** are all equal to 1 and are the only nonzero elements. This can be represented by the equation

$$e_{ij} = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j. \end{cases}$$

The quantity δ_{ij} is called the *Kronecker delta*.

EXERCISE 9.15 ▶ Show by explicit matrix multiplication that

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{31} & a_{41} \\ a_{31} & a_{31} & a_{31} & a_{41} \\ a_{41} & a_{41} & a_{31} & a_{41} \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{21} & a_{31} & a_{41} \\ a_{31} & a_{31} & a_{31} & a_{41} \\ a_{41} & a_{41} & a_{31} & a_{41} \end{bmatrix}.$$

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Just as in operator algebra, we do not define division by a matrix. In operator algebra we defined an inverse operator, which undoes the effect of a given operator. We define now the *inverse of a matrix*. Only square matrices have inverses. We denote the inverse of **A** by $\mathbf{A}^{-1}$, so that

$$\boxed{\mathbf{A}\mathbf{A}^{-1} = \mathbf{E}}. \tag{9.51}$$

This multiplication of a matrix by its inverse is commutative, so that **A** is also the inverse of $\mathbf{A}^{-1}$.

From Eq. (9.45) we can write the second equality in Eq. (9.51) in terms of matrix elements:

$$\sum_{k=1}^{n} a_{ik}(A^{-1})_{kj} = \delta_{ij}, \tag{9.52}$$

where we write $(\mathbf{A}^{-1})_{kj}$ for the kj element of $\mathbf{A}^{-1}$. This equation represents a set of simultaneous linear algebraic equations, one for each value of i and each value of j, so that there are just enough equations to determine the elements of $\mathbf{A}^{-1}$.

One method for finding $\mathbf{A}^{-1}$ is called *Gauss–Jordan elimination*, which is a method of solving simultaneous linear algebraic equations. It consists of a set of operations to be applied to Eq. (9.51). In order maintain a valid equation, these operations must be applied to both sides of the equation. The first operation is applied to the matrix **A** and to the matrix **E** on the right-hand side of the equation, but not to the unknown matrix $\mathbf{A}^{-1}$. This is analogous to the fact that if you have an equation $ax = c$, you would multiply a and c by some factor, but not multiply

both a and x by the factor to maintain a valid equation. The goal of the operations is to transform Eq. (9.51) into

$$\mathbf{E}(\mathbf{A}^{-1}) = \mathbf{D} \tag{9.53}$$

so that $\mathbf{A}^{-1}$ will be the same matrix as $\mathbf{D}$.

In order to carry out the procedure conveniently, we write the matrix $\mathbf{A}$ and the matrix $\mathbf{E}$ explicitly side by side and carry out operations on each element of the same row in each matrix. For example, we might multiply every element in a given row of $\mathbf{A}$ by some constant and multiply every element in the same row of $\mathbf{E}$ by the same constant. This is an example of a *row operation*. If we carry it out we still have a valid equation. Another row operation that we can apply is to subtract one row of $\mathbf{A}$ from another row of $\mathbf{A}$, element by element, while doing the same thing to E. This amounts to subtracting the left-hand sides of pairs of equations and subtracting at the same time the right-hand sides of the equations, which produces valid equations. We can then replace one of the row by the difference of two rows. Successive application of these two row operations is sufficient to transform the left factor of a matrix product into the identity matrix. If we apply them in the appropriate way to Eq. (9.51), we can transform it into Eq. (9.53). We illustrate the procedure in the following example.

EXAMPLE 9.10 Find the inverse of the matrix

$$\mathbf{A} = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 2 \\ 0 & 1 & 1 \end{bmatrix}.$$

SOLUTION ► Our version of Eq. (9.51) is

$$\begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} \begin{bmatrix} (A^{-1})_{11} & (A^{-1})_{12} & (A^{-1})_{13} \\ (A^{-1})_{21} & (A^{-1})_{22} & (A^{-1})_{23} \\ (A^{-1})_{22} & (A^{-1})_{32} & (A^{-1})_{33} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

In order to carry out the row operations we write the two matrices on which we operate side by side and perform the same operations on the same row of both matrices. The matrix that is not operated on, $\mathbf{A}^{-1}$, is not written. We don't know what its elements are so we couldn't operate on it.

$$\left[\begin{array}{ccc:ccc} 2 & 1 & 0 & 1 & 0 & 0 \\ 1 & 2 & 1 & 0 & 1 & 0 \\ 0 & 1 & 2 & 0 & 0 & 1 \end{array}\right]$$

It is usual to clear out the columns from left to right. We first want to get a zero in the place of a_{21}, which is now equal to 1. We multiply the first row by $\frac{1}{2}$, obtaining

$$\left[\begin{array}{ccc:ccc} 1 & \frac{1}{2} & 0 & \frac{1}{2} & 0 & 0 \\ 1 & 2 & 1 & 0 & 1 & 0 \\ 0 & 1 & 2 & 0 & 0 & 1 \end{array}\right].$$

We subtract the first row from the second and replace the second row by this difference. The result is

$$\left[\begin{array}{ccc:ccc} 1 & \frac{1}{2} & 0 & \frac{1}{2} & 0 & 0 \\ 0 & \frac{3}{2} & 1 & -\frac{1}{2} & 1 & 0 \\ 0 & 1 & 2 & 0 & 0 & 1 \end{array}\right].$$

We say that we have used the element a_{11} as the *pivot element* in this procedure. The left column is now as we want it to be. We now use the a_{22} element as the pivot element to clear the second column. We multiply the second row by $\frac{1}{3}$ and replace the first row by the difference of the first row and the second to obtain

$$\left[\begin{array}{ccc:ccc} 1 & 0 & -\frac{1}{3} & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & \frac{1}{2} & \frac{1}{3} & -\frac{1}{6} & \frac{1}{3} & 0 \\ 0 & 1 & 2 & 0 & 0 & 1 \end{array}\right].$$

We now multiply the second row by 2, subtract this row from the third row, and replace the third row by the difference. The result is

$$\left[\begin{array}{ccc:ccc} 1 & 0 & -\frac{1}{3} & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & 1 & \frac{2}{3} & -\frac{1}{3} & \frac{2}{3} & 0 \\ 0 & 0 & \frac{4}{3} & \frac{1}{3} & -\frac{2}{3} & 1 \end{array}\right].$$

We now multiply the third row by $\frac{1}{2}$ in order to use the a_{33} element as the pivot element. We subtract the third row from the second and replace the second row by the difference, obtaining

$$\left[\begin{array}{ccc:ccc} 1 & 0 & -\frac{1}{3} & \frac{2}{3} & -\frac{1}{3} & 0 \\ 0 & 1 & 0 & -\frac{1}{2} & 1 & -\frac{1}{2} \\ 0 & 0 & \frac{2}{3} & \frac{1}{6} & -\frac{1}{3} & \frac{1}{2} \end{array}\right].$$

We now multiply the third row by $\frac{1}{2}$, add it to the first row, and replace the first row by the sum. The result is

$$\left[\begin{array}{ccc:ccc} 1 & 0 & 0 & \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ 0 & 1 & 0 & -\frac{1}{2} & 1 & -\frac{1}{2} \\ 0 & 0 & \frac{1}{3} & \frac{1}{12} & -\frac{1}{6} & \frac{1}{4} \end{array}\right].$$

The final row operation is multiplication of the third row by 3 to obtain

$$\left[\begin{array}{ccc:ccc} 1 & 0 & 0 & \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ 0 & 1 & 0 & -\frac{1}{2} & 1 & -\frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{array}\right].$$

We now reconstitute the matrix equation by placing the identity matrix on the left to the left of the $\mathbf{A}^{-1}$matrix. This produces a matrix equation such that the left-hand side of the equation is $\mathbf{E}\mathbf{A}^{-1}$ and the right-hand side is the right half of the double matrix. Therefore, the right half of this double matrix is $\mathbf{A}^{-1}$:

$$\mathbf{A}^{-1} = \left[\begin{array}{ccc} \frac{3}{4} & -\frac{1}{2} & \frac{1}{4} \\ -\frac{1}{2} & 1 & -\frac{1}{2} \\ \frac{1}{4} & -\frac{1}{2} & \frac{3}{4} \end{array}\right].$$

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EXERCISE 9.16 ▶ a. Show that $\mathbf{A}\mathbf{A}^{-1} = \mathbf{E}$ and that $\mathbf{A}^{-1}\mathbf{A} = \mathbf{E}$ for the matrices of the preceding example.
b. Find the inverse of the matrix

$$\mathbf{A} = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$$

◀

Only square matrices have inverses, but not all square matrices have inverses. Associated with each square matrix is a determinant, which we define in the next section. If the determinant of a square matrix vanishes, the matrix is said to be *singular*. A singular matrix has no inverse.

We conclude this section with the definition of several terms that apply to square matrices. The *trace* of a matrix is the sum of the diagonal elements of the matrix:

$$\mathrm{Tr}(\mathbf{A}) = \sum_{i=1}^{n} a_{ii}. \tag{9.54}$$

The trace is sometimes called the *spur*, from the German word *Spur*, which means track or trace. For example, the trace of the n by n identity matrix is equal to n. A matrix in which all the elements below the diagonal elements vanish is called an *upper triangular matrix*. A matrix in which all the elements above the diagonal elements vanish is called a *lower triangular matrix*, and a matrix in which all the elements except the diagonal elements vanish is called a *diagonal matrix*. The matrix in which all of the elements vanish is called the *null matrix* or the *zero matrix*. The *transpose* of a matrix is obtained by replacing the first column by the first row, the second column by the second row of the original matrix, and so on. The transpose of A is denoted by $\tilde{\mathbf{A}}$ (pronounced "A tilde"),

$$(\tilde{\mathbf{A}})_{ij} = \tilde{a}_{ij} = a_{ji}. \tag{9.55}$$

If a matrix is equal to its transpose, it is a *symmetric matrix*. The matrix in Example 9.10 is symmetric, and its inverse is also symmetric.

The *hermitian conjugate* of a matrix is obtained by taking the complex conjugate of each element and then taking the transpose of the resulting matrix. If a matrix has only real elements, the hermitian conjugate is the same as the transpose. The hermitian conjugate is also called the *adjoint* (mostly by physicists) and the *associate* (mostly by mathematicians, who use the term "adjoint" for something else). The hermitian conjugate is denoted by $\mathbf{A}^\dagger$.

$$(\mathbf{A}^\dagger)_{ij} = a^*_{ji}. \tag{9.56}$$

A matrix that is equal to its hermitian conjugate is said to be a *hermitian matrix*.

An *orthogonal matrix* is one whose inverse is equal to its transpose. If A is orthogonal, then

$$\mathbf{A}^{-1} = \tilde{\mathbf{A}} \quad \text{(orthogonal matrix)}. \tag{9.57}$$

A *unitary matrix* is one whose inverse is equal to its hermitian conjugate. If A is unitary, then

$$\mathbf{A}^{-1} = \mathbf{A}^\dagger = \tilde{\mathbf{A}}^* \quad \text{(unitary matrix)}. \tag{9.58}$$

EXERCISE 9.17 ► Which of the following matrices are diagonal, symmetric, hermitian, orthogonal, or unitary?

a. $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ b. $\begin{bmatrix} 1 & 0 \\ 1 & 1 \end{bmatrix}$ c. $\begin{bmatrix} i & i \\ 0 & 1 \end{bmatrix}$ d. $\begin{bmatrix} 0 & i \\ -i & 1 \end{bmatrix}$. ◄

Determinants

Associated with every square matrix is a quantity called a *determinant*. If the elements of the matrix are constants, the determinant is a single constant, defined as a certain sum of products of subsets of the elements. If the matrix has n rows and columns, each term in the sum making up the determinant will have n factors in it. The determinant of a 2 by 2 matrix is defined as the product of the diagonal elements minus the product of the off-diagonal elements:

$$\det(\mathbf{A}) = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}. \tag{9.59}$$

The determinant is written in much the same way as the matrix, except that straight vertical lines are used on the left and right instead of brackets.

EXAMPLE 9.11 Find the value of the determinant

$$\begin{vmatrix} 3 & -17 \\ 1 & 5 \end{vmatrix}.$$

SOLUTION ► $\begin{vmatrix} 3 & -17 \\ 1 & 5 \end{vmatrix} = (3)(5) - (-17)(1) = 15 + 17 = 32.$ ◄

Finding the value of a determinant larger than 2 by 2 requires a number of operations. One way to do it is by *expanding by minors*, as follows:

1. Pick a row or a column of the determinant. Any row or column will do, but one with zeros in it will minimize the work.
2. The determinant is equal to a sum of terms, one for each element in this row or column. Each term consists of an element of the chosen row or column times the *minor* of that element, with an assigned sign, either positive or negative. The minor of an element in a determinant is obtained by deleting the row and the column containing that element. It is a determinant with one less row and one less column than the original determinant.
3. Determine the sign assigned to a term as follows: Count the number of steps of one row or one column required to get from the upper left element to the element whose minor is desired. If the number of steps is odd, the sign is negative. If the number of steps is even (including zero), the sign is positive.
4. Repeat the entire process with each determinant in the expansion until you have a sum of 2 by 2 determinants, which can be evaluated by Eq. (9.59).

The *cofactor* of an element in a determinant is the minor multiplied by the appropriate factor of 1 or -1, determined as in step 3. In addition to the minor which we have defined, other minors of different order are defined, in which two or more rows and columns are deleted. We do not need to use these and will not discuss them.

EXAMPLE 9.12 Expand the 3 by 3 determinant of the matrix **A** by minors.

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11} \begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12} \begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13} \begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}.$$

$$= a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} + a_{12}a_{23}a_{31} + a_{13}a_{21}a_{32} - a_{13}a_{22}a_{31}.$$

EXERCISE 9.18 ► Expand the following determinant by minors:

$$\begin{vmatrix} 3 & 2 & 0 \\ 7 & -1 & 5 \\ 2 & 3 & 4 \end{vmatrix}.$$

◄

EXERCISE 9.19 ► Expand the 4 by 4 determinant by minors

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix}$$

◄

Determinants have a number of important properties:

1. If two rows of a determinant are interchanged, the result will be a determinant whose value is the negative of the original determinant. The same is true if two columns are interchanged.

2. If two rows or two columns of a determinant are identical, the determinant has value zero.

3. If each element in one row or one column of a determinant is multiplied by the same quantity c the value of the new determinant is c times the value of the original determinant. Therefore, if an n by n determinant has every element multiplied by c, the new determinant is c^n times the original determinant.

4. If every element in any one row or in any one column of a determinant is zero, the value of the determinant is zero.

5. If any row is replaced, element by element, by that row plus a constant times another row, the value of the determinant is unchanged. The same is true for

two columns. For example,

$$\begin{vmatrix} a_{11}+ca_{12} & a_{12} & a_{13} \\ a_{21}+ca_{22} & a_{22} & a_{13} \\ a_{31}+ca_{32} & a_{32} & a_{33} \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}. \tag{9.60}$$

6. The determinant of a triangular matrix (a *triangular determinant*) is equal to the product of the diagonal elements. For example,

$$\begin{vmatrix} a_{11} & 0 & 0 \\ a_{22} & a_{22} & 0 \\ a_{21} & a_{32} & a_{33} \end{vmatrix} = a_{11}a_{22}a_{33}. \tag{9.61}$$

7. The determinant of a matrix is equal to the determinant of the transpose of that matrix.

$$\det(\tilde{\mathbf{A}}) = \det(\mathbf{A}). \tag{9.62}$$

These properties can be verified using the expansion of a determinant by minors.

EXERCISE 9.20 ► (a) Find the value of the determinant

$$\begin{vmatrix} 3 & 4 & 5 \\ 2 & 1 & 6 \\ 3 & -5 & 10 \end{vmatrix}.$$

(b) Interchange the first and second columns and find the value of the resulting determinant.

(c) Replace the second column by the sum of the first and second columns and find the value of the resulting determinant.

(d) Replace the second column by the first, thus making two identical columns, and find the value of the resulting determinant.

◄

There is an application of determinants in quantum chemistry that comes from Property 1. The electronic wave function of a system containing two or more electrons must change sign but keep the same magnitude if the coordinates of two of the electrons are interchanged (the wave function must be *antisymmetric*). For example, if $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of two electrons and Ψ is a multi-electron wave function, then the wave function must obey

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots, \mathbf{r}_n) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_4, \ldots, \mathbf{r}_n) \tag{9.63}$$

with similar equations for exchanging any other pair of electrons' coordinates. Many approximate multi-electron wave functions are constructed as a product of

one-electron wave functions, or *orbitals*. If ψ_1, ψ_2, and so on, are orbitals such a wave function for n electrons is written as

$$\Psi = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_3(\mathbf{r}_3)\psi_4(\mathbf{r}_4)\cdots\psi_n(\mathbf{r}_n). \tag{9.64}$$

where $\mathbf{r}_1$, $\mathbf{r}_2$, $\cdots$ represent the coordinates of electron 1, electron 2, and so on. This wave function does not obey the antisymmetry condition of Eq. (9.63). A wave function that does obey this equation can be constructed as a *Slater determinant*.[3] The elements of this determinant are the orbital functions, so the determinant is equal to a function of the coordinates of all electrons:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) & \cdots & \psi_1(\mathbf{r}_n) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) & \cdots & \psi_2(\mathbf{r}_n) \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) & \cdots & \psi_3(\mathbf{r}_n) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_n(\mathbf{r}_1) & \psi_n(\mathbf{r}_2) & \psi_n(\mathbf{r}_3) & \cdots & \psi_n(\mathbf{r}_n) \end{vmatrix}. \tag{9.65}$$

The factor $1/\sqrt{n!}$ is a normalizing factor, which is not important to us now. The Slater determinant obeys the antisymmetry property, since interchanging $\mathbf{r}_1$ and $\mathbf{r}_2$, for example, is the same as interchanging two columns, which changes the sign of the determinant. If we attempt to write such a wave function with two electrons in the same orbital (two of the ψ factors identical), then two rows of the determinant are identical, and the entire determinant vanishes by Property 2. This is the *Pauli exclusion principle*, which states that no two electrons in the same atom or molecule can occupy the same orbital.[4]

9.4 Matrix Algebra with Mathematica

As you have seen, matrix algebra can be tedious. Mathematica has all of the matrix operations built into it, so that you can form matrix products and carry out matrix inversion automatically. Mathematica treats matrices as lists of lists, with the elements of each row entered as a list. A list is entered inside curly brackets ("braces") with the elements separated by commas. A list of lists requires braces around the set of lists with braces and commas. For example, to enter the following 3 by 3 matrix

$$\mathbf{A} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}, \tag{9.66}$$

you would type in the following:

```
Clear[a]
a={{1, 2, 3}, {4, 5, 6},{7, 8, 9}}
```

and press the "Enter" key or a "Shift-Return." Mathematica will type the following:

```
In[1]:= a={{1, 2, 3}, {4, 5, 6},{7, 8, 9}}
```

[3] After John C. Slater, 1900–1976, a prominent American physicist and chemist.

[4] The Pauli exclusion principle is named for Wolfgang Pauli, 1900–1958, who received the 1945 Nobel Prize in physics for his contributions to quantum mechanics.

Note that the symbol that we chose for the matrix name is in lower case and requires no auxiliary labels. You should start the names of all Mathematica variables with lowercase letters to avoid possible confusion with Mathematica operators and functions. If you want to see the matrix **A** in standard form, type the statement MatrixForm[a] and press the "Enter" key or the "Shift-Return."

Mathematica treats vectors as a single list. It does not distinguish between row vectors and column vectors. If you want to enter a vector $v = (2, 4, 6)$, you enter the components inside curly brackets separated by commas as follows:

v={2, 4, 6}

followed by pressing the "Enter" key or a "Shift-return." A diagonal matrix is entered as a single list inside square brackets. To enter the diagonal matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 4 \end{bmatrix}, \tag{9.67}$$

use the statement

DiagonalMatrix[{1,2,4}]

When you press "Enter" or "Shift-Return" you get the output

Out[1]={{1,0,0,},{0,2,0,},{0,0,4}}

After two matrices A and B have been entered, a matrix multiplication is carried out by the statement

a.b

where you type a period between the symbols for the matrices. The product of a row vector with a matrix is accomplished with the statement

v.a

and a product of a matrix and a column vector is accomplished with the statement

a.v

The inverse of a matrix is obtained with the statement

Inverse[a]

If the matrix is singular and does not have an inverse, Mathematica will tell you so. To obtain the determine of a square matrix **A**, use the statement

Det[a]

Remember the capitalization. Mathematica does not allow alternate choices to its statements.

EXERCISE 9.21 ► Obtain the inverse of the following matrix by hand. Then use Mathematica to verify your answer. ◄

$$\begin{bmatrix} 1 & 3 & 0 \\ 3 & 0 & 4 \\ 1 & 2 & 0 \end{bmatrix}$$

Mathematica is a large and powerful program, and you can refer to the book by Wolfram listed at the end of this book to learn more about its use.

9.5 An Elementary Introduction to Group Theory

A mathematical *group* is a collection of elements with a single method for combining two elements of the group. We call the method multiplication in order to exploit the similarities of this operation with matrix and operator multiplication. The following requirements must be met:

1. If **A** and **B** are members of the group, and **F** is the product **AB**, then **F** must be a member of the group.
2. The group must contain the identity element, **E**, such that

$$\mathbf{AE} = \mathbf{EA} = \mathbf{A}. \tag{9.68}$$

3. The inverse of every element of the group must be a member of the group.
4. The associative law must hold:

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C}. \tag{9.69}$$

It is not necessary that the elements of the group commute with each other. That is, it is possible that

$$\mathbf{AB} \neq \mathbf{BA} \quad \text{(possible but not required)} \tag{9.70}$$

If all the members of the group commute, the group is called *abelian*.[5]

The set of symmetry operators which "belong" to a symmetrical object in the sense of Section 9.3 form a group if we define operator multiplication to be the method of combining two elements of the group.

We illustrate this fact for the ammonia molecule, NH_3. In its equilibrium conformation, the molecule is a triangular pyramid.[6] Figure 9.4a shows the nuclear framework as viewed from the first octant of the coordinate system, and Fig. 9.4b shows the framework as viewed from the positive end of the z axis. The molecule is placed in the coordinate system in the conventional way, with the center of mass at the origin and the rotation axis of highest order (largest value of n) along the z axis.

The symmetry elements of the molecule are shown in the figure. The symmetry operators that belong to the nuclear framework are $\hat{E}$, $\hat{C}_3$, $\hat{C}_3^2$ and the three reflection operators corresponding to vertical mirror planes passing through each of the three hydrogen nuclei, which we call $\hat{\sigma}_a$, $\hat{\sigma}_b$, and $\hat{\sigma}_c$. The square of the $\hat{C}_3$ operator is included because we must include the inverse of all operators in the group and $\hat{C}_3^2$ is the inverse of $\hat{C}_3$.

We now satisfy ourselves that the four conditions to have a group are met:

Condition 1. The product of any two members of the group must be a member of the group. We show this by constructing a multiplication table, as shown in Table 9.1. The operators listed in the first column of the table are used as the left factor, and the operators listed in the first row of the table are used as the right factor

[5] After Niels Henrik Abel, 1802–1829, a great Norwegian mathematician, who was the first to show that a general fifth-degree algebraic equation cannot be solved by a radical expression.

[6] This discussion is adapted from Ira N. Levine, *Molecular Spectroscopy*, pp. 390ff, Wiley, New York, 1975.

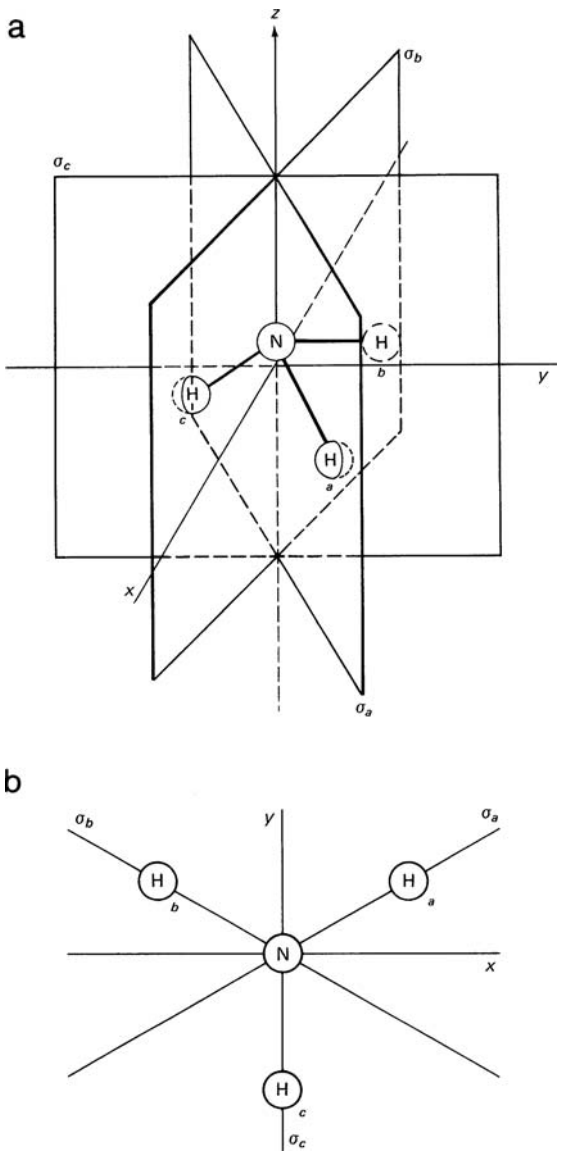

Figure 9.4 ► (a) The NH_3 molecule in its coordinate axes, with symmetry elements shown (after Levine). (b) The NH_3 molecule viewed from the positive z axis (after Levine).

TABLE 9.1 ► Multiplication Table for the Symmetry Operators of the NH_3 Molecule

	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$
$\hat{E}$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$
$\hat{C}_3$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{E}$	$\hat{\sigma}_c$	$\hat{\sigma}_a$	$\hat{\sigma}_b$
$\hat{C}_3^2$	$\hat{C}_3^2$	$\hat{E}$	$\hat{C}_3$	$\hat{\sigma}_b$	$\hat{\sigma}_c$	$\hat{\sigma}_a$
$\hat{\sigma}_a$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{\sigma}_c$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$
$\hat{\sigma}_b$	$\hat{\sigma}_b$	$\hat{\sigma}_c$	$\hat{\sigma}_a$	$\hat{C}_3^2$	$\hat{E}$	$\hat{C}_3$
$\hat{\sigma}_c$	$\hat{\sigma}_c$	$\hat{\sigma}_a$	$\hat{\sigma}_b$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{E}$

in a product. We must specify which factor comes first because the operators do not necessarily commute. The entries in the table are obtained as in the example:

EXAMPLE 9.13 Find the product $\hat{\sigma}_c\hat{C}_3$.

SOLUTION ► Both of these operators leave the nitrogen nucleus in its original location. The $\hat{C}_3$ operator moves the hydrogen nucleus originally at the σ_a plane to the σ_b plane, the nucleus originally at the σ_b plane to the σ_c plane, and the nucleus originally at the σ_c plane to the σ_a plane. The $\hat{\sigma}_c$ operator reflects in the σ_c plane, so that it exchanges the nuclei at the σ_a and σ_b planes. It thus returns the nucleus originally at the σ_c plane to its original position and moves the nucleus originally at the σ_c plane to the σ_b plane. This is the same as the effect that the $\hat{\sigma}_a$ operator would have, so

$$\hat{\sigma}_c\hat{C}_3 = \hat{\sigma}_a.$$

◄

EXERCISE 9.22 ► Verify several of the entries in Table 9.1. ◄

Some pairs of operators in this group commute, whereas others do not. For example, $\hat{C}_3\hat{\sigma}_c = \hat{\sigma}_b$, whereas $\hat{\sigma}_c\hat{C}_3 = \hat{\sigma}_a$.

Condition 2. The group does contain the identity operator, $\hat{E}$.

Condition 3. The inverse of every operator is in the group. Each reflection operator is its own inverse, and the inverse of $\hat{C}_3$ is $\hat{C}_3^2$.

Condition 4. The multiplication operation is associative, because operator multiplication is always associative.

A group that consists of point symmetry operators is called a *point group*. There is only a limited number of point groups that exist, and each is assigned a symbol, called a *Schoenflies symbol*. The point group of the NH_3 molecule is called the C_{3v} group. This symbol is chosen because the principal rotation axis is a C_3 axis, and because there are vertical mirror planes. You can communicate what the symmetry properties of the NH_3 molecule are by saying that it has C_{3v} symmetry. Flow charts have been constructed for the routine assignment of Schoenflies symbols.[7]

The H_2O molecule belongs to the C_{2v} point group, which contains the operators $\hat{E}$, $\hat{C}_2$, and two reflection operators, one whose mirror plane is the plane of the nuclei and one whose mirror plane bisects the angle between the bonds and is perpendicular to the first.

EXERCISE 9.23 ► Obtain the multiplication table for the C_{2v} point group and show that it satisfies the conditions to be a group. ◄

Symmetry Operators and Matrices

Operator algebra and matrix algebra are quite similar, and matrices can be used to represent symmetry operators. A set of matrices that represent all of the elements of a group is called a *representation* of that group. Equation (9.28) represents the action of a general symmetry operator, $\hat{A}$, on the location of a point. Let the original location of the point be given by the Cartesian coordinates (x, y, z), and the final coordinates be given by (x', y', z'):

$$\hat{A}(x, y, z) = (x', y', z'). \tag{9.71}$$

[7] See, for example, P. W. Atkins, *Physical Chemistry*. 6th ed. p. 433, Freeman, New York, 1998.

If we represent the position vectors by 3 by 1 matrices (column vectors) this can be written as a matrix equation:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \tag{9.72}$$

Equation (9.72) is the same as three ordinary equations:

$$a_{11}x + a_{12}y + a_{13}z = x' \tag{9.73a}$$
$$a_{21}x + a_{22}y + a_{23}z = y' \tag{9.73b}$$
$$a_{31}x + a_{32}y + a_{33}z = z'. \tag{9.73c}$$

We can obtain the elements of the matrix that represents $\hat{A}$ by comparing these equations with the equations obtained in Section 9.2 for various symmetry operators. For example, in the case of the identity operator, $x = x'$, $y = y'$, and $z = z'$, so that the matrix for the identity symmetry operator is the 3 by 3 identity matrix.

$$\hat{E} \leftrightarrow \mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{9.74}$$

The double-headed arrow means that the symmetry operator $\hat{E}$ and the matrix **E** are equivalent. That is, the matrix product in Eq. (9.72) and the operator expression in Eq. (9.71) give the same result. We sometimes say that there is a *one-to-one correspondence* between this operator and this matrix.

EXAMPLE 9.14 Find the matrix that represents $\hat{C}_n(z)$.

SOLUTION ► Let $\alpha = 2\pi/n$ radians, the angle through which the operator rotates a particle,

$$x' = \cos(\alpha)x - \sin(\alpha)y$$
$$y' = \sin(\alpha)x + \cos(\alpha)y$$
$$z' = z.$$

Comparison of this with Eq. (9.73a) gives

$$\hat{C}_n(z) \leftrightarrow \begin{bmatrix} \cos(\alpha) & -\sin(\alpha) & 0 \\ \sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{9.75}$$

◄

EXERCISE 9.24 ►

(a) Verify Eqs. (9.74) and (9.75) by matrix multiplication.

(b) Use Eq. (9.75) to find the matrix for $\hat{C}_2(z)$.

(c) Find the matrices equivalent to $\hat{S}_3(z)$ and $\hat{\sigma}_h$.

◄

The matrices that represent a group of symmetry operators have the same effect as the symmetry operators, so they must multiply together in the same way. We can show this for our present representation by carrying out the matrix multiplications. The matrices for the C_{3v} group are

$$\hat{E} \leftrightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{E},\ \hat{C}_3 \leftrightarrow \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{A} \tag{9.76}$$

$$\hat{C}_3^2 \leftrightarrow \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{B},\ \hat{\sigma}_a \leftrightarrow \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{C}$$

$$\hat{\sigma}_b \leftrightarrow \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{D},\ \hat{\sigma}_c \leftrightarrow \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{F},$$

where we have given each matrix an arbitrarily chosen letter symbol.

EXERCISE 9.25 ▶

(a) By transcribing Table 9.1 with appropriate changes in symbols, generate the multiplication table for the matrices in Eq. (9.76).

(b) Verify several of the entries in the multiplication table by matrix multiplication.

◀

Each of the matrices in Eq. (9.76) is equivalent to one of the symmetry operators in the C_{3v} group, but it is not exactly identical to it, being only one possible way to represent the symmetry operator. Any set of matrices that obeys the same multiplication table as a given group is called a *representation* of that group. Our set of matrices forms another group of the same *order* (same number of members) as the C_{3v} point group. The fact that it obeys the same multiplication table is expressed by saying that it is *isomorphic* with the group of symmetry operators. A group of matrices that is isomorphic with a group of symmetry operators is called a *faithful representation* of the group. Our group of matrices consists of 3 by 3 matrices and is said to be of *dimension 3*.

The representation of the C_{3v} group that we have presented is said to have the coordinates x, y, and z as its *basis*. Other representations can be obtained by using other functions as a basis and determining how the symmetry operators change these functions. The matrices in a representation do not have to have any physical interpretation, but they must multiply in the same way as do the symmetry operators, must be square, and all must have the same number of rows and columns. In some representations, called *unfaithful* or *homomorphic*, there are fewer matrices than there are symmetry operators, so that one matrix occurs in the places in the multiplication table where two or more symmetry operators occur.

Group representations are divided into two kinds, *reducible* and *irreducible*. In a reducible representation, the matrices are "block-diagonal" or can be put into block-diagonal form by a *similarity transformation*. A similarity transformation

means forming the matrix product

$$\mathbf{P} = \mathbf{X}^{-1}\mathbf{Q}\mathbf{X} \tag{9.77}$$

where **P**, **X**, and **Q** are square matrices. A *block-diagonal matrix* is one in which all elements are zero except those in square regions along the diagonal. The following matrix has two 2 by 2 blocks and a 1 by 1 block

$$\begin{vmatrix} 1 & 2 & 0 & 0 & 0 \\ 3 & 2 & 0 & 0 & 0 \\ 0 & 0 & 4 & 3 & 0 \\ 0 & 0 & 3 & 3 & 0 \\ 0 & 0 & 0 & 0 & 2 \end{vmatrix}.$$

All the matrices in a reducible representation have the same size blocks in the same order. The representation of the group C_{3v} given in Eq. (9.76) is reducible, since each matrix has a 2 by 2 block and a 1 by 1 block. When two block-diagonal matrices with the same size blocks are multiplied together, the result is a matrix that is block-diagonal with the same size blocks in the same order. This is apparent in the case of the matrices in Eq. (9.76), which produce only each other when multiplied together.

EXERCISE 9.26 ▶ Show by matrix multiplication that two matrices with a 2 by 2 block and two 1 by 1 blocks produce another such matrix when multiplied together. ◀

Because of the way in which block-diagonal matrices multiply, the 2 by 2 blocks in the matrices in Eq. (9.76) if taken alone form another representation of the C_{3v} group. When a reducible representation is written with its matrices in block-diagonal form, the block submatrices form irreducible representations, and the reducible representation is said to be the *direct sum* of the irreducible representations. Both the representations obtained from the submatrices are irreducible. The 1 by 1 blocks form an unfaithful or homomorphic representation, in which every operator is represented by the 1 by 1 identity matrix. This one-dimensional representation is called the *totally symmetric representation*. In this particular case we could not get three one-dimensional representations, because the $\hat{C}_3(z)$ operator mixes the x and y coordinates of a particle, preventing the matrices from being diagonal.

EXERCISE 9.27 ▶ Pick a few pairs of 2 by 2 submatrices from Eq. (9.76) and show that they multiply in the same way as the 3 by 3 matrices. ◀

In any representation of a symmetry group, the trace of a matrix is called the *character* of the corresponding operator for that representation.

EXERCISE 9.28 ▶ Find the characters of the operators in the C_{3v} group for the representation in Eq. (9.76). ◀

The two irreducible representations of the C_{3v} group that we have obtained thus far are said to be *nonequivalent*, since they have different dimensions. There are several theorems governing irreducible representations for a particular group.[8]

[8] Ira N. Levine, *Quantum Chemistry*, Vol. II, p. 389, Allyn & Bacon, Boston, 1970.

These theorems can be used to determine that three irreducible representations of the C_{3v} group occur, and that their dimensions are 2, 1, and 1. The other one-dimensional representation is

$$\begin{array}{cccc} \hat{E} \leftrightarrow 1 & \hat{C}_3 \leftrightarrow 1 & \hat{C}_3^2 \leftrightarrow 1 \\ \hat{\sigma}_a \leftrightarrow -1 & \hat{\sigma}_b \leftrightarrow -1 & \hat{\sigma}_c \leftrightarrow -1. \end{array} \tag{9.78}$$

EXERCISE 9.29 ► Show that the 1 by 1 matrices (scalars) in Eq. (9.78) obey the same multiplication table as does the group of symmetry operators. ◄

Group theory can be applied to several different areas of molecular quantum mechanics, including the symmetry of electronic and vibrational wave functions and the study of transitions between energy levels.[9] There is also a theorem which says that there is a correspondence between an energy level and some one of the irreducible representations of the symmetry group of the molecule, and that the degeneracy (number of states in the level) is equal to the dimension of that irreducible representation.

SUMMARY

We discussed three topics in this chapter: operator algebra, matrix algebra, and group theory. A mathematical operator is a symbol standing for the carrying out of a mathematical operation. Operating on a function with an operator produces a new function. Operator symbols can be manipulated in a way similar to the algebra of ordinary variables, without reference to any function that might be operated on. We defined the sum and the product of two operators. The product of two operators was defined as successive operation with the operators. The quotient of two operators was not defined, but we defined the inverse of an operator, which undoes the effect of that operator. The principal difference between operator algebra and ordinary algebra is that multiplication of two operators is not necessarily commutative. We discussed symmetry operators, a useful class of operators which move points in space relative to a symmetry element.

A matrix is a list of quantities, arranged in rows and columns. Matrix algebra is similar to operator algebra in that multiplication of two matrices is not necessarily commutative. The inverse of a matrix is similar to the inverse of an operator. If $\mathbf{A}^{-1}$ is the inverse of $\mathbf{A}$, then $\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{E}$, where $\mathbf{E}$ is the identity matrix. We presented the Gauss-Jordan method for obtaining the inverse of a nonsingular square matrix.

Group theory is a branch of mathematics that involves elements with defined properties and a single method to combine two elements called multiplication. The symmetry operators belonging to any symmetrical object form a group. The theorems of group theory can provide useful information about electronic wave functions for symmetrical molecules, spectroscopic transitions, and so forth.

[9] See P. W. Atkins, *Physical Chemistry*, 6th ed., Chap. 15, Freeman, New York, 1998.

PROBLEMS

1. Find the following commutators, where $D_x = d/dx$:

a) $[\hat{D}_x, \sin(x)]$;

b) $[\hat{D}_x^3, x]$;

2. Find the following commutators, where $D_x = d/dx$:

a) $[\hat{D}_x^3, x^2]$;

b) $[\hat{D}_x^2, f(x)]$.

3. Show that the x and z components of the angular momentum have quantum mechanical operators that do not commute and find their commutator:

$$\hat{L}_x = \frac{\hbar}{i}\left(\hat{y}\frac{d}{dz} - \hat{z}\frac{d}{dy}\right), \quad \hat{L}_z = \frac{\hbar}{i}\left(\hat{x}\frac{d}{dy} - \hat{y}\frac{d}{dx}\right).$$

4. The Hamiltonian operator for a one-dimensional harmonic oscillator moving in the x direction is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{kx^2}{2}.$$

Find the value of the constant a such that the function e^{-ax^2} is an eigenfunction of the Hamiltonian operator. The quantity k is the force constant, m is the mass of the oscillating particle, and $\hbar$ is Planck's constant divided by 2π.

5. In quantum mechanics, the *expectation value* of a mechanical quantity is given by

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi \, dx}{\int \psi^* \psi \, dx},$$

where $\hat{A}$ is the operator for the mechanical quantity and ψ is the wave function for the state of the system. The integrals are over all permitted values of the coordinates of the system. The expectation value is defined as the prediction of the mean of a large number of measurements of the mechanical quantity, given that the system is in the state corresponding to ψ prior to each measurement.

For a particle moving in the x direction only and confined to a region on the x axis from $x = 0$ to $x = a$, the integrals are single integrals from 0 to a and $\hat{p}_x$ is given by $(\hbar/i)\partial/\partial x$. Find the expectation value of p_x and of p_x^2 if the wave function is

$$\psi = C \sin\left(\frac{\pi x}{a}\right),$$

where C is a constant.

6. If $\hat{A}$ is the operator corresponding to the mechanical quantity A and ϕ_n is an eigenfunction of $\hat{A}$, such that

$$\hat{A}\phi_n = a_n \phi_n$$

show that the expectation value of A is equal to a_n if the state of the system corresponds to ϕ_n. See Problem 5 for the formula for the expectation value.

7. If x is an ordinary variable, the Maclaurin series for $1/(1-x)$ is

$$\frac{1}{1-x} = 1 + x^2 + x^3 + x^4 + \cdots .$$

If $\hat{X}$ is some operator, show that the series

$$1 + \hat{X} + \hat{X}^2 + \hat{X}^3 + \hat{X}^4 + \cdots$$

is the inverse of the operator $1 - \hat{X}$.

8. Find the result of each operation on the given point (represented by Cartesian coordinates):

a) $\hat{\imath}(2, 4, 6)$

b) $\hat{C}_2(y)(1, 1, 1)$

c) $\hat{C}_3(z)(1, 1, 1)$

9. Find the result of each operation on the given point (represented by Cartesian coordinates):

a) $\hat{S}_4(z)(1, 1, 1)$

b) $\hat{C}_2(z)\hat{\imath}\hat{\sigma}_h(1, 1, 1)$

c) $\hat{S}_2(y)\hat{\sigma}_h(1, 1, 0)$.

10. Find the 3 by 3 matrix that is equivalent in its action to each of the symmetry operators:

a) $\hat{S}_2(z)$

b) $\hat{C}_2(x)$

11. Find the 3 by 3 matrix that is equivalent in its action to each of the symmetry operators:

a) $\hat{C}_8(x)$

b) $\hat{S}_6(x)$

12. Give the function that results if the given symmetry operator operates on the given function for each of the following:

a) $\hat{C}_4(z)x^2$

b) $\hat{\sigma}_h x \cos(x/y)$

13. Give the function that results if the given symmetry operator operates on the given function for each of the following:

a) $\hat{\imath}(x + y + z^2)$

b) $\hat{S}_4(x)(x + y + z)$

14. Find the matrix products. Use Mathematica to check your result.

a) $\begin{bmatrix} 0 & 1 & 2 \\ 4 & 3 & 2 \\ 7 & 6 & 1 \end{bmatrix} \begin{bmatrix} 1 & 2 & 3 \\ 6 & 8 & 1 \\ 7 & 4 & 3 \end{bmatrix}$

b) $\begin{bmatrix} 6 & 3 & 2 & -1 \\ -7 & 4 & 3 & 2 \\ 1 & 3 & 2 & -2 \\ 6 & 7 & -1 & -3 \end{bmatrix} \begin{bmatrix} 4 & 7 & -6 & -8 \\ 3 & -6 & 8 & -6 \\ 2 & 3 & -3 & 4 \\ -1 & 4 & 2 & 3 \end{bmatrix}$

15. Find the matrix products. Use Mathematica to check your result.

a) $\begin{bmatrix} 3 & 2 & 1 & 4 \end{bmatrix} \begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix}$

b) $\begin{bmatrix} 1 & 2 & 3 \\ 0 & 3 & -4 \\ 1 & -2 & 1 \\ 3 & 1 & 0 \end{bmatrix} \begin{bmatrix} 3 \\ 2 \\ 1 \\ 4 \end{bmatrix}$

c) $\begin{bmatrix} 6 & 3 & -1 \\ 7 & 4 & -2 \end{bmatrix} \begin{bmatrix} 1 & 4 & -7 & 3 \\ 2 & 5 & 8 & -2 \\ 3 & 6 & -9 & 1 \end{bmatrix}$

16. Show that $(\mathbf{AB})\mathbf{C} = \mathbf{A}(\mathbf{BC})$ for the matrices:

$$\mathbf{A} = \begin{bmatrix} 0 & 1 & 2 \\ 3 & 1 & -4 \\ 2 & 3 & 1 \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} 3 & 1 & 4 \\ -2 & 0 & 1 \\ 3 & 2 & 1 \end{bmatrix} \quad \mathbf{C} = \begin{bmatrix} 0 & 3 & 1 \\ -4 & 2 & 3 \\ 3 & 1 & -2 \end{bmatrix}$$

17. Show that $\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{AB} + \mathbf{AC}$ for the example matrices in the previous problem.

18. Test the following matrices for singularity. Find the inverses of any that are nonsingular. Multiply the original matrix by its inverse to check your work. Use Mathematica to check your work.

a) $\begin{bmatrix} 0 & 1 & 2 \\ 2 & 3 & 1 \\ 2 & 4 & 3 \end{bmatrix}$

b) $\begin{bmatrix} 6 & 8 & 1 \\ 7 & 3 & 2 \\ 4 & 6 & -9 \end{bmatrix}$

19. Test the following matrices for singularity. Find the inverses of any that are nonsingular. Multiply the original matrix by its inverse to check your work. Use Mathematica to check your work.

a) $\begin{bmatrix} 3 & 2 & -1 \\ -4 & 6 & 3 \\ 7 & 2 & -1 \end{bmatrix}$

b) $\begin{bmatrix} 0 & 2 & 3 \\ 1 & 1 & 1 \\ 2 & 0 & 1 \end{bmatrix}$

20. Find the matrix $\mathbf{P}$ that results from the similarity transformation

$$\mathbf{P} = \mathbf{X}^{-1}\mathbf{Q}\mathbf{X},$$

where

$$\mathbf{Q} = \begin{bmatrix} 1 & 2 \\ 2 & 1 \end{bmatrix}, \ \mathbf{X} = \begin{bmatrix} 2 & 3 \\ 4 & 3 \end{bmatrix}.$$

21. The H_2O molecule belongs to the point group C_{2v}, which contains the symmetry operators $\hat{E}$, $\hat{C}_2$, $\hat{\sigma}_a$, and $\hat{\sigma}_b$, where the C_2 axis passes through the oxygen nucleus and midway between the two hydrogen nuclei, and where the σ_a mirror plane contains the three nuclei and the σ_b mirror plane is perpendicular to the σ_a mirror plane.

a) Find the 3 by 3 matrix that is equivalent to each symmetry operator.

b) Show that the matrices obtained in part (a) have the same multiplication table as the symmetry operators, and that they form a group. The multiplication table for the group was to be obtained in Exercise 9.23.

22. Permutation operators are operators that interchange objects. Three objects can be arranged in $3! = 6$ different ways, or permutations. From a given arrangement, all six permutations can be attained by application of the six operators: $\hat{E}$, the identity operator; $\hat{P}_{12}$, which interchanges objects 1 and 2; $\hat{P}_{23}$, which interchanges objects 2 and 3; $\hat{P}_{13}$, which interchanges objects 1 and 3; $\hat{P}_{23}\hat{P}_{12}$, which interchanges objects 1 and 2 and then interchanges objects 2 and 3, and $\hat{P}_{23}\hat{P}_{13}$, which interchanges objects 1 and 3 and then interchanges objects 2 and 3. Satisfy yourself that each of these operators produces a different arrangement. Show that the six operators form a group. Construct a multiplication table for the group.

10

The Solution of Simultaneous Algebraic Equations

Preview

If there are two variables in an equation, such as $F(x, y) = 0$, then the equation can be solved for y as a function of x or x as a function of y, but in order to solve for constant values of both variables, a second equation, such as $G(x, y) = 0$, is required, and the two equations must be solved simultaneously. If there are n variables, n independent and consistent equations are required. In this chapter, we discuss various methods for finding the roots to sets of simultaneous equations.

Principal Facts and Ideas

1. To solve for n variables, n equations are required, and these equations must be independent and consistent.
2. Simultaneous linear inhomogeneous equations can be solved with various techniques, including elimination, use of Cramer's formula, and by matrix inversion.
3. Linear homogeneous simultaneous equations have a nontrivial solution only when a certain dependence condition is met.

Objectives

After studying this chapter, you should be able to:

1. solve any fairly simple set of several simultaneous linear equations by the method of elimination;
2. solve a set of linear inhomogeneous simultaneous equations by Cramer's method and by matrix inversion;

3. solve a set of linear homogeneous simultaneous equations using the dependence condition.

10.1 Simultaneous Equations with More than Two Unknowns

In Chapter 3, we discussed the use of the method of substitution and the method of elimination to solve the linear inhomogeneous set of two simultaneous equations:

$$a_{11}x + a_{12}y = c_1 \tag{10.1a}$$
$$a_{21}x + a_{22}y = c_2, \tag{10.1b}$$

where the a 's and the c's are constants. Systems of several equations are similar to pairs of equations for two unknowns. For a unique solution, you must have n independent and consistent equations to solve for n unknowns. Sometimes in practical calculations you will have more equations than you have unknowns. If the equations are not all consistent, you have what is called an *overdetermined system of equations*, which has no solution. If the equations arise from experimental measurements, the source of inconsistency is likely experimental error. In this case, you can pick various sets of n equations and solve them separately, presumably getting slightly different answers for different sets because of experimental error. The variation between different answers can be used to get an idea of the effects of the errors.

10.2 Cramer's Rule

This method is a systematic method for solving linear inhomogeneous equations. We illustrate the method with the set of two linear inhomogeneous equations in Eq. (10.1). Written in matrix form these equations are

$$\mathbf{AX} = \mathbf{C}, \tag{10.2}$$

where $\mathbf{A}$ is a square matrix, and $\mathbf{X}$ and $\mathbf{C}$ are column vectors (matrices with only one column):

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \tag{10.3}$$

EXERCISE 10.1 ▶ Use the rules of matrix multiplication to show that Eq. (10.2) is identical with Eq. (10.1). ◀

Cramer's rule states that the solutions to this set of equations are written as quotients of determinants:

$$x = \frac{\begin{vmatrix} c_1 & a_{12} \\ c_2 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} \tag{10.4}$$

$$y = \frac{\begin{vmatrix} a_{11} & c_1 \\ a_{21} & c_2 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}}. \tag{10.5}$$

The solutions are constructed as follows: The denominator in each expression is the determinant of the matrix **A**, and the numerator is the determinant of this matrix with one of the columns replaced by the column vector $\binom{c_1}{c_2}$. In the expression for x, the column of coefficients for x is replaced, and in the expression for y, the column of coefficients for y is replaced.

EXERCISE 10.2 ▶ Use Cramer's rule to solve the simultaneous equations

$$\begin{aligned} 4x + y &= 14 \\ 2x - 3y &= 0. \end{aligned}$$

◀

If there are more than two variables and more than two linear inhomogeneous equations, Cramer's rule uses exactly the same pattern. If we have a set of three equations

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = c_3 \tag{10.6}$$
$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = c_2 \tag{10.7}$$
$$a_{31}x_1 + a_{32}x_2 + a_{33}x_3 = c_3, \tag{10.8}$$

where we call the unknown quantities x_1, x_2, and x_3 instead of x, y, and z. This equation can be written in matrix notation:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} \tag{10.9}$$

or

$$\mathbf{AX} = \mathbf{C},$$

where **X** and **C** are the column vectors shown.

According to Cramer's rule the value of x_1 is given by

$$\boxed{x_1 = \frac{\begin{vmatrix} c_1 & a_{12} & a_{13} \\ c_2 & a_{22} & a_{23} \\ c_3 & a_{32} & a_{33} \end{vmatrix}}{\det(\mathbf{A})}}, \tag{10.10}$$

where $\det(\mathbf{A})$ is the determinant of the 3 by 3 matrix of the a coefficients. The determinant in the numerator is obtained by replacing the first column by the constants c_1, c_2, and c_3 (the column vector **C)**. The value of x_2 is given by a similar expression with the second column in the determinant in the numerator replaced by the constants c_1, c_2, and c_3. The value of x_3 is given by an expression with the third column in the determinant replaced by the column vector **C**.

EXAMPLE 10.1 Use Cramer's rule to find the value of x_1 that satisfies

$$\begin{bmatrix} 2 & 4 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} 21 \\ 4 \\ 10 \end{bmatrix}. \tag{10.11}$$

SOLUTION ►

$$x_1 = \frac{\begin{bmatrix} 21 & 4 & 1 \\ 4 & -1 & 1 \\ 10 & 1 & 1 \end{bmatrix}}{\begin{bmatrix} 2 & 4 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & 1 \end{bmatrix}} = \frac{21\begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} - 4\begin{bmatrix} 4 & 1 \\ 1 & 1 \end{bmatrix} + 10\begin{bmatrix} 4 & 1 \\ -1 & 1 \end{bmatrix}}{2\begin{bmatrix} -1 & 1 \\ 1 & 1 \end{bmatrix} - 1\begin{bmatrix} 4 &] \\ 1 & 1 \end{bmatrix} + 1\begin{bmatrix} 4 &] \\ -1 & 1 \end{bmatrix}}$$

$$= \frac{21(-1-1) - 4(4-1) + 10(4+1)}{2(-1-1) - (4-1) + (4+1)} = \frac{-4}{-2} = 2.$$

◄

EXERCISE 10.3 ► Find the values of x_2 and x_3 for the previous example. ◄

Cramer's rule for more than three linear inhomogeneous equations is completely analogous to this. We write the equations in matrix form

$$\mathbf{AX} = \mathbf{C},$$

where the matrices now have more than three rows and columns. In order to have a solution, the matrix $\mathbf{A}$ must be square and have the same number of rows and columns as the column vectors $\mathbf{X}$ and $\mathbf{C}$ have rows. Let $\mathbf{A}_n$ be the matrix that is obtained from $\mathbf{A}$ by replacing the nth column by the column vector $\mathbf{C}$. Cramer's rule is now written

$$\boxed{x_n = \frac{\det(\mathbf{A}_n)}{\det(\mathbf{A})}}. \tag{10.12}$$

Linear Dependence and Inconsistency

In Chapter 3 we discussed linear dependence and inconsistency in the case of two equations. We will not discuss completely the questions of consistency and independence for sets of more than two equations, but we will make the following comments, which apply to sets of linear inhomogeneous equations:

1. A set of n equations is said to be *linearly dependent* if a set of constants $b_1, b_2, \ldots, b_n$, not all equal to zero, can be found such that if the first equation is multiplied by b_1, the second equation by b_2, the third equation by b_3, and so on, the equations add to zero for all values of the variables. A simple example of linear dependence is for two of the equations to be identical. In this case, we could multiply one of these equations by $+1$ and the other by -1 and all of the remaining equations by 0 and have the equations sum to zero. If two equations are identical, one has only $n - 1$ usable equations and cannot solve

for n variables. More complicated types of linear dependence also occur, and in any case one has only $n - 1$ usable equations or fewer.

2. In the case of two identical equations, the determinant of the matrix **A** vanishes, from property 2 of determinants, described in Chapter 9. The determinant of **A** will also vanish in more complicated types of linear dependence. If det(**A**) vanishes, either the equations are linearly dependent or they are inconsistent.

3. It is possible for a set of equations to appear to be overdetermined and not actually be overdetermined if some of the set of equations are linearly dependent.

EXERCISE 10.4 ▶ See if the set of four equations in three unknowns can be solved:

$$\begin{aligned} x_1 + x_2 + x_3 &= 6 \\ x_1 + x_2 + x_3 &= 0 \\ 3x_1 + 3x_2 + x_3 &= 12 \\ 2x_1 + x_2 + 4x_3 &= 16 \end{aligned}$$

◀

10.3 Solution by Matrix Inversion

We write a set of linear inhomogeneous equations in matrix form:

$$\boxed{\mathbf{AX} = \mathbf{C}}, \tag{10.13}$$

where **A** is now an n by n square matrix, **X** is an n by 1 column vector containing the unknowns, and **C** is another n by 1 column vector containing constants. If we possess the inverse of **A**, we can multiply both sides this equation on the left by $\mathbf{A}^{-1}$ to get

$$\boxed{\mathbf{A}^{-1}\mathbf{AX} = \mathbf{X} = \mathbf{A}^{-1}\mathbf{C}}. \tag{10.14}$$

The solution is represented by a column vector that is equal to the matrix product $\mathbf{A}^{-1}\mathbf{C}$. In order for a matrix to possess an inverse, it must be *nonsingular*, which means that its determinant does not vanish. If the matrix is singular, the system of equations cannot be solved because it is either linearly independent or inconsistent. We have already discussed the inversion of a matrix in Chapter 9. The difficulty with carrying out this procedure by hand is that it is probably more work to invert an n by n matrix than to solve the set of equations by other means. However, with access to Mathematica, BASIC, or another computer language that automatically inverts matrices, you can solve such a set of equations very quickly.

EXERCISE 10.5 ► Solve the following set of simultaneous equations by matrix inversion:

$$\begin{aligned} 2x_1 + x_2 &= 1 \\ x_1 + 2x_2 + x_3 &= 2 \\ x_2 + 2x_3 &= 3. \end{aligned}$$

The inverse of the relevant matrix has already been obtained in Example 9.10. ◄

Gauss–Jordan Elimination

This is a systematic procedure for carrying out the method of elimination. It is very similar to the Gauss–Jordan method for finding the inverse of a matrix, described in Chapter 9. If the set of equations is written in the vector form

$$\mathbf{AX} = \mathbf{C},$$

we write an *augmented matrix* consisting of the **A** matrix and the **C** column vector written side by side. For a set of four equations, the augmented matrix is

$$\left[\begin{array}{cccc:c} a_{11} & a_{12} & a_{13} & a_{14} & c_1 \\ a_{21} & a_{22} & a_{23} & a_{24} & c_2 \\ a_{31} & a_{32} & a_{33} & a_{34} & c_3 \\ a_{41} & a_{42} & a_{42} & a_{44} & c_4 \end{array}\right]. \tag{10.15}$$

Row operations are carried out on this augmented matrix: a row can be multiplied by a constant, and one row can be subtracted from or added to another row. These operations will not change the roots to the set of equations, since such operations are equivalent to multiplying one of the equations by a constant or to taking the sum or difference of two equations. In Gauss–Jordan elimination, our aim is to transform the left part of the augmented matrix into the identity matrix, which will transform the right column into the four roots, since the set of equations will then be

$$\mathbf{EX} = \mathbf{C}'. \tag{10.16}$$

The row operations are carried out exactly as in Section 9.4 except for having only one column in the right part of the augmented matrix.

EXERCISE 10.6 ► Use Gauss–Jordan elimination to solve the set of simultaneous equations in the previous exercise. The same row operations will be required that were used in Example 9.10. ◄

There is a similar procedure known as *Gauss elimination*, in which row operations are carried out until the left part of the augmented matrix is in upper triangular form. The bottom row of the augmented matrix then provides the root for one variable. This is substituted into the equation represented by the next-to-bottom row, and it is solved to give the root for the second variable. The two values are substituted into the next equation, and so on.

Linear Homogeneous Equations

In Chapter 3 we discussed pairs of linear homogeneous equations for two variables. We found that such a pair of equations needed to be linearly dependent in order to have a solution other than the *trivial solution* $x = 0$, $y = 0$. The same is true of sets with more than two variables.

A set of three homogeneous equations in three unknowns is written

$$a_{11}x_1 + a_{12}x_2 + a_{13}x_3 = 0 \tag{10.17a}$$
$$a_{21}x_1 + a_{22}x_2 + a_{23}x_3 = 0 \tag{10.17b}$$
$$a_{31}x_2 + a_{32}x_2 + a_{33}x_3 = 0. \tag{10.17c}$$

If we attempt to apply Cramer's rule to this set of equations, without asking whether it is legitimate to do so, we find for example that

$$x_1 = \frac{\begin{vmatrix} 0 & a_{12} & a_{13} \\ 0 & a_{22} & a_{23} \\ 0 & a_{32} & a_{33} \end{vmatrix}}{\det(\mathbf{A})}. \tag{10.18}$$

If $\det(\mathbf{A}) \neq 0$, this yields $x_1 = 0$, and similar equations will also give $x_2 = 0$ and $x_3 = 0$. This trivial solution is all that we can have if the determinant of $\mathbf{A}$ is nonzero (i.e., if the three equations are independent). To have a nontrivial solution, the equations must be linearly dependent. In order to find a possible nontrivial solution, we investigate the condition

$$\det(\mathbf{A}) = 0, \tag{10.19}$$

which in the 3 by 3 case is the same as

$$a_{11}a_{22}a_{33} - a_{11}a_{23}a_{32} - a_{12}a_{21}a_{33} - a_{13}a_{22}a_{31} + a_{12}a_{23}a_{31} - a_{13}a_{21}a_{32} = 0 \tag{10.20}$$

This condition must be satisfied for a nontrivial solution to exist.

Matrix Eigenvalues and Eigenvectors

One case in which a set of linear homogeneous equations arises is the *matrix eigenvalue problem*. This problem is very similar to an eigenvalue equation for an operator, as in Eq. (9.3). The problem is to find a column vector, $\mathbf{X}$ and a scalar *eigenvalue* b, such that

$$\mathbf{BX} = b\mathbf{X}, \tag{10.21}$$

where $\mathbf{B}$ is the square matrix for which we want to find an eigenvector and $\mathbf{X}$ is a column vector (the *eigenvector*). Since the right-hand side of Eq. (10.21) is the same as $b\mathbf{EX}$ where $\mathbf{E}$ is the identity matrix, we can rewrite Eq. (10.21) as

$$(\mathbf{B} - b\mathbf{E})\mathbf{X} = 0, \tag{10.22}$$

which is a set of linear homogeneous equations written in the notation of Eq. (10.13). The equations must be linearly dependent in order to have a solution, so there are only $n - 1$ independent equations if this condition is satisfied.

EXAMPLE 10.2 Find the values of b and $\mathbf{X}$ that satisfy the eigenvalue equation

$$\begin{bmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \\ 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = b \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} \tag{10.23}$$

and also satisfy a "normalization" condition:

$$x_1^2 + x_2^2 + x_3^2 = 1. \tag{10.24}$$

Since the equations must be linearly dependent, this additional equation will provide unique values for the three variables.

SOLUTION ► In the form of Eq. (10.22),

$$\begin{bmatrix} 1-b & 1 & 0 \\ 1 & 1-b & 1 \\ 0 & 1 & 1-b \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = 0. \tag{10.25}$$

The condition that corresponds to Eq. (10.19) is

$$\begin{vmatrix} y & 1 & 0 \\ 1 & y & 1 \\ 0 & 1 & y \end{vmatrix} = y \begin{vmatrix} y & 1 \\ 1 & y \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & y \end{vmatrix} = y^3 - 2y = 0, \tag{10.26}$$

where we temporarily let $y = 1 - b$. Equation (10.26) is a cubic equation that can be solved by factoring. It has the three roots

$$y = 0, \quad y = \sqrt{2}, \quad y = -\sqrt{2}$$

or

$$b = 1, \quad b = 1 - \sqrt{2}, \quad b = 1 + \sqrt{2}. \tag{10.27}$$

The three roots in Eq. (10.27) are three different eigenvalues. It is only when b is equal to one of these three values that Eq. (10.23) has a nontrivial solution. Since we have three values of b, we have three different eigenvectors. We find the eigenvectors by substituting each value of b in turn into Eq. (10.25) and solving the set of equations. We begin with $b = 1$ and write

$$0 + x_2 + 0 = 0 \tag{10.28a}$$
$$x_1 + 0 + x_3 = 0 \tag{10.28b}$$
$$0 + x_2 + 0 = 0. \tag{10.28c}$$

It is now obvious that this set of equations is linearly dependent, as required, since the first and third equations are the same. Our solution is now

$$x_2 = 0 \tag{10.28d}$$
$$x_1 = -x_3. \tag{10.28e}$$

We have solved for two of the variables in terms of the third. Since we have only two independent equations, we do not have definite values for x_1 and x_3 until we apply the normalization condition of Eq. (10.24). Imposing it, we find for our first eigenvector

$$\mathbf{X} = \begin{bmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{bmatrix}. \tag{10.29}$$

The negative of this eigenvector could also have been taken.

We now seek the second eigenvector, for which $y = \sqrt{2}$, or $b = 1 - \sqrt{2}$. Equation (10.25)

becomes

$$\begin{aligned} \sqrt{2}x_1 + x_2 + 0 &= 0 \\ x_1 + \sqrt{2}x_2 + x_3 &= 0 \\ 0 + x_2 + \sqrt{2}x_3 &= 0. \end{aligned} \tag{10.30}$$

With the normalization condition, the solution to this is

$$\mathbf{X} = \begin{bmatrix} 1/2 \\ -1/\sqrt{2} \\ 1/2 \end{bmatrix}. \tag{10.31}$$

◄

EXERCISE 10.7 ►

(a) Verify Equation (10.31). Show that this is an eigenvector.

(b) Find the third eigenvector for the problem of the previous example.

◄

In various methods in quantum chemistry orbital functions are represented as linear combinations of functions from a basis set containing several functions. A set of simultaneous equations very similar to Eq. (10.22) arises that is to be solved for the coefficients in the linear combinations. The condition analogous to Eq. (10.19) is called a *secular equation*, and the eigenvalue b in Eq. (10.22) is replaced by the orbital energy. The simplest theory using this representation for molecular orbitals is the Hückel method,[1] which is known as a semi-empirical method because it relies on experimental data to establish values for certain integrals that occur in the theory while assuming that certain other integrals vanish.

10.4 The Use of Mathematica to Solve Simultaneous Equations

In Chapter 3, we introduced the use of Mathematica to solve a single algebraic equation, using the Solve statement and the NSolve statement. The Solve statement can also be used to solve simultaneous equations. The equations are typed inside curly brackets with commas between them, and the variables are listed inside curly brackets. To solve the equations

$$ax + by = c$$
$$gx + hy = k$$

we type the input entry

```
Solve[{a x + b y == c, g x + h y == k},{x,y}]
```

and press the "Enter" key. Notice the use of braces to notify Mathematica that we have a list of two equations and a list of two variables and the use of a space to indicate multiplication. The output is

Out[1] ={{$x \to ca + \frac{b(c\ g\ -\ a\ k)}{a(-(b\ g)\ +\ a\ h)}$, $y \to -\frac{(cg-ak}{-(b\ g)\ +\ a\ h)}$}}

To simplify the expressions for x and y, we use the fact that the percent symbol represents the last line of output and type

```
Simplify[%]
```

[1] Donald J. Royer, *Bonding Theory*, pp. 154–163, McGraw-Hill, New York, 1968.

We receive the output

Out[2]={{$x \to \frac{-(c\ h) + b\ k}{b\ g - a\ h}$, $y \to -\frac{-(c\ g) + a\ k}{-(b\ g) + a\ h}$}}

which is the expression obtained from Cramer's rule.

The *Eliminate statement* is used to eliminate one or more of the variables in a set of simultaneous equations. For example, to obtain a single equation in x from the set of equations above, you would type the input entry (note the double equal signs):

```
Eliminate[{a x + b y == c, g x + h y == k},y]
```

and would receive the output:

Out[1]=c h == b k – b g x + a h x

we solve this equation for x by typing

```
Solve[%,x]
```

We receive the output:

Out[2]={{$x \to \frac{-(c\ h) + b\ k}{b\ g - a\ h}$}}

The Use of Mathematica to Find Matrix Eigenvalues and Eigenvectors

Mathematica finds matrix eigenvalues and eigenvectors by use of the statements Eigenvalues[m] and Eigenvectors[m], where m denotes a matrix that has already been typed into the program.

EXAMPLE 10.3 Use Mathematica to find the eigenvalues and eigenvectors of the matrix in the previous example.

SOLUTION ► We open Mathematica and type the input statement

```
m={{1,1,0},{1,1,1},{0,1,1}}
```

We press the "Enter" key and see the output

```
Out[1]={{1,1,0},{1,1,1},{0,1,1}}
```

We then type the statement

```
Eigenvalues[m]
```

We press the "Enter" key and see the output

Out[2]={$1 + \sqrt{2}, 1, 1 - \sqrt{2}$}

We type the statement

```
Eigenvectors[m]
```

and see the output

Out[3]={{$1, \sqrt{2}, 1$}, {$-1, 0, 1$}, {$1, \sqrt{2}, 1$}} ◄

SUMMARY

To solve for numerical values of two variables, two equations are required, and they must be solved simultaneously, and similarly for more variables. We presented several methods for solving simultaneous equations. First was the method of substitution, which is not limited to linear equations, but which is not practical for more than two or three equations. We then presented several methods which can apply to sets of linear inhomogeneous equations. Cramer's method is a method

which uses determinants to obtain the roots. A set of linear equations can be written in matrix form and can be solved by finding the inverse of the matrix of the coefficients. The methods of Gauss elimination and Gauss–Jordan elimination were presented.

Finally, we examined linear homogeneous equations. With such a set, the equations possess only a trivial solution if the equations are linearly independent. The condition of dependence that must occur in order to have a nontrivial solution is represented by an equation in which the determinant of the matrix of the coefficients is set equal to zero. Matrix eigenvalue equations fall into this category, and we discussed the determination of the eigenvalues and eigenvectors, including the use of Mathematica to find the eigenvalues and eigenvectors.

PROBLEMS

1. Solve the set of simultaneous equations.

$$\begin{aligned} 3x + 4y + 5z &= 1 \\ 4x - 3y + 6z &= 3 \\ 7x + 2y - 6z &= 2 \end{aligned}$$

2. Solve the set of simultaneous equations.

$$\begin{aligned} y + z &= 1 \\ x + z &= 2 \\ x + y &= 3 \end{aligned}$$

3. Solve the set of equations, using Cramer's rule.

$$\begin{aligned} 3x_1 + x_2 + x_3 &= 19 \\ x_1 - 2x_2 + 3x_3 &= 13 \\ x_1 + 2x_2 + 2x_3 &= 23 \end{aligned}$$

Verify your result using Mathematica.

4. Solve the set of equations, using Gauss or Gauss-Jordan elimination.

$$\begin{aligned} x_1 + x_2 + x_3 &= 9 \\ 2x_1 - x_2 - x_3 &= 9 \\ x_1 + 2x_2 - x_3 &= 9 \end{aligned}$$

Use Mathematica to confirm your solution.

5. Solve the sets of equations.

a) $\begin{aligned} 3x_1 + 4x_2 + 5x_3 &= 25 \\ 4x_1 + 3x_2 - 6x_3 &= -7 \\ x_1 + x_2 + x_3 &= 6 \end{aligned}$

b)
$$\begin{bmatrix} 1 & 1 & 1 & 3 \\ 2 & 1 & 1 & 1 \\ 1 & 2 & 3 & 4 \\ 2 & 0 & 1 & 4 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} 6 \\ 5 \\ 10 \\ 7 \end{bmatrix}.$$

6. Decide whether the following set of equations has a solution. Solve the equations if it does.

$$\begin{aligned} 3x + 4y + z &= 13 \\ 4x + 3y + 2z &= 10 \\ 7x + 7y + 3z &= 23 \end{aligned}$$

7. Solve the set of equations by matrix inversion. If available, use Mathematica to invert the matrix.

$$\begin{aligned} 2x_1 + 4x_2 + x_3 &= 40 \\ x_1 + 6x_2 + 2x_3 &= 55 \\ 3x_1 + x_2 + x_3 &= 23 \end{aligned}$$

8. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}.$$

9. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}.$$

10. Find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \\ 1 & 0 & 1 \end{bmatrix}.$$

Does this matrix have an inverse?

11. In the Hückel method for finding approximate orbitals for electrons in a conjugated system of pi bonds, each orbital is represented as a linear combination of several basis functions. In the treatment of the cyclopropenyl radical, the basis functions are the three 2pz atomic orbitals, which we denote by f_1, f_2, and f_3.

$$\psi = c_1 f_1 + c_2 f_2 + c_3 f_3$$

The orbital energy, denoted by W, is expressed as a certain quotient of integrals and the minimum value of W is sought as a function of the c coefficients

by differentiating with respect to each c and setting The three simultaneous equations are

$$\begin{aligned} xc_1 + c_2 + c_3 &= 0 \\ c_1 + xc_2 + c_3 &= 0 \\ c_1 + c_2 + xc_3 &= 0, \end{aligned}$$

where $x = (\alpha - W)/\beta)$ and where α and β are certain integrals whose values are to be determined later.

a) The determinant of the c coefficients must be set equal to zero in order for a nontrivial solution to exist. This is the *secular equation*. Solve the secular equation, which will yield three different values of x.

b) Solve the three simultaneous equations, once for each value of x. Since there are only two independent equations, express c_2 and c_3 in terms of c_1.

c) Impose the normalization condition

$$c_1^2 + c_2^2 + c_3^2 = 1$$

to find the values of the c coefficients for each value of W.

d) Check your work by using Mathematica to find the eigenvalues and eigenvectors of the matrix

$$\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}.$$

11

The Treatment of Experimental Data

Preview

Some quantities in which we are interested can be measured directly. More often, a quantity must be calculated from other quantities that can be measured. This calculation process is called *data reduction*. The simplest form of data reduction is the use of a formula into which measured values are substituted. Other forms of data reduction include analysis of a set of data that can be represented by data points on a graph. Construction of such a graph and analysis of features of the graph, such as slopes and intercepts of lines, can provide values of variables. Statistical analysis done numerically can replace graphical analysis, providing better accuracy with less effort. We discuss both of these approaches.

We also discuss the analysis of the accuracy of experimental data. In the case that we can directly measure some desired quantity, we need to estimate the accuracy of the measurement. If data reduction must be carried out, we must study the propagation of errors in measurements through the data reduction process. The two principal types of experimental errors, random errors and systematic errors, are discussed separately. Random errors are subject to statistical analysis, and we discuss this analysis.

Principal Facts and Ideas

1. Every measured quantity is subject to experimental error.

2. When the value of a measured quantity is reported, an estimate of the expected error should be included.

3. Random experimental errors can be analyzed statistically if the measurement can be repeated a number of times.

4. Systematic errors must usually be estimated by educated guesswork.

5. The mean of a set of repeated measurements is a better estimate of the correct value of a variable than is a single measurement.

6. The probable random error in the mean of a set of repeated measurements can be determined statistically.

7. When a variable is calculated by substitution of measured quantities into a formula, the estimated errors in the measured quantities can be propagated through the calculation.

8. Another type of data reduction involves fitting a set of data to a formula. This can be done graphically or numerically by use of the least-squares (regression) procedure.

Objectives

After studying the chapter, you should be able to:

1. identify probable sources of error in a physical chemistry experiment and classify the errors as systematic or random;

2. calculate the mean and standard deviation of a sample of numbers;

3. calculate the probable error in the measured value of a directly measured quantity;

4. carry out data reduction using mathematical formulas and do an error propagation calculation to determine the probable error in the final calculated quantity;

5. carry out data reduction using graphical methods and determine the probable error in quantities obtained from the graphs;

6. carry out data reduction numerically using least squares and other numerical methods and determine probable errors in quantities obtained by these methods.

11.1 Experimental Errors in Measured Quantities

Once we have obtained a value for a measured quantity, we should try to determine how accurate that value is, since experimental error is always present. If a measurement can be repeated a number of times and if the repetitions agree well with each other, the set of data is said to have good *precision*. If a measurement agrees well with the correct value, it is said to have good *accuracy*. It is tempting to assume that a set of repetitions of a measurement that has high precision also has high accuracy, but this can be a poor assumption.

We divide experimental errors into two categories: *Systematic errors* recur with the same direction and with the same magnitude on every repetition of an experiment, so they can affect the accuracy of a measurement without affecting the precision. *Random errors* do not have the same direction and magnitude every time, so they affect the precision as well as the accuracy. Systematic errors are generally produced by limitations in the apparatus, whereas random errors usually arise from limitations in the technique used to carry out the experiment.

EXAMPLE 11.1 A simple apparatus for measuring the melting temperature of a substance consists of a small bath containing a liquid in which the sample can be suspended in a small capillary tube held next to a thermometer. The bath is slowly heated and the thermometer reading at the time of melting of the sample is recorded. List some of the possible experimental error sources in this determination. Classify each as systematic or random and guess its relative magnitude.

SOLUTION ► (a) Faulty thermometer calibration. This is systematic. With an inexpensive thermometer, this error might be as large as several tenths of a degree.

(b) Lack of thermal equilibration between the liquid of the bath, the sample, and the thermometer. If the experimental procedure is the same for all repetitions, this will be systematic. If the thermometer is larger than the sample, it will likely be heated more slowly than the sample if the heating is done too rapidly. This error will probably be less than 1°C.

(c) Failure to read the thermometer correctly. This is random. There are two kinds of error here. The first is more of a blunder than an experimental error and amounts to counting the marks on the thermometer incorrectly and, for example, recording 87.5 °C instead of 88.5 °C, and so on. The other kind of error is due to *parallax*, or looking at the thermometer at some angle other than a right angle. This might produce an error of about two-tenths of a degree Celsius.

(d) Presence of impurities in the sample. This is systematic, since impurities that dissolve in the liquid always lower the melting point. If carefully handled samples of purified substances are used, this error should be negligible.

(e) Failure to observe the onset of melting. This error is variable in magnitude, although always in the same direction. If the heating is done slowly, it should be possible to reduce this error to a few tenths of a degree.

◄

Some of the errors in this example can be minimized by reducing the rate of heating. This suggests a possible procedure: an initial rough determination establishes the approximate value, and a final heating is done with slow and careful heating near the melting point.

EXERCISE 11.1 ► List as many sources of error as you can for some of the following measurements. Classify as systematic or random and estimate the magnitude of each source of error.

(a) The measurement of the diameter of a copper wire with a micrometer caliper.

(b) The measurement of the length of a piece of glass tubing with a meter stick.

(c) The measurement of the mass of a porcelain crucible using a digital balance.

(d) The measurement of the mass of a silver chloride precipitate in a porcelain crucible using a digital balance.

(e) The measurement of the resistance of an electrical heater using a Wheatstone bridge.

(f) The measurement of the time required for an automobile to travel the distance between two highway markers 1 km apart, using a stopwatch.

◄

The usual approach to systematic errors is to make an educated guess about the inherent accuracy of the apparatus. For example, if we use a wooden meter stick we might conclude that its length is probably accurate to 0.2% or 0.3% because of shrinkage or swelling of the wood or poor calibration when the meter stick was manufactured. If we use a mercury-in-glass thermometer, we might conclude that it is accurate to about 0.3 °C because of faulty manufacture or calibration. Although it is useful to engage in educated guesswork, it is better to have some kind of objective way to estimate the magnitude of experimental errors. There are two principal ways to gain information about systematic errors. One is to modify the apparatus and repeat the measurement or to repeat the measurement with a different apparatus. For example, in making a voltage measurement with a potentiometer, one compares the voltage with that of a standard cell. One could see if the same result is obtained with a different standard cell. If the result is different, you can assume that at least one of the standard cells is contributing a systematic error that is likely as large as the difference in the values. Another possibility a change in the design of the apparatus. For example, the apparatus may include some insulation that minimizes unwanted heat transfer. If the measurement gives a different value when the insulation is improved, there was probably a systematic error at least as big as the change in the result. It is even better to use a totally different apparatus, possibly in a different laboratory. There have been cases in the literature in which some quantity was measured in one laboratory and a certain probable error was specified. When the measurement was made in a different laboratory a value was obtained that differed significantly from the first value, exposing the existence of systematic error in one or both of the measurements.

The other approach to the study of systematic errors is to use the same apparatus to measure a well-known quantity, observing the actual experimental error. For example, if you are measuring the melting temperature of an unknown substance, you could also measure the melting temperature of a known substance and compare your result with the accepted result. Any discrepancy could be due to systematic error, although if only one measurement is made you cannot separate the effects

of systematic and random errors. These methods of estimating systematic errors are usually not available in physical chemistry laboratory courses. In this event, educated guesswork is nothing to be ashamed of.

11.2 Statistical Treatment of Random Errors

Statistics is the study of a large set of people, objects, or numbers, called a *population*. The population is not studied directly, because of its large size or inaccessibility. A subset from the population, called a *sample*, is studied and the likely properties of the population are inferred from the properties of the sample. If several repetitions of a measurement can be made, this set of measurements can be considered to be a sample from a population. The population is an imaginary set of infinitely many repetitions of the measurement. Statistical analysis can be used to study the properties of the sample and to infer likely properties of the population.

Properties of a Population

The infinitely many members in a population of numerical quantities will be distributed among all values in some range according to some probability distribution. We have discussed probability distributions in Chapter 5. A *probability density* or *probability distribution* $f(x)$ is defined such that

$$(\text{probability of values of } x \text{ between } x' \text{ and } x' + dx) = f(x')dx \tag{11.1}$$

If the probability distribution is *normalized* the total probability of all occurrences equals unity:

$$\boxed{\int_a^b f(x)\,dx = 1}, \tag{11.2}$$

where a is the smallest possible value of x and b is the largest possible value. for convenience we will sometimes assume that $a = -\infty$ and that $b = +\infty$. This is generally not correct for measured quantities, but the probability of values of x with large magnitude is small so that this assumption will not introduce significant errors

The most important property of a population of numerical quantities is its *mean value*. If there are no systematic errors, the mean of the population of measurements will equal the correct value of the measured quantity, since random errors are equally likely in either direction and will cancel in taking the mean. If the probability distribution $f(x)$ is normalized the *population mean* μ is given by Eq. (5.69),

$$\boxed{\mu = \int_a^b xf(x)\,dx}. \tag{11.3}$$

The *population standard deviation* is a measure of the spread of the distribution, and is given by Eq. (5.74)

$$\boxed{\sigma_x = \left[\int_a^b (x-\mu)^2 f(x)dx\right]^{1/2}}, \tag{11.4}$$

where we add a subscript x to remind us that x is the variable being discussed.

EXERCISE 11.2 ▶ Show that the definition of the standard deviation in Eq. (11.4) is the same as that in Eq. (5.74). That is, show that

$$\int_a^b (x-\mu)^2 f(x)dx = \int_a^b x^2 f(x)dx - \left(\int_a^b xf(x)dx\right)^2. \qquad (11.5)$$

◀

We will assume that any population of experimental results is governed by the *Gaussian probability distribution* (also called the *normal distribution*), introduced in Chapter 5. The important properties of that distribution are as listed in that chapter:

1. A total of 68.3% of the members of the population have their values of x lying within one standard deviation of the mean: in the interval $\mu - \sigma_x < x < \mu + \sigma_x$.
2. A total of 95% of the members of the population have their values of x lying within 1.96 standard deviations of the mean: in the interval $\mu - 1.96\sigma_x < x < \mu + 1.96\sigma_x$.
3. The fraction of the population with value of x in the interval $\mu - x_1 < x < \mu + x_1$ is $\text{erf}(x_1/\sqrt{2}\sigma)$ where $\text{erf}(\cdots)$ stands for the error function, discussed in Appendix G.

If a random experimental error arises as the sum of many contributions, the *central limit theorem of statistics* gives some justification for assuming that our experimental error will be governed by the Gaussian distribution. This theorem states that if a number of *random variables* (independent variables) $x_1, x_2, \ldots, x_n$ are governed by some probability distributions with finite means and finite standard deviations, then a *linear combination* (weighted sum) of them

$$y = \sum_{i=1}^{n} a_i x_i \qquad (11.6)$$

is governed by a probability distribution that approaches a Gaussian distribution as n becomes large. If experimental errors arise from multiple sources, they should be at least approximately described by a Gaussian distribution.

There are other probability distributions that are used in statistics, including the *binomial distribution*, the *Poisson distribution*, and the *Lorentzian distribution*.[1] We will not discuss these distributions. However, all of them have properties that are qualitatively similar to those of the Gaussian distribution.

Properties of a Sample

Our sample is a set of repetitions of a measurement, which we think of as being selected randomly from a large population of many imaginary repetitions. From

[1] See Philip R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, Chap. 3, McGraw-Hill, New York, 1969, or Hugh D. Young, *Statistical Treatment of Experimental Data*, McGraw-Hill, New York, 1962, for discussions of various distributions.

this sample, we need to estimate the correct value of the measured quantity and the probable error in this estimate. We will assume that an average of our set of measurements gives the best estimate of the population mean, which is equal to the correct value if there are no systematic errors. There are several common averages. The *median* is a value such that half of the members of a set are greater than the median and half are smaller than the median. The *mode* is the value that occurs most frequently in a set. The *mean* of a set of N values is defined by Eq. (5.59)

$$\boxed{\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i}, \tag{11.7}$$

where $x_1, x_2, \ldots$ are the members of the set. In a population governed by the Gaussian distribution, the population median, the population mode, and the population mean all have the same value. In a sample of finite size the median, mode, and mean are not necessarily equal to each other. The mean of a sample taken from a population is said by statisticians to be an unbiased estimate of the population mean. We will use the mean of a set of repetitions as our estimate of the population mean, which is equal to the correct value if systematic errors are absent.

The *sample standard deviation* is defined by

$$\boxed{s_x = \left[\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2\right]^{1/2}}, \tag{11.8}$$

where $\bar{x}$ is the sample mean. The square of the standard deviation is called the *variance*. In Eq. (11.8), every term in the sum is positive or zero, since it is the square of a real quantity. The standard deviation can vanish only if every member of the sample is equal to the mean, and otherwise must be positive. The larger the differences between members of the set, the larger the standard deviation will be. In most cases, about two-thirds of the members of a sample will have values between $\bar{x} - s$ and $\bar{x} + s$.

It has been shown that if we use the $N - 1$ denominator of Eq. (11.8) instead of a denominator equal to N then s is an unbiased estimate of the population standard deviation σ. This has to do with the fact that in a sample of N members, there are N pieces of information, which means that there are $N - 1$ independent pieces of information in addition to the mean, or $N - 1$ *degrees of freedom* in addition to the mean.[2]

EXAMPLE 11.2 Find the mean and the standard deviation of the set of numbers

32.41, 33.76, 32.91, 33.04, 32.75, 33.23.

[2]These $N - 1$ degrees of freedom were illustrated once in a physical chemistry class that included one student who did not want the other students to know her score on an exam. The other students took their scores and the announced mean score and calculated the score of the first student.

SOLUTION ►

$$\bar{x} = \frac{1}{6}(32.41 + 33.76 + 32.91 + 33.04 + 32.75 + 33.23) = 33.02$$

$$s = \left\{\frac{1}{5}\left[(0.39)^2 + (0.74)^2 + (-0.11)^2 + (0.02)^2 + (0.27)^2 + (0.21)^2\right]\right\}^{1/2}$$
$$= 0.41.$$

One of the six numbers lies below 32.61, and one lies above 33.43, so that two-thirds of them lie between $\bar{x} - s$ and $\bar{x} + s$. ◄

EXERCISE 11.3 ► Find the mean, $\bar{x}$, and the sample standard deviation, s, for the following set of values: 2.876m, 2.881m, 2.864m, 2.879m, 2.872m, 2.889 m, 2.869m. Determine how many values lie below $\bar{x} - s$ and how many lie above $\bar{x} + s$. ◄

Numerical Estimation of Random Errors

A common practice among scientific workers is to make statements that have a 95% probability of being correct. Such a statement is said to be at the 95% *confidence level*. For example, we want to make a statement of the form

$$\text{correct value} = \mu = \bar{x} \pm \varepsilon \tag{11.9}$$

that has a 95% chance of being right. That is, we want to state an interval $\bar{x} - \varepsilon < x < \bar{x} + \varepsilon$ that has a 95% chance of containing the correct value μ, which we do not know. We call such an interval the 95% *confidence interval*, and we call the positive number ε the *probable error at the* 95% *confidence level* or the *estimated error*. If we knew the value of σ, the population standard deviation, we could make this statement after a single measurement. Since a single measurement has a 95% change of being within 1.96σ of μ, we could say with 95% confidence that

$$\mu = x \pm 1.96\sigma, \tag{11.10}$$

where x is the outcome of our single measurement. If we have no opportunity to repeat our measurement, the only thing we can do is to make educated guess of the value of σ.

However, let us assume that we can make N measurements of the same quantity. Think of our set of N measurements as only one possible set of N measurements from the same population. If we could take infinitely many sets of N measurements from our population, the means of these sets would themselves form a new population. If the original population is governed by a Gaussian distribution, the population of sample means will also be governed by a Gaussian distribution (although we do not prove this fact). The mean of this new population is the same as the mean of the original population, and σ_m, the standard deviation of the population of sample means, is given by

$$\sigma_m = \frac{\sigma}{\sqrt{N}}, \tag{11.11}$$

where σ is the standard deviation of the original population. The new population of sample means has a smaller spread than the original population, and its spread

becomes smaller as N becomes larger. That is, the means of the sets of measurements cluster more closely about the population mean if the number of members of each sample is made larger. If $N = 10$, $\sigma_m = 0.3162\sigma$, and if $N = 100$, $\sigma_m = 0.100\sigma$. Most people intuitively agree with the notion that the average of a set of measurements is more likely to come close to the correct value than is a single measurement.

If we knew the standard deviation of the original population, we would now be able to write an expression for the expected error in the mean of a set of N measurements:

$$\varepsilon = 1.96\sigma_m = \frac{1.96\sigma}{\sqrt{N}}. \tag{11.12}$$

However, we do not know the population standard deviation. Since we use the sample standard deviation as our estimate of the population standard deviation, we could write as a first approximation

$$\varepsilon = \frac{1.96s}{\sqrt{N}} \quad \text{(first approximation)}, \tag{11.13}$$

where s is the sample standard deviation. However, there is better estimate. A statistically correct formula was derived by Gossett.[3] Gossett defined the *Student t factor*

$$t = \frac{(\bar{x} - \mu)N^{1/2}}{s}, \tag{11.14}$$

where μ is the population mean, $\bar{x}$ is the sample mean, and s is the sample standard deviation. There is a different value of t for every sample. Although μ is not known, Gossett derived the probability distribution that t obeys.[4] From this distribution, which is called *Student's t distribution*, the maximum value of t corresponding to a given confidence level can be calculated for any value of N. The notation used is $t(\nu, 0.05)$. The quantity ν is the number of degrees of freedom, equal to $N - 1$, and 0.05 represents the confidence level of 95%. Table 11.1 gives these values for various values of N and for four different confidence levels. Notice that as N becomes large the maximum Student t value for 95% confidence (also called 0.05 significance) approaches 1.96, the factor in Eq. (11.13). For fairly small values of N the Student t distribution corresponds to larger probability for large values of $x - \mu$ than does the Gaussian distribution. However, as N becomes large the Student t distribution approaches a Gaussian distribution. Unfortunately, some authors use a different notation for the critical value of t, such as $t_\nu(0.025)$ to represent the Student t factor for $\nu + 1$ data points at the 95% confidence level.[5]

Using a value from Table 11.1, we can write a formula for the expected error in the mean at the 95% confidence level

$$\boxed{\varepsilon = \frac{t(\nu, 0.05)s}{\sqrt{N}}} \tag{11.15}$$

for a sample of $\nu + 1$ members (N members).

[3]William Sealy Gossett, 1876–1937, English chemist and statistician who published under the pseudonym "Student" in order to keep the competitors of his employer, a brewery, from knowing what statistical methods he was applying to quality control.

[4]See Walter Clark Hamilton, *Statistics in Physical Science*, pp. 78ff, The Ronald Press Company, New York, 1964.

[5]John A. Rice, *Mathematical Statistics and Data Analysis*, Wadsworth & Brooks/Cole, Pacific Grove, CA, 1988.

TABLE 11.1 ► Some Values of Student's t Factor*

Number of Degrees of Freedom	Maximum Value of Student's t Factor for the Significance Levels Indicated			
ν	$t(\nu, 0.60)$	$t(\nu, 0.10)$	$t(\nu, 0.05)$	$t(\nu, 0.01)$
1	1.376	6.314	12.706	63.657
2	1.061	2.920	4.303	9.925
3	0.978	2.353	3.182	5.841
4	0.941	2.132	2.776	4.604
5	0.920	2.015	2.571	4.032
6	0.906	1.943	2.447	3.707
7	0.896	1.895	2.365	3.499
8	0.889	1.860	2.306	3.355
9	0.883	1.833	2.262	3.250
10	0.879	1.812	2.228	3.169
11	0.876	1.796	2.201	3.106
12	0.873	1.782	2.179	3.055
13	0.870	1.771	2.160	3.012
14	0.868	1.761	2.145	2.977
15	0.866	1.753	2.131	2.947
16	0.865	1.746	2.120	2.921
17	0.863	1.740	2.110	2.898
18	0.862	1.734	2.101	2.878
19	0.861	1.729	2.093	2.861
20	0.860	1.725	2.086	2.845
21	0.859	1.721	2.080	2.831
22	0.858	1.717	2.074	2.819
23	0.858	1.714	2.069	2.807
24	0.857	1.711	2.064	2.797
25	0.856	1.708	2.060	2.787
26	0.856	1.706	2.056	2.479
27	0.855	1.703	2.052	2.771
28	0.855	1.701	2.048	2.763
29	0.854	1.699	2.045	2.756
30	0.854	1.697	2.042	2.750
40	0.851	1.684	2.021	2.704
60	0.848	1.671	2.000	2.660
∞	0.842	1.645	1.960	2.576

* John A. Rice, *Mathematical Statistics and Data Analysis*, Wadsworth & Brooks/Cole, Pacific Grove, CA, 1988, p. 560

EXAMPLE 11.3 Assume that the melting temperature of calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, has been measured 10 times, and that the results are 42.70 °C, 42.60 °C, 42.78 °C, 42.83 °C, 42.58 °C, 42.68 °C, 42.65 °C, 42.76 °C, 42.73 °C, and 42.71 °C. Ignoring systematic errors, determine the 95% confidence interval for the set of measurements.

SOLUTION ► Our estimate of the correct melting temperature is the sample mean:

$$\begin{aligned}\bar{T}_{melt} &= \frac{1}{10}(42.70\,^\circ\text{C} + 42.60\,^\circ\text{C} + 42.78\,^\circ\text{C} + 42.83\,^\circ\text{C} + 42.58\,^\circ\text{C} + 42.68\,^\circ\text{C} + \\ &\quad 42.65^\circ\text{C} + 42.76\,^\circ\text{C} + 42.73\,^\circ\text{C} + 42.71\,^\circ\text{C}) \\ &= 42.70\,^\circ\text{C}\end{aligned}$$

The sample standard deviation is

$$\begin{aligned}s &= \left\{ \begin{array}{l} \frac{1}{9}[(0.00\,^\circ\text{C})^2 + (0.10\,^\circ\text{C})^2 + (0.08\,^\circ\text{C})^2 + (0.13\,^\circ\text{C})^2 + (0.12\,^\circ\text{C})^2 + \\ \quad (0.02\,^\circ\text{C})^2 + (0.05\,^\circ\text{C})^2 + (0.16^\circ\text{C})^2 + (0.13\,^\circ\text{C})^2 + (0.01\,^\circ\text{C})^2] \end{array} \right\}^{1/2} \\ &= 0.08\,^\circ\text{C}\end{aligned}$$

◄

The value of $t\,(9, 0.05)$ is found from Table 11.1 to equal 2.26, so that

$$\varepsilon = \frac{(2.26)(0.08\,^\circ\text{C})}{\sqrt{10}} = 0.06\,^\circ\text{C}\,.$$

Therefore, at the 95% confidence level, $T_{melt} = 42.70\,^\circ\text{C} \pm 0.06\,^\circ\text{C}$.

EXERCISE 11.4 ► Assume that the H–O–H bond angles in various crystalline hydrates have been measured to be 108°, 109°, 110°, 103°, 111°, and 107°. Give your estimate of the correct bond angle and its 95% confidence interval. ◄

Rejection of Discordant Data

Sometimes a repetition of a measurement yields a value that differs greatly from the other members of the sample (a *discordant value*). For example, say that we repeated the measurement of the melting temperature of $Ca(NO_3)_2 \cdot 4H_2O$ in the previous example one more time and obtained a value of 39.75 °C. If we include this eleventh data point, we get a sample mean of 42.43 °C and a sample standard deviation of 0.89 °C. Using the table of Student's t values, we obtain a value for ε of 0.60 °C at the 95% confidence level. Some people think that the only honest thing to do is to report the melting temperature as $42.4 \pm 0.6\,^\circ\text{C}$.

If we assume that our sample standard deviation of 0.89 °C is a good estimate of the population standard deviation, our data point of 39.75 °C is 3.01 standard deviations away from the mean. From the table of the error function in Appendix G, the probability of a randomly chosen member of a population differing from the mean by this much or more is 0.003, or 0.3%. There is considerable justification for asserting that such an improbable event was due not to random experimental errors but to some kind of a mistake, such as misreading a thermometer. If you assume this, you discard the suspect data point and recompute the mean and standard deviation just as though the discordant data point had not existed. Do not discard more than one data point from a set of data. If two or more apparently discordant data points occur in a set, you should regard it as a signal that the data simply have low precision.

There are several rules for deciding whether to discard a data point. Some people discard data points that are more than 2.7 standard deviations from the mean (this means 2.7 standard deviations calculated with the discordant point left in). This discards points that have less than a 1% chance of having arisen through

TABLE 11.2 ► Critical Q Values at the 95% Confidence Level

N	3	4	5	6	7	8	9	10	20	30
Q	0.97	0.84	0.72	0.63	0.58	0.53	0.50	0.47	0.36	0.30

normal experimental error. Pugh and Winslow[6] suggest that for a sample of N data points, a data point should be discarded if there is less than one chance in $2N$ that the point came from the same population. This rule discards more points than the first rule for a sample of 10 measurements, since it would discard a point lying 1.96 standard deviations from the mean in a sample of 10 measurements. Since you would expect such a point to occur once in 20 times, the probability that it would occur in a sample of 10 by random chance is fairly large.

There is a test called the *Q test*, in which Q is defined as the difference between an "outlying" data point and its nearest neighbor divided by the difference between the highest and the lowest values in the set:

$$Q = \boxed{\frac{\text{(outlying value)} - \text{(value nearest the outlying value)}}{\text{(highest value)} - \text{(lowest value)}}}. \tag{11.16}$$

An outlying data point is discarded if its value of Q of exceeds a certain critical value, which depends on the number of members in the sample. Table 11.2 contains the critical value of Q at the 95% confidence level for samples of N members.[7]

EXERCISE 11.5 ► Apply the Q test to the 39.75 °Cdata point appended to the data set of Example 11.2. ◄

11.3 Data Reduction and the Propagation of Errors

Many values that are obtained by measurement in a physical chemistry laboratory are used along with other values to calculate some quantity that is not directly measured. Such a calculation is call *data reduction*. An experimental error in a measured quantity will affect the accuracy of any quantity that is calculated from it. This is called *propagation of errors*.

The Combination of Errors

Assume that we have measured two quantities, a and b, and have established a probable value and a 95% confidence interval for each:

$$a = \bar{a} \pm \varepsilon_a \tag{11.17a}$$
$$b = \bar{b} \pm \varepsilon_b, \tag{11.17b}$$

where $\bar{a}$ is our probable value of a, perhaps from a single measurement or perhaps from a mean of several measurements, and ε_a is our expected error in a, perhaps

[6] Emerson M. Pugh and George H. Winslow, *The Analysis of Physical Measurements*, Addison-Wesley, Reading, MA, 1966.

[7] W. J. Dixon, *Ann. Math. Statist.* **22**, 68 (1951); and R. B. Dean and W. J. Dixon, *Anal. Chem.* **23**, 636 (1951).

computed from Eq. (11.15) or perhaps obtained by educated guesswork. Analogous quantities are defined for b. Assume that we want to obtain a probable value and a 95% confidence interval for c, the sum of a and b. The probable value of c is the sum of $\bar{a}$ and $\bar{b}$:

$$\bar{c} = \bar{a} + \bar{b}. \tag{11.18}$$

A simple estimate of the probable error in c is the sum of ε_a and ε_b, which corresponds to the assumption that the errors in the two quantities always add together:

$$\varepsilon_c = \varepsilon_a + \varepsilon_b \quad \text{(simple preliminary estimate)}. \tag{11.19}$$

However, Eq. (11.19) provides an overestimate, because there is some chance that errors in a and in b will be in opposite directions. If a and b are both governed by Gaussian distributions, mathematicians have shown that c is also governed by a Gaussian distribution, and that the probable error in c is given by

$$\boxed{\varepsilon_c = (\varepsilon_a^2 + \varepsilon_b^2)^{1/2}}. \tag{11.20}$$

This formula allows for the statistically correct probability of cancellation of errors.

EXAMPLE 11.4 Two lengths have been measured as $24.8\,\text{m} \pm 0.4\,\text{m}$ and $13.6\,\text{m} \pm 0.3\,\text{m}$. Find the probable value of their sum and its probable error.

SOLUTION ► The probable value of the sum is $24.8\,\text{m} + 13.6\,\text{m} = 38.4\,\text{m}$, and the probable error is $\varepsilon = [(0.4\,\text{m})^2 + (0.3\,\text{m})^2]^{1/2} = 0.5\,\text{m}$. Therefore, the sum is reported as $38.4\,\text{m} \pm 0.5\,\text{m}$. ◄

EXERCISE 11.6 ► Two time intervals have been clocked as $56.57\,\text{s} \pm 0.13\,\text{s}$ and $75.12\,\text{s} \pm 0.17\,\text{s}$. Find the probable value of their sum and its probable error. ◄

The Combination of Random and Systematic Errors

Statistics can be used to determine the probable error due to random errors if the measurements can be repeated. The probable error due to systematic errors can be estimated by apparatus modification or by guesswork. These errors combine in the same way as the errors in Eq. (11.20). If ε_r is the probable error due to random errors and ε_s is the probable error due to systematic errors, the total probable error is given by

$$\boxed{\varepsilon_t = (\varepsilon_s^2 + \varepsilon_r^2)^{1/2}}. \tag{11.21}$$

In using this formula, you must try to make your estimate of the systematic error conform to the same level of confidence as your random error. If you use the 95% confidence level for the random errors, do not estimate the systematic errors at the 50% confidence level, which is what most people instinctively tend to do when asked what they think a probable error is. You might make a first guess at your systematic errors and then double it to avoid this underestimation.

EXAMPLE 11.5 Assume that you estimate the total systematic error in the melting temperature measurement of Example 11.3 as 0.20 °C at the 95% confidence level. Find the total expected error.

SOLUTION ►

$$\varepsilon_t = [(0.06\,^\circ\text{C})^2 + (0.20\,^\circ\text{C})^2]^{1/2} = 0.21\,^\circ\text{C}.$$

◄

Notice that if two sources of error combine additively and if one is much larger than the other, the smaller error makes a much smaller contribution after the errors are squared. If the error from one source is five times as large as the other, its contribution is 25 times as large, and the smaller error source can be neglected.

Error Propagation in Data Reduction Using Mathematical Formulas

In the Dumas method for determining the molar mass of a volatile liquid,[8] one uses the formula

$$M = \frac{wRT}{PV}, \tag{11.22}$$

where M is the molar mass, w is the mass of the sample of the substance contained in volume V at pressure P and temperature T, and R is the ideal gas constant. We think of Eq. (11.22) as being an example of a general formula,

$$y = y(x_1, x_2, x_3, \ldots, x_n). \tag{11.23}$$

Let us assume that we have a 95% confidence interval for each of the independent variables $x_1, x_2, \cdots$ such that

$$x_i = \bar{x}_i \pm \varepsilon_i \quad (i = 1, 2, \cdots, n). \tag{11.24}$$

Our problem is to take the uncertainties in x_1, x_2, and so on, and calculate the uncertainty in y, the dependent variable. This is called the *propagation of errors*. If the errors are not too large, we can take an approach based on a differential calculus. The fundamental equation of differential calculus is Eq. (7.9),

$$dy = \left(\frac{\partial y}{\partial x_1}\right) dx_1 + \left(\frac{\partial y}{\partial x_2}\right) dx_2 + \left(\frac{\partial y}{\partial x_3}\right) dx_3 + \cdots + \left(\frac{\partial y}{\partial x_n}\right) dx_n. \tag{11.25}$$

This equation gives an infinitesimal change in the dependent variable y due to arbitrary infinitesimal changes in the independent variables $x_1, x_2, x_3, \ldots, x_n$.

If finite changes Δx_1, Δx_2, and so on, are made in the independent variables, we could write as an approximation

$$\Delta y \approx \left(\frac{\partial y}{\partial x_1}\right) \Delta x_1 + \left(\frac{\partial y}{\partial x_2}\right) \Delta x_2 + \cdots + \left(\frac{\partial y}{\partial x_n}\right) \Delta x_n. \tag{11.26}$$

If we had some known errors in x_1, x_2, and so on, we could use Eq. (11.26) to calculate a known error in y. Since all we have is probable errors in the independent variables and do not know whether the actual errors are positive or negative, one

[8] Lawrence J. Sacks, *Experimental Chemistry*, pp. 26–29, Macmillan Co., New York, 1971.

cautious way to proceed would be to assume that the worst might happen and that all the errors would add:

$$\varepsilon_y \approx \left|\left(\frac{\partial y}{\partial x_1}\right)\varepsilon_1\right| + \left|\left(\frac{\partial y}{\partial x_2}\right)\varepsilon_2\right| + \cdots + \left|\left(\frac{\partial y}{\partial x_n}\right)\Delta x_n\right| \text{(first estimate)}, \quad (11.27)$$

where $\varepsilon_1, \varepsilon_2, \cdots \varepsilon_n$, represent the expected errors in the independent variables and ε_y represents the expected error in y. This equation overestimates the error in y because there is some probability that the errors in the x values will cancel instead of adding. An equation that incorporates the statistical probability of error cancellation is

$$\boxed{\varepsilon_y \approx \left[\left(\frac{\partial y}{\partial x_1}\right)^2 \varepsilon_1^2 + \left(\frac{\partial y}{\partial x_2}\right)^2 \varepsilon_2^2 + \cdots + \left(\frac{\partial y}{\partial x_n}\right)^2 \varepsilon_n^2\right]^{1/2} \quad \text{(final formula)}}. \quad (11.28)$$

This equation is analogous to Eq. (11.21). It will be our working equation for the propagation of errors through formulas. Since it is based on a differential formula, it becomes more nearly exact if the errors are small.

EXAMPLE 11.6 (a) Find the expression for the propagation of errors for the Dumas molar mass determination.
(b) Apply this expression to the following set of data for *n*-hexane:

$$\begin{aligned} T &= 373.15 \pm 0.25\text{K} \\ V &= 206.34 \pm 0.15\,\text{ml} \\ P &= 760 \pm 0.2\ \text{torr} \\ w &= 0.585 \pm 0.005\ \text{g}. \end{aligned}$$

SOLUTION ► (a) The analogue of Eq. (11.28) for our equation is

$$\varepsilon_M \approx \left[\left(\frac{RT}{PV}\right)^2 \varepsilon_w^2 + \left(\frac{wR}{PV}\right)^2 \varepsilon_T^2 + \left(\frac{wRT}{P^2V}\right)^2 \varepsilon_P^2 + \left(\frac{wRT}{PV^2}\right)^2 \varepsilon_V^2\right]^{1/2}$$

◄

Substituting the numerical values, we obtain

$$M = \frac{(0.585\ \text{g})(0.082057\,\text{l atm K}^{-1}\ \text{mol}^{-1})(373.15\ \text{K})}{(1.000\ \text{atm})(0.20634\,\text{l})} = 86.81\ \text{g mol}^{-1}.$$

We do not report the numerical calculation of the expected error, but the result is

$$\begin{aligned} \varepsilon_M &= 0.747\ \text{g mol}^{-1} \\ M &= 86.8 \pm 0.7\ \text{g mol}^{-1}. \end{aligned}$$

One significant digit suffices in an expected error. The digit 8 after the decimal point in the value of M in the previous example is not quite significant, but since the error is smaller than 1.0 g mol^{-1}, it provides a little information, and we include it. The accepted value is 86.17g mol^{-1}, so that our expected error is larger than our actual error, as it should be about 95% of the time.

EXERCISE 11.7 ▶ In the cryoscopic determination of molar mass,[a] the molar mass in kg mol^{-1} is given by

$$M = \frac{wK_f}{W\Delta T_f}(1 - k_f \Delta T_f),$$

where W is the mass of the solvent in kilograms, w is the mass of the unknown solute in kilograms, ΔT_f is the amount by which the freezing point of the solution is less than that of the pure solvent, and K_f and k_f are constants characteristic of the solvent. Assume that in a given experiment, a sample of an unknown substance was dissolved in benzene, for which $K_f = 5.12\,\mathrm{K\,kg\,mol^{-1}}$ and $k_f = 0.011\,\mathrm{K^{-1}}$. For the following data, calculate M and its probable error:

$$\begin{aligned} W &= 13.185 \pm 0.003 \text{ g} \\ w &= 0.423 \pm 0.002 \text{ g} \\ \Delta T_f &= 1.263 \pm 0.020 \text{ K}. \end{aligned}$$

◀

[a] Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., p. 182, McGraw-Hill, New York, 2003.

11.4 Graphical and Numerical Data Reduction

There are a number of functional relationships in physical chemistry that require data reduction that is more involved that substituting values into a formula. For example, thermodynamic relations imply that the equilibrium pressure of a two-phase system containing one substance is a function of the temperature. If we control the temperature and measure the pressure, we write

$$P = P(T). \tag{11.29}$$

This equation represents a function that we assume to be piecewise continuous.

Table 11.3 contains a set of student data for the vapor pressure of ethanol, which is the pressure observed when the liquid and the vapor are at equilibrium. Error estimates are included in the table.

Figure 11.1 is a graph on which these data have been plotted. A fairly smooth curve has been drawn near the points, passing through or nearly through the confidence intervals given in the table. The curve in Fig. 11.1 is an approximate representation of the function of Eq. (11.29). It gives us a means to interpolate between the data points, and it can give us "smoothed" values at the data points. However, we can extract more information from these data. The *Clapeyron equation* for any

TABLE 11.3 ► Experimental Vapor Pressures of Pure Ethanol at Various Temperature

t/°C	T/K	Vapor Pressure/torr	Expected Error/torr
25.00	298.15	55.9	3.0
30.00	303.15	70.0	3.0
35.00	308.15	93.8	4.2
40.00	313.15	117.5	5.5
45.00	318.15	154.1	6.0
50.00	323.15	190.7	7.6
55.00	328.15	241.9	8.0
60.00	333.15	304.15	8.8
65.00	338.15	377.9	9.5

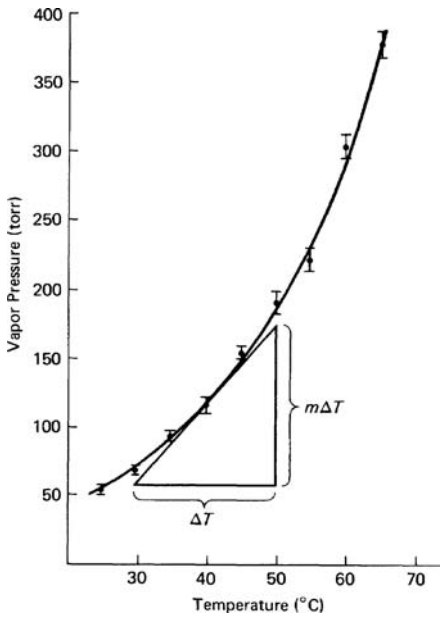

Figure 11.1 ► The vapor pressure of ethanol as a function of temperature.

phase transition is

$$\frac{dP}{dT} = \frac{\Delta H_m}{T\Delta V_m}, \tag{11.30}$$

where P is the pressure, ΔH_m is the molar enthalpy change of the phase transition, T is the absolute temperature, and ΔV_m is the molar volume change of the phase transition. If ΔV_m is known and the value of the derivative dP/dT can be determined, then the enthalpy change of vaporization can be calculated. The derivative dP/dT is the slope of the tangent line at the point being considered (see Chapter 4). After a smooth curve has been drawn as in Fig. 11.1, a tangent line can be constructed. Two line segments can be drawn parallel to the coordinate axes, forming a right triangle with the tangent line, as is shown in the figure.

EXAMPLE 11.7 Determine the value of dP/dT from the triangle in Fig. 11.1

SOLUTION ► The slope of the tangent line is equal to the height of the triangle divided by its base ("rise" over "run"). This gives

$$\frac{dP}{dT} = \frac{115\,\text{torr}}{20.0\,\text{K}} = 5.75\,\text{torr}\,\text{K}^{-1} \tag{11.31}$$

◀

Numerical Differentiation

Drawing a graph and constructing a tangent by hand in is tedious. There are numerical procedures that can be carried out on a computer. The first procedure is "smoothing" data. The idea is that the mathematical function that the data should conform to is continuous and smooth, so that if we adjust the data points so that they lie closer to a smooth curve, we have probably reduced the experimental errors. One procedure is based on choosing polynomial functions that provide smoothed values of the function. If we have the set of data points (x_1, y_1), (x_2, y_2), (x_3, y_3), and so on, such that the x values are equally spaced, a smoothed value for the dependent variable y_i is given by[9]

$$y_i = \frac{1}{35}\left[17y_i + 12(y_{i+1} + y_{i-1}) - 3(y_{i+2} + y_{i-2})\right]. \tag{11.32}$$

This equation corresponds to the value of the 3rd-degree polynomial that most nearly fits the five data points included in the formula and is valid only for equally spaced values of x. There are also similar formulas that involve a larger number of points.

We now define a set of *differences*, which are used to calculate numerical approximations to derivatives for a set of equally spaced data points. The *first difference* for the ith point is defined by

$$\Delta y_i = y_{i+1} - y_i. \tag{11.33a}$$

The *second difference* for the ith point is defined by

$$\Delta^2 y_i = \Delta y_{i+1} - \Delta y_i = y_{i+2} - 2y_{i+1} + y_i. \tag{11.33b}$$

The *third difference* for the ith point is defined by

$$\Delta^3 y_i = \Delta^2 y_{i+1} - \Delta^2 y_i. \tag{11.33c}$$

Higher-order differences are defined in a similar way. For data sets of ordinary accuracy, the values of y in Eqs. (11.33a) should be the smoothed values given by Eq. (11.32). This set of differences for point number i involves only points with subscripts greater than or equal to i. Other schemes can be defined that use points on both sides of the ith data point.

A numerical value for the derivative dy/dx at the ith point is given by[10]

$$\left.\frac{dy}{dx}\right|_{x=x_i} = \frac{1}{w}\left(\Delta y_i - \frac{1}{2}\Delta^2 y_i + \frac{1}{3}\Delta^3 y_i - \frac{1}{4}\Delta^4 y_i + \cdots\right), \tag{11.34}$$

where w is the spacing between values of x:

$$w = x_{i+1} - x_i. \tag{11.35}$$

Equation (11.34) is based on the *Gregory–Newton interpolation formula*.[11] The second derivative is given by

[9] C. W. Garland, J. W. Nibler and D. P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., pp. 770ff, McGraw-Hill, Boston, 2003.

[10] *Ibid*.

[11] *Ibid*.

$$\left.\frac{d^2y}{dx^2}\right|_{x=x_i} = \frac{1}{w^2}\left(\Delta^2 y_i - \Delta^3 y_i + \frac{11}{12}\Delta^4 y_i - \frac{10}{12}\Delta^5 y_i + \cdots\right). \qquad (11.36)$$

EXAMPLE 11.8 Smooth the data of Table 11.3. Find the value of the derivative dP/dT at 40 °C and find the value of ΔH_m.

SOLUTION ► The data were entered into an Excel spreadsheet and smoothed. The first three differences were calculated, and the derivative was calculated for the 40 °C data point.

$$\frac{dP}{dT} = 5.75\,\text{torr K}^{-1} \qquad (11.37)$$

The enthalpy change of vaporization was calculated using the approximation

$$\Delta V_m = V_m(gas) - V_m(liquid) \approx V_m(gas) = \frac{RT}{P} \qquad (11.38)$$

$$\Delta H_m = TV_m\frac{dP}{dT} = \frac{RT^2}{P}\frac{dP}{dT} = \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(313.15\,\text{K})^2(5.75\,\text{torr K}^{-1})}{119.7\,\text{torr}} \qquad (11.39)$$

$$= 39200\,\text{J mol}^{-1} = 39.2\,\text{kJ mol}^{-1} \qquad (11.40)$$

Notice that we did not use SI units for all quantities, but that the torr unit canceled, so that the correct answer was obtained. ◄

EXERCISE 11.8 ► The rate of a first-order chemical reaction obeys the equation

$$-\frac{dc}{dt} = kc, \qquad (11.41)$$

where c is the concentration of the reactant and k is a function of temperature called the *rate constant*. The following is a set of data for the following reaction at 25 °C.[a]

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

Time/h	$[(\mathbf{CH}_3)_3\mathbf{CBr}]$/mol l^{-1}
0	0.1051
5	0.0803
10	0.0614
15	0.0470
20	0.0359
25	0.0274
30	0.0210
35	0.0160
40	0.0123

Smooth the data using Eq. (11.32). Using Excel, make a table of the first, second, third, and fourth differences. Use Eq. (11.34) to evaluate the derivative dc/dt at $t = 20$ h. Use this value to evaluate the rate constant. ◄

[a] L. C. Bateman, E. D. Hughes, and C. K. Ingold, "Mechanism of Substitution at a Saturated Carbon Atom. Part XIX. A Kinetic Demonstration of the Unimolecular Solvolysis of Alkyl Halides," *J. Chem. Soc.* 960 (1940).

Linearization

In some cases, a variable obeys a mathematical relation that can be *linearized*. This means finding new variables such that the curve in a graph of our data is expected to be a line instead of some other curve. In our vapor pressure example, these variables are found by manipulation of the Clapeyron equation. We assume that the volume of the liquid is negligible compared to that of the gas, and that the gas is ideal:

$$\Delta V_m = V_m(gas) - V_m(liquid) \approx V_m(gas) \approx \frac{RT}{P} \tag{11.42}$$

We also assume that ΔH_m is equal to a constant. After separation of variables and integration, we obtain the *Clausius–Clapeyron equation*

$$\ln(P) = -\frac{\Delta H_m}{RT} + C, \tag{11.43}$$

where C is a constant of integration.

EXERCISE 11.9 ► Multiply both sides of Eq. (11.30) by dT, separate the variables do an indefinite integration to obtain Eq. (11.43), using the stated assumptions. ◄

Equation (11.43) represents a linear function if we use $1/T$ as the independent variable and $\ln(P)$ as the dependent variable. Figure 11.2 is a graph of the same data as Fig. 11.1, using these variables.

A straight line passing nearly through the points has been drawn in the figure. The expected errors in $\ln(P)$ were also plotted. They were obtained by use of Eq.

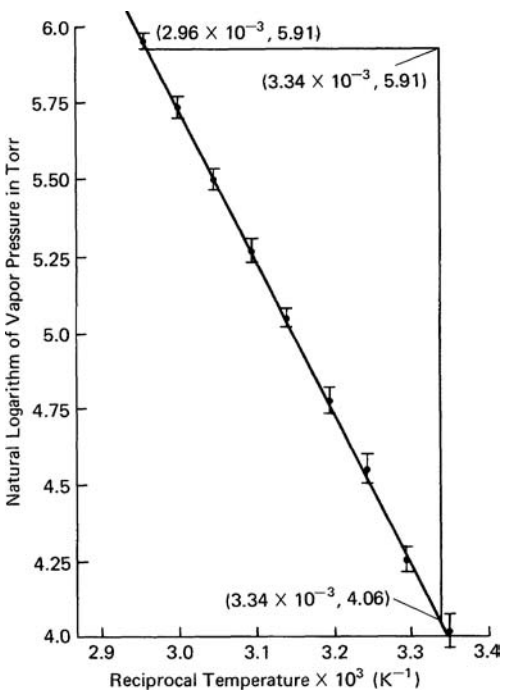

Figure 11.2 ► The natural logarithm of the vapor pressure of ethanol as a function of the reciprocal of the absolute temperature.

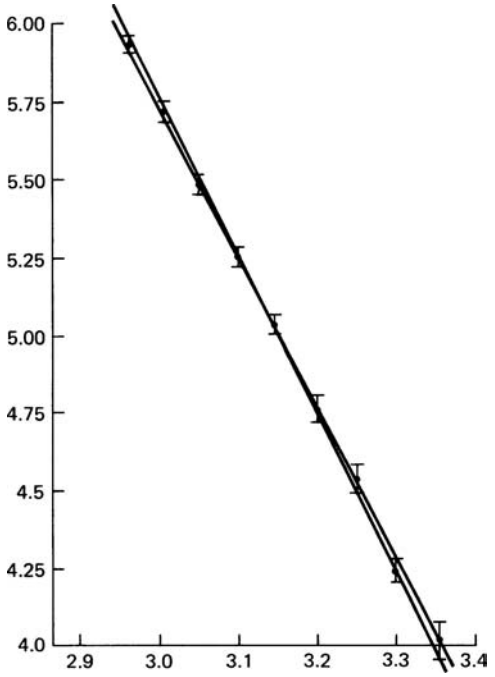

Figure 11.3 ► The lines of maximum and minimum slope in Figure 11.2.

(11.28), with $y = \ln(P)$.

$$\varepsilon(\ln(P)) = \varepsilon_y = \left(\left(\frac{dy}{dP}\right)^2 \varepsilon_P^2\right)^{1/2} = \left|\left(\frac{dy}{dP}\right)\varepsilon_P\right| = \frac{1}{P}\varepsilon_P. \qquad (11.44)$$

EXERCISE 11.10 ► Calculate the expected error in $\ln(P)$ for a few data points in Table 11.3, using Eq. (11.44). ◄

EXAMPLE 11.9 Find the enthalpy change of vaporization of ethanol from the graph in Fig. 11.2.

SOLUTION ► The necessary right triangle has been drawn in Fig. 11.2 and the coordinates of the vertices are given in the figure. If m is the slope, then

$$\begin{aligned}\Delta H_m &= -mR = -(-4.87 \times 10^3 \text{ K})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 40.5 \times 10^3 \text{ J mol}^{-1} = 40.5 \text{ kJ mol}^{-1}.\end{aligned}$$

◄

EXERCISE 11.11 ► Construct the graph of the data in Exercise 11.8. Do this by solving Eq. (11.41) to obtain

$$\ln(c) = -kt + K. \qquad (11.45)$$

Find the value of the rate constant k. ◄

11.5 Numerical Curve Fitting: The Method of Least Squares (Regression)

Graphical techniques have lost favor because of the availability of computers and software packages that make numerical procedures much less tedious than graphical techniques. Furthermore, numerical procedures are less subjective and are usually more accurate than graphical procedures. The method of least squares is a numerical procedure for finding a continuous function to represent a set of data points. Our data points are represented by ordered pairs of numbers, (x_1, y_1), (x_2, y_2), (x_3, y_3), etc. where x is the independent variable. We assume that there is some function

$$y = y(x) \tag{11.46}$$

governing the behavior of y as a function of x, and that we know a family of functions to which the correct function belongs,

$$y = f(x, a_1, a_2, \ldots, a_p), \tag{11.47}$$

where the a's are parameters that have different values for different members of the family. We want to find the values of the parameters for the member of the assumed family that most nearly fits the data points. For example, a family of linear functions is

$$y = mx + b, \tag{11.48}$$

where the slope m and the intercept b are the parameters that have different values for different members of the family.

We define the *residual* for the ith data point as the difference between the measured value and the value of the function at that point:

$$r_i = y_i - f(x_i, a_1, a_2, \ldots, a_p). \tag{11.49}$$

When a function has been chosen that fits the points well, these residuals will collectively be small. Under certain conditions, it has been shown by mathematicians that the best fit is obtained when the sum of the squares of the residuals is minimized. The method of finding the best curve to fit a set of data points by minimizing this sum is called the *method of least squares*. The method is also called *regression*. It was first applied by Sir Francis Galton (1822–1911), a famous geneticist who studied the sizes of plants and their offspring, and also the heights of fathers and sons. He found in both these cases that there was a correlation between the trait in the second generation and the earlier generation. However, he also found that the offspring tended to be closer to the mean of the trait than the earlier generation. He called this tendency "regression toward mediocrity" and it has also been called "regression toward the mean." The name "regression" has stuck to the method.

We seek the minimum of R, the sum of the squares of the residuals,

$$R = \sum_{i=1}^{N} \left[y_i - f(x_i, a, a_2, \ldots, a_p) \right]^2, \tag{11.50}$$

where N is the number of data points. This minimum occurs where all of the partial derivatives of R with respect to $a_1, a_2, \ldots, a_p$ vanish:

$$\frac{\partial R}{\partial a_i} = 0 \qquad (i = 1, 2, \ldots, p). \tag{11.51}$$

This is a set of simultaneous equations, one for each parameter. For some families of functions, these simultaneous equations are nonlinear equations and are solved by successive approximations.[12] For linear functions or polynomial functions, the equations are linear equations, and we can solve them by the methods of Chapter 10.

In the method of *linear least squares* or *linear regression*, we find the linear function that best fits our points. If we have a nonlinear function, we might have a theory that produces a linear dependence (*linearize*) by changing variables. The family of *linear functions* is given by

$$y = mx + b. \tag{11.52}$$

We seek that value of the slope m and that value of the intercept b that give us the best fit to our data points (possibly after linearization). For the linear function of Eq. (11.52), the sum of the squares of the residuals is

$$R = \sum_{i=1}^{N} (y_i - mx_i - b)^2. \tag{11.53}$$

The simultaneous equations are

$$\frac{\partial R}{\partial m} = 2\sum_{i=1}^{N} (y_i - mx_i - b)(-x_i) = 0 \tag{11.54a}$$

$$\frac{\partial R}{\partial b} = 2\sum_{i=1}^{N} (y_i - mx_i - b)(-1) = 0. \tag{11.54b}$$

This is a set of linear inhomogeneous simultaneous equations in m and b. We write them in the form

$$S_{x^2} m + S_x b = S_{xy} \tag{11.55a}$$

$$S_x m + Nb = S_y, \tag{11.55b}$$

where

$$S_x = \sum_{i=1}^{N} x_i \tag{11.56a}$$

$$S_y = \sum_{i=1}^{N} y_i \tag{11.56b}$$

$$S_{xy} = \sum_{i=1}^{N} x_i y_i \tag{11.56c}$$

$$S_{x^2} = \sum_{i=1}^{N} x_i^2. \tag{11.56d}$$

These linear inhomogeneous equations can be solved by any of the techniques of Chapter 10. *Cramer's rule* is the easiest method in this case. From Eqs. (10.4) and

[12] Garland, Nibler, and Shoemaker, *op. cit.*, pp. 724ff

(10.5),

$$\boxed{m = \frac{1}{D}(N S_{xy} - S_x S_y)} \tag{11.57}$$

$$\boxed{b = \frac{1}{D}(S_{x^2} S_y - S_x S_{xy})}, \tag{11.58}$$

where

$$\boxed{D = N S_{x^2} - S_x^2} \tag{11.59}$$

These are our working equations. The calculation of the four sums can be carried out by hand if there are not too many data points, but many handheld calculators carry out the calculation automatically, and we will describe how to do the calculation with the Excel spreadsheet later in this section.

EXAMPLE 11.10 Calculate the slope m and the intercept b for the least-squares line for the data in Table 11.3, using $\ln(P)$ as the dependent variable and $1/T$ as the independent variable. Calculate the enthalpy change of vaporization from the slope.

SOLUTION ► When the numerical work is done, the results are

$$\begin{aligned} m &= -4854 \text{ K} \\ b &= 20.28 \\ \Delta H_m &= -mR = (-4854 \text{ K})(8.3145 \text{J K}^{-1} \text{ mol}^{-1}) \\ &= 40.36 \times 10^3 \text{J mol}^{-1}. \end{aligned}$$

This value compares with the accepted value of 40.3×10^3 J mol^{-1}, and is somewhat closer to the accepted value than the result obtained from the derivative dP/dT in an earlier example. ◄

EXERCISE 11.12 ► The following data give the vapor pressure of water at various temperatures.[a]

(a) Find the least-squares line for the data, using $\ln(P)$ for the dependent variable and $1/T$ for the independent variable. Calculate the four sums by hand. Find the molar enthalpy change of vaporization.

Temperature/°C	Vapor pressure/torr
0	4.579
5	6.543
10	9.209
15	12.788
20	17.535
25	23.756

(b) Verify your results using Excel. ◄

[a] R. Weast, Ed., *Handbook of Chemistry and Physics*, 51st ed., p. D-143, CRC Press, Boca Raton, FL, 1971–1972.

In some problems, it is not certain in advance what variables should be used for a linear least-squares fit. In the vapor pressure case, we had the Clausius-Clapeyron equation, Eq. (11.43), which indicated that $\ln(P)$ and $1/T$ were the variables that should produce a linear relationship. In the analysis of chemical rate data, it may be necessary to try two or more hypotheses to determine which gives the best fit. In a reaction involving one reactant, the concentration c of the reactant is given by Eq.(11.45) if there is no back reaction and if the reaction is a *first-order reaction*. If there is no back reaction and the reaction is a *second-order* reaction, the concentration of the reactant is given by

$$\frac{1}{c} = kt + C, \tag{11.60}$$

where k is the rate constant and C is a constant of integration. If there is no back reaction and the reaction is *third order*, the concentration c of the reactant is given by

$$\frac{1}{2c^2} = kt + C. \tag{11.61}$$

If the order of a reaction is not known, it is possible to determine the order by trying different linear least-squares fits and finding which one most nearly fits the data. One way to see whether a given hypothesis produces a linear fit is to examine the residuals. Once the least-squares line has been found, m and b are known. The residuals can be calculated from

$$r_i = y_i - mx_i - b. \tag{11.62}$$

If a given dependent variable and independent variable produce a linear fit, the points will deviate from the line only because of experimental error, and the residuals will be either positive or negative without any pattern. However, if there is a general curvature to the data points in a graph, the residuals will have the same sign near the ends of the graph and the other sign in the middle. This indicates that a different pair of variables should be tried or a nonlinear least-squares fit attempted.

EXAMPLE 11.11 The following is a fictitious set of data for the concentration of the reactant in a chemical reaction with one reactant. Determine whether the reaction is first, second, or third order. Find the rate constant and the initial concentration.

Time/min	Concentration/mol l^{-1}
5.0	0.715
10.0	0.602
15.0	0.501
20.0	0.419
25.0	0.360
30.0	0.300
35.0	0.249
40.0	0.214
45.0	0.173

SOLUTION ► We first test for first order by attempting a linear fit using $\ln(c)$ as the dependent variable and t as the independent variable. The result is

$$\begin{aligned} m &= -0.03504\,\text{min}^{-1} = -k \\ b &= -0.1592 = \ln[c(0)] \\ c(0) &= 0.853\,\text{mol l}^{-1}. \end{aligned}$$

The following set of residuals was obtained:

$$\begin{aligned} r_1 &= -0.00109 & r_6 &= 0.00634 \\ r_2 &= 0.00207 & r_7 &= -0.00480 \\ r_3 &= -0.00639 & r_8 &= 0.01891 \\ r_4 &= -0.00994 & r_9 &= -0.01859. \\ r_5 &= 0.01348 \end{aligned}$$

This is a good fit, with no pattern of general curvature shown in the residuals.

We test the hypothesis that the reaction is second order by attempting a linear fit using $1/c$ as the dependent variable and t as the independent variable. The result is

$$\begin{aligned} m &= 0.1052\,\text{l mol}^{-1} = k \\ b &= 0.4846\,\text{l mol}^{-1} = \frac{1}{c(0)} \\ c(0) &= 2.064\,\text{mol l}^{-1}. \end{aligned}$$

The following set of residuals was obtained:

$$\begin{aligned} r_1 &= 0.3882 & r_6 &= -0.3062 \\ r_2 &= 0.1249 & r_7 &= -0.1492 \\ r_3 &= -0.0660 & r_8 &= -0.0182 \\ r_4 &= -0.2012 & r_9 &= 0.5634. \\ r_5 &= -0.3359 \end{aligned}$$

This is not such a satisfactory fit as in part a, since the residuals show a general curvature, beginning with positive values, becoming negative, and then becoming positive again.

We now test the hypothesis that the reaction is third order by attempting a linear fit using $1/(2c^2)$ as the dependent variable and t as the independent variable. The results are

$$\begin{aligned} m &= 0.3546\,\text{l}^2\,\text{mol}^{-2}\,\text{min}^{-1} = k \\ b &= -3.054\,\text{l}^2\,\text{mol}^{-2}. \end{aligned}$$

This is obviously a bad fit, since the intercept b should not be negative. The residuals are

$$\begin{aligned} r_1 &= 2.2589 & r_6 &= -2.0285 \\ r_2 &= 0.8876 & r_5 &= -1.2927 \\ r_3 &= -0.2631 & r_8 &= -0.2121 \\ r_4 &= -1.1901 & r_9 &= 3.8031. \\ r_5 &= -1.9531 \end{aligned}$$

Again, there is considerable curvature. The reaction is apparently first order, with the rate constant and initial concentration given in part a of the solution. ◄

In addition to inspecting the residuals, we can calculate the *correlation coefficient*, which gives information about the closeness of a least-squares fit. For linear least squares, the correlation coefficient is defined by

$$\boxed{r = \frac{NS_{xy} - S_x S_y}{[(NS_{x^2} - S_x^2)(NS_{y^2} - S_y^2)]^{1/2}}}, \tag{11.63}$$

where S_x, S_y, S_{xy}, and S_{x^2} are defined in Eq. (11.55a) and where

$$S_{y^2} = \sum_{i=1}^{N} y_i^2. \tag{11.64}$$

If the data points lie exactly on the least-squares line, the correlation coefficient will be equal to 1 if the slope is positive or to -1 if the slope is negative. If the data points are scattered randomly about the graph so that no least-squares line can be found, the correlation coefficient will equal zero. The magnitude of the correlation coefficient will be larger for a close fit than for a poor fit. In a fairly close fit, its magnitude might equal 0.99. Some software packages give the square of the correlation coefficient rather than the correlation coefficient itself.

EXAMPLE 11.12 Calculate the correlation coefficients for the three linear fits in the previous example.

SOLUTION ► Use of Eq. (11.63) gives the results:
(a) For the first-order fit, $r = -0.9997$.
(b) For the second-order fit, $r = 0.9779$.
(c) For the third-order fit, $r = 0.9257$.
Again, the first-order fit is the best. ◄

EXERCISE 11.13 ► Do three linear least-squares fits on the data of Exercise 11.8. Calculate the correlation coefficients for the three fits and show that the reaction is first order. If you wish, you can use a spreadsheet such as Excel, which will plot the data and carry out the least-squares fit for you. The procedure is described later in this section. ◄

The correlation coefficient is related to a quantity called the *covariance*, defined by[13]

$$s_{x,y} = \frac{1}{N-1}\sum_{i-1}^{N}(x_i - \bar{x})(y_i - \bar{y}), \tag{11.65}$$

where $\bar{x}$ is the average of the x's,

$$\bar{x} = \frac{1}{N}S_x, \tag{11.66}$$

and where y is the average of the y's,

$$\bar{y} = \frac{1}{N}S_y. \tag{11.67}$$

The covariance has the same general behavior as the correlation coefficient. If large values of x tend to occur with small values of y, the covariance will be negative, and if large values of x tend to occur with large values of y, the covariance will be positive. If there is no relationship between x and y, the covariance will equal zero.

Error Propagation in Linear Least Squares

We discuss two cases: (1) the expected error in each value of the dependent variable is known, and (2) the expected error in these values is not known. In both cases, we assume that the errors in the values of the independent variable x are negligible.

[13] John E. Freund, *Modern Elementary Statistics*, 7th ed., p. 459, Prentice-Hall, Englewood Cliffs, NJ, 1988.

Case 1. Let the expected error in the value of y_i be denoted by ε_i. Equations for the slope and the intercept of the least-squares line are given in Eqs. (11.57) and (11.58). The y's can be considered to be independent variables, so we can apply Eq. (11.28). The expected error in the slope is given by

$$\varepsilon_m = \left[\sum_{i=1}^{N}\left(\frac{\partial m}{\partial y_i}\right)^2 \varepsilon_i^2\right]^{1/2} = \left[\frac{1}{D^2}\sum_{i=1}^{N}(Nx_i - S_x)^2\varepsilon_i^2\right]^{1/2}, \qquad (11.68)$$

where D and S_x are given in Eqs. (11.59) and (11.56d). In the case that all of the expected errors in the y's are equal to each other,

$$\boxed{\varepsilon_m = \left(\frac{N}{D}\right)^{1/2}\varepsilon_y}, \qquad (11.69)$$

where ε_y is the value of all the ε_i's.

The expected error in the intercept is

$$\varepsilon_b = \left[\sum_{i=1}^{N}\left(\frac{\partial b}{\partial y_i}\right)^2 \varepsilon_i^2\right]^{1/2} = \left[\frac{1}{D^2}\sum_{i=1}^{N}(S_{x^2} - S_x x_i)^2\varepsilon_i^2\right]^{1/2}. \qquad (11.70)$$

For the case that all of the ε_i's are assumed to be equal,

$$\boxed{\varepsilon_b = \left(\frac{S_{x^2}}{D}\right)^{1/2}\varepsilon_y}, \qquad (11.71)$$

where S_{x^2} is given in Eq. (11.56d).

EXERCISE 11.14 ► Verify Eqs. (11.69) and (11.71). ◄

EXAMPLE 11.13 Assume instead of the given expected errors that the expected error in the logarithm of each vapor pressure in Table 11.3 is equal to 0.040. Find the expected error in the least-squares slope and in the enthalpy change of vaporization.

SOLUTION ► From the data,

$$D = 1.327 \times 10^{-6}\ \mathrm{K}^{-2}$$

so that

$$\varepsilon_m = \left(\frac{9}{1.327 \times 10^{-6}\ \mathrm{K}^{-2}}\right)^{1/2}(0.040) = 104\ \mathrm{K}$$

$$\varepsilon_{\triangle H_m} = R\varepsilon_m = 870\ \mathrm{J\,mol^{-1}} = 0.87\ \mathrm{kJ\,mol^{-1}}.$$

◄

EXERCISE 11.15 ► Assume that the expected error in the logarithm of each concentration in Example 11.10 is equal to 0.010. Find the expected error in the rate constant, assuming the reaction to be first order. ◄

Case 2. If we do not have information about the expected errors in the dependent variable, we assume that the residuals are a sample from the population of actual experimental errors. This is a reasonable assumption if systematic errors can be ignored. The variance of the N residuals is given by

$$s_r^2 = \frac{1}{N-2}\sum_{i=1}^{N} r_i^2. \tag{11.72}$$

The standard deviation of the residuals is the square root of the variance:

$$s_r = \left(\frac{1}{N-2}\sum_{i=1}^{N} r_i^2\right)^{1/2}. \tag{11.73}$$

This differs from Eq.(11.8) in that a factor of $N-2$ occurs in the denominator instead of $N-1$. The number of degrees of freedom is $N-2$ because we have calculated two quantities, a least-squares slope and a least-squares intercept from the set of numbers, "consuming" two of the degrees of freedom. The mean of the residuals does not enter in the formula, because the mean of the residuals in a least-squares fit always vanishes.

EXERCISE 11.16 ► Sum the residuals in Example 11.11 and show that this sum vanishes in each of the three least-square fits. ◄

Equation (11.73) provides an estimate of the standard deviation of the population of experimental errors. We assume that the errors in y are distributed according to the Student t distribution, so the expected error in y at the 95% confidence level is given by

$$\boxed{\varepsilon_y = t(\nu, 0.05)s_r}, \tag{11.74}$$

where $t(v, 0.05)$ is the Student t factor for $\nu = N-2$; the number of degrees of freedom for N data points after the slope and the intercept have been calculated. If there were a very large number of data points, the Student t distribution would approach the Gaussian distribution, and this factor would approach 1.96.

We can now write expressions similar to Eqs. (11.69) and (11.70) for the expected errors at the 95% confidence level:

$$\varepsilon_m = \left(\frac{N}{D}\right)^{1/2} t(\nu, 0.05)s_r \tag{11.75}$$

and

$$\varepsilon_b = \left(\frac{1}{D}\sum_{i=1}^{N} x_i^2\right)^{1/2} t(\nu, 0.05)s_r. \tag{11.76}$$

The standard deviations of the slope and intercept are given by similar formulas without the Student t factor:

$$s_m = \left(\frac{1}{D}\sum_{i=1}^{N} x_i^2\right)^{1/2} s_r \tag{11.77}$$

$$s_b = \left(\frac{N}{D}\right)^{1/2} s_r. \tag{11.78}$$

The slope and the intercept of a least-squares line are not independent of each other, since they are derived from the same set of data, and their *covariance* is given by[14]

$$Cov(m, b) = s_{m,b} = \frac{-s_r^2 S_x}{D}. \tag{11.79}$$

EXAMPLE 11.14 Calculate the residuals for the linear least-squares fit of Example 11.10. Find their standard deviation and the probable error in the slope and in the enthalpy change of vaporization, using the standard deviation of the residuals.

SOLUTION ► Numbering the data points from the 25 °C point (number 1) to the 65 °C point (number 9), we find the residuals:

$$\begin{aligned} r_1 &= 0.0208 & r_6 &= -0.0116 \\ r_2 &= -0.0228 & r_7 &= -0.0027 \\ r_3 &= 0.0100 & r_8 &= 0.0054 \\ r_4 &= -0.0162 & r_9 &= 0.0059. \\ r_5 &= 0.0113 \end{aligned}$$

The standard deviation of the residuals is found to be

$$s_r = 0.0154.$$

Using the value of D from the previous example, the uncertainty in the slope is

$$\varepsilon_m = \left(\frac{9}{1.327 \times 10^{-6}\ \mathrm{K}^{-2}}\right)^{1/2} (2.365)(0.0154) = 94.9\,\mathrm{K},$$

where we have used the value of the Student's t factor for seven degrees of freedom from Table 11.1. The uncertainty in the enthalpy change of vaporization is

$$\varepsilon_{\triangle H_m} = R\varepsilon_m = (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})(96.9\,\mathrm{K}) = 789\ \mathrm{J\,mol^{-1}}.$$

◄

EXERCISE 11.17 ► Assuming that the reaction in Exercise 11.12 is first order, find the expected error in the rate constant, using the residuals. ◄

Expected Errors in the Dependent Variable

If the linear least-squares method is used to find the line that best represents a set of data, this line can be used to predict a value for the dependent variable corresponding to any given value of the independent variable. We now consider the probable error in such a prediction.[15] Since the dependent variable y is a function of the slope m and the intercept b, we might try to apply Eq. (11.28):

$$\varepsilon_y = \left(\left(\frac{\partial y}{\partial m}\right)^2 \varepsilon_m^2 + \left(\frac{\partial y}{\partial b}\right)^2 \varepsilon_b^2\right)^{1/2} \qquad \text{(NOT APPLICABLE)}. \tag{11.80}$$

[14] John A. Rice., *op. cit.*, p. 460.

[15] Edwin F. Meyer, *J. Chem. Educ.* **74**, 1339 (1997). The author of this article refers to a software package by Ramette, called FLEXFIT, which is available on JCE Online at http.//jchemed.chem.wisc.edu/. This package can be manipulated to give the covariance of m and b.

However, this equation is incorrect, because m and b have been derived from the same set of data and are not independent of each other, as was assumed in obtaining Eq. (11.28).

The correct equation is obtained by including the covariance of m and b. We consider the standard deviation of y,

$$s_y^2 = \left(\frac{\partial y}{\partial m}\right)^2 s_m^2 + \left(\frac{\partial y}{\partial b}\right)^2 s_b^2 + 2\left(\frac{\partial y}{\partial m}\right)\left(\frac{\partial y}{\partial b}\right) s_{m,b} \tag{11.81}$$

$$= x^2 s_m^2 + s_b^2 + 2x s_{m,b}, \tag{11.82}$$

where s_m is the standard deviation of m, s_b is the standard deviation of b, and $s_{m,b}$ is the covariance of m and b. In this equation, x stands for the value of x for which we want the value of y. The expected error in y at the 95% confidence level is

$$\varepsilon_y = t(N-2, 0.05)s_y. \tag{11.83}$$

If you want to determine a value of x for a given value of y, a similar analysis can be carried out, considering that for a given value of y, x is a function of m and b.

EXERCISE 11.18 ►

(a) From the least-squares fit of Example 11.10, find the predicted value of the vapor pressure of ethanol at 70.0 °C. Find the expected error in the natural logarithm of the vapor pressure. Compare the values of the three terms in Eq. (11.81). Find the expected error in the predicted value of the vapor pressure.

(b) From the least-squares fit of Example 11.10, find the predicted temperature at which the vapor pressure of ethanol is equal to 350.0 torr. Find the expected error in the reciprocal of the absolute temperature. Compare the values of the three terms analogous to those in Eq. (11.81).

◄

Carrying Out Least Squares Fits with Excel

The following instructions are written for Excel 2003 for Windows. If you have a later version or an earlier version of this spreadsheet, there might be small differences in the procedure. There are also small differences in Excel for the Macintosh computer. The Excel spreadsheet will carry out least squares fits in two different ways. You can carry out linear least squares in a worksheet, or you can carry out linear and various nonlinear least squares procedures on a graph. The advantage of

the worksheet procedure is that expected errors in the slope and intercept of the linear fit are provided by the software. The disadvantage of the worksheet procedure is that nonlinear least squares fits apparently cannot be carried out.

Doing Linear Least Squares Fits in a Worksheet

The first step in carrying out linear least squares fits in a worksheet after opening the worksheet is to enter the data points into columns of the worksheet. The values of the variable that will go on the x axis go into one column and the corresponding values of the variable that will go on the y axis go into another column. This column does not have to be immediately to the right of the first column as it does in making a graph. If necessary, use formulas to transform your original data into variables that will give a linear fit. Go to the Tools menu and select Data Analysis. If Data Analysis does not show up as one of the items on the menu, select Add-Ins. A list of tools should appear, and you should check Analysis ToolPak and click on OK. After you select Data Analysis, a list of techniques appears. Select Regression and click on OK. A window appears with several blanks. In the Input Y Range blank, type in the first and last cell addresses of the dependent variable, separated by a colon (:). If the values are in the first ten rows of column B, you type B1:B10. The software will change this to $B$1:$B$10 or you can type in the absolute addresses (with $ signs). In the Input X Range blank, type in the cell addresses for the independent variable, such as A1:A10. In the Confidence Level blank, make sure that 95% is chosen. Choose 95% if it is not already chosen. You will probably want to see a list of the residuals, so check the Residuals box. If you want to see a plot of the residuals, check the Residuals Plot box. You can specify where you want to put the output. The output occupies several columns and several rows, so it is probably best to check the New Worksheet Ply box. Otherwise, specify a location on your worksheet for the upper left corner of the area where you want the output. Click on OK.

When you click on OK, the computer carries out the procedure and puts the output on the screen. A number of statistical parameters are exhibited. You can find the value of correlation coefficient and its square (in the R Square cell). At the bottom of the output are the parameters of the fit. There are columns labeled Coefficient, Standard Error, t Stat, P-Value, Lower 95%, and Upper 95%. There are two rows for the intercept and slope. The intercept row is labeled Intercept, and the slope row is labeled X Variable. The Coefficient column contains the parameter. The Standard Error column contains the error based on the standard deviation (about 68% confidence). The Lower 95% column contains the parameter decremented by the expected error at the 95% confidence level, and the Upper 95% column contains the parameter incremented by the expected error. To obtain the expected error, you will have to do a subtraction. You should look at the list of residuals to see it there is a systematic curvature in the data, which shows up with residuals having one sign at the ends of the fit and the other sign in the middle.

Least Squares Fits on a Graph with Excel

With Excel, it appears that only linear least squares fits can be carried out on a worksheet, but various functions can be fit to your data on a graph. Unfortunately,

residuals and expected errors in the parameters are not provided when you work from the graph. The correlation coefficient is provided. To begin a fit, you make the graph in the usual way, using the X-Y Scatter option. Do not choose the option that places a curve in the graph. When you finish the graph, go to the Chart menu and select Add Trendline. A window appears with two tab-like areas at the top. The Type tab should already be selected. You can choose from linear, polynomial, logarithmic, power, exponential, and moving average fits. If you choose polynomial, you must specify the degree (highest power) in the polynomial. After you select the type of fit, click on the Options tab. Click on the "Display Eq. on Chart" area and on the "Display R-Squared Value on Chart" area. If you want the displayed curve to extend past your first and last data points, click on Forecast and specify how far on the x axis your want the curve to extend in the forward and back directions. Click on OK and the computer carries out the curve fit. The least-squares curve, the equation of the fitting function and the square of the correlation coefficient appear on the graph. If you want more digits for the equation parameters or want scientific notation, double-click on the equation. A window appears. Click on Number. A window appears in which you can choose whether you want scientific notation or ordinary notation (click on "number") and can specify the number of digits after the decimal point. Click on OK and look at your results.

Some Warnings about Least-Squares Procedures

It is a poor idea to rely blindly on a numerical method. You should always determine whether your results are reasonable. It is possible to spoil your results by entering one number incorrectly or by failing to recognize a bad data point. Remember the first maxim of computing: "*Garbage in, garbage out*." You should always look at your correlation coefficient. A low magnitude usually indicates a problem. Another way to make sure that a linear least-squares procedure has given you a good result is to inspect the graph. If you carry out the fit on an Excel worksheet, you should also make the graph. If you have an incorrectly entered data point you will probably be able to tell by looking at the graph. If the data points show a general curvature, you will probably be able to tell that as well from the graph.

A final warning is that in making a change in variables in order to fit a set of data to a straight line rather than to some other function, you are changing the relative importance, or weight, of the various data points.[16] In analyzing reaction rate data, fitting $\ln(c)$ to a straight line $\ln(c) = -kt + C$ will not necessarily give the same value of k as will fitting c to the function $c = e^C e^{-kt}$. We now discuss a way to compensate for this and also to compensate for errors of different sizes in different data points.

Weighting Factors in Linear Least Squares

Consider the case that we want to make a linear least-squares fit to a set of data in which the probable errors in the values of the dependent variable are not all of the same size. In this case, instead of minimizing the sum of the squares of the residuals, it has been shown that one should minimize the sum of the squares of the residuals divided by the square of the standard deviation of the population of errors

[16] Donald E. Sands, "Weighting Factors in Least Squares," *J. Chem. Educ*. **51**, 473 (1974).

from which the residual is drawn. If σ_i is the standard deviation of this population for data point number i, we should minimize[17]

$$R' = \sum_{i=1}^{N} \frac{r_i^2}{\sigma_i^2} = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(y_i - mx_i - b)^2. \tag{11.84}$$

The factors $1/\sigma_i^2$ in the sum are called *weighting factors*. The effect of this weighting is to give a greater importance (greater weight) to those points that have smaller expected errors.[18] The standard deviations are generally unknown, so if we have expected error values for the different data points, we use the expected error ε_i in place of the standard deviation σ_i:

$$R' = \sum_{i=1}^{N} \frac{1}{\varepsilon_i^2}(y_i - mx_i - b)^2 \tag{11.85}$$

We can now minimize R'. The equations are very similar to Eqs. (11.54a)–(11.59), except that each sum includes the weighting factors. The results for the slope and intercept are

$$m = \frac{1}{D'}(S_1' S_{xy}' - S_x' S_y') \tag{11.86}$$

$$b = \frac{1}{D'}(S_{x^2}' S_y' - S_x' S_{xy}'), \tag{11.87}$$

where

$$D' = S_1' S_{x^2}' - S_x'^2, \tag{11.88}$$

and where

$$S_1' = \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \tag{11.89}$$

$$S_x' = \sum_{i=1}^{N} \frac{x_i}{\sigma_i^2} \tag{11.90}$$

$$S_y' = \sum_{i=1}^{N} \frac{y_i}{\sigma_i^2} \tag{11.91}$$

$$S_{xy}' = \sum_{i=1}^{N} \frac{x_i y_i}{\sigma_i^2} \tag{11.92}$$

$$S_{x^2}' = \sum_{i=1}^{N} \frac{x_i^2}{\sigma_i^2}. \tag{11.93}$$

The standard deviations in these formulas could be replaced by the expected errors.

[17] P. R. Bevington and D. K. Robinson, *Data Reduction and ErrorAnalysis for the Physical Sciences*, 2nd ed., McGraw-Hill, New York, 1992.

[18] R. deLevie, *J. Chem. Educ.* **63**, 10 (1986).

EXAMPLE 11.15 Find the least-squares line for the data of Table 11.3, assuming that the weighting factors are inversely proportional to the squares of the expected errors in the logarithms.

SOLUTION ► The expected errors in $\ln(P)$ were calculated by Eq. (11.44) from the expected errors in the pressures given in the table. These were substituted into Eqs. (11.86)–(11.88) in place of the σ_i's. The results were

$$\begin{aligned} m &= -4872\,\mathrm{K} \\ b &= 20.34 \end{aligned}$$

These figures differ slightly from those of Example 11.9, and since the expected errors in the logarithms are not all equal to each other, these values are likely more nearly correct. The slope gives a value of the enthalpy change of vaporization

$$\begin{aligned} \Delta H_m &= -Rm = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(-4872\,\mathrm{J\,mol^{-1}}) \\ &= 40501\,\mathrm{J\,mol^{-1}} = 40.51\,\mathrm{kJ\,mol^{-1}}\,. \end{aligned} \tag{11.94}$$

◄

In the following example, we see what an inaccurate point can do if the unweighted least-squares procedure is used.

EXAMPLE 11.16 Change the data set of Table 11.3 by adding a value of the vapor pressure at 70 °C of 421 torr ±40 torr. Find the least-squares line using both the unweighted and weighted procedures.

SOLUTION ► After the point was added, the unweighted procedure was carried out as in Example 11.10, and the weighted procedure was carried out as in Example 11.15. The results were: For the unweighted procedure,

$$\begin{aligned} m &= \text{slope} = -4752\,\mathrm{K} \\ b &= \text{intercept} = 19.95. \end{aligned}$$

For the weighted procedure,

$$\begin{aligned} m &= \text{slope} = -4855\,\mathrm{K} \\ b &= \text{intercept} = 20.28. \end{aligned}$$

The data point of low accuracy has done more damage in the unweighted procedure than in the procedure with weighting factors. ◄

If the values of the original dependent variable have equal expected errors, an unweighted least-squares fit is appropriate if we use that variable in our procedure. However, if we take a function of the original variable in order to use a linear fit, then the original expected errors, which are all equal, will not generally produce equal errors in the new variable, and the weighted least-squares procedure is preferred.

This discussion suggests a possible procedure to use if you carry out a least squares fit and a few points lie a long way from the line: Carry out the fit a second time using weighting factors, utilizing the residuals from the first fit in place of the σ_i's of Eq. (11.88). This procedure should give a better fit than use of the unweighted procedure alone. If there is only one data point with a residual that is much larger in magnitude that the others, a reasonable procedure would be to calculate the standard deviation of the residuals after an initial fit and to disregard

the data point if its residual is at least as large as the standard deviation of the residuals times 2.7, which correspond to a probability of less than 1% that the data point arose from experimental error.

Linear Least Squares with Fixed Slope or Intercept

At times it is necessary to do a linear least-squares fit with the constraint that the slope or the intercept must have a specific value. For example, the Bouguer–Beer law states that the absorbance of a solution is proportional to the concentration of the colored substance. In fitting the absorbance of several solutions to their concentrations, one would specify that the intercept of the least-squares line had to be zero.

In the minimization of the sum of the squares of the residuals, one minimizes only with respect to the slope m if the intercept b is fixed. This is the same as given in Eq. (11.54a):

$$\frac{dR}{dm} = 2\sum_{i=1}^{N}(y_i - mx_i - b)(-x_i) = 0. \tag{11.95}$$

The solution to this is

$$m = \frac{S_{xy} - bS_x}{S_{x^2}}. \tag{11.96}$$

If the slope m is required to have a fixed value, we have only one equation, which is the same as Eq. (11.54a).

$$\frac{dR}{db} = 2\sum_{i=1}^{N}(y_i' - mx_i - b)(-1) = 0. \tag{11.97}$$

The solution to this is

$$b = \frac{S_y - mS_x}{N}. \tag{11.98}$$

If the required slope is equal to zero, the resulting intercept is equal to the mean of the y values and can be calculated

$$b = \frac{S_y}{N} = \bar{y}. \tag{11.99}$$

The Excel spreadsheet will carry out fits on a graph with the intercept required to have a specific value. After finishing the graph and selecting "Trendline," click on the "Options" tab, and then click on the "Set intercept" box and specify 0 or another appropriate value for the intercept. You should include the equation for the curve and the square of the correlation coefficient.

EXERCISE 11.19 ► Using Excel or by hand calculation carry out a linear least squares fit on the following data, once with the intercept fixed at zero and one without specifying the intercept:

x	0	1	2	3	4	5
y	0.10	0.98	2.00	2.99	4.02	4.98

(11.100)

Compare your slopes and your correlation coefficients for the two fits. ◄

SUMMARY

We discussed several related techniques in this chapter. The first is the estimation of probable errors in directly measured quantities. We assumed the existence of a population of infinitely many repetitions of the measurement. If several repetitions of the measurement can be made, we considered this set of measurements to be a sample from the population. We took the sample standard deviation to be an unbiased estimate of the population standard deviation and the sample mean to be an estimate of the population mean (which is the correct value if systematic error is absent). The probable error in the mean was determined by a formula of Student.

If a formula is used to calculate values of some variable from measured values of other variables, it is necessary to propagate the errors in the measured quantities through the calculation. We provided a scheme to calculate the expected error in the dependent variable, based on the total differential of the dependent variable.

We also discussed graphical and numerical data reduction procedures. The most important numerical data reduction procedure is the least squares, or regression, method, which finds the best member of a family of functions to represent a set of data. We discussed the propagation of errors through this procedure and presented a version of the procedure in which different data points are given different weights, or importances, in the procedure.

PROBLEMS

1. Assume that a sample of 10 sheets of paper has been selected randomly from a ream (500 sheets) of paper. Regard the ream as a population, even though it has only a finite number of members. The width and length of each sheet of the sample were measured, with the following results:

Sheet number	**Width**/in	**Length**/in
1	8.50	11.03
2	8.48	10.99
3	8.51	10.98
4	8.49	11.00
5	8.50	11.01
6	8.48	11.02
7	8.52	10.98
8	8.47	11.04
9	8.53	10.97
10	8.51	11.00

a) Calculate the sample mean length and its sample standard deviation, and the sample mean width and its sample standard deviation.

b) Give the expected ream mean length and width, and the expected error in each at the 95% confidence level.

c) Calculate the expected ream mean area from the width and length, and give the 95% confidence interval for the area.

d) Calculate the area of each sheet in the sample. Calculate from these areas the sample mean area and the standard deviation in the area.

e) Give the expected ream mean area and its 95% confidence interval from the results of part d.

f) Compare the results of parts c and e. Would you expect the two results to be identical? Why (or why not)?

2. The intrinsic viscosity $[\eta]$ of a set of solutions of polyvinyl alcohol is defined as the limit[19]

$$\lim_{c\to 0}\left(\frac{1}{c}\ln\left(\frac{\eta}{\eta_0}\right)\right), \tag{11.101}$$

where c is the concentration of the polymer in grams per deciliter, η is the viscosity of a solution of concentration c, and η_0 is the viscosity of the pure solvent (water in this case). The intrinsic viscosity and the viscosity-average molar mass are related by the formula

$$[\eta] = (2.00\times 10^{-4}\ \text{dl g}^{-1})\left(\frac{M}{M_0}\right)^{0.76}, \tag{11.102}$$

where M is the molar mass and $M_0 = 1\ \text{g mol}^{-1}$ (1 dalton). Find the molar mass if $[\eta] = 0.86\ \text{dl g}^{-1}$. Find the expected error in the molar mass if the expected error in $[\eta]$ is $0.03\ \text{dl g}^{-1}$.

3. Assuming that the ideal gas law holds, find the amount in moles of nitrogen gas in a container if

$$\begin{aligned} P &= 0.856\,\text{atm} \pm 0.003\,\text{atm} \\ V &= 0.01785\,\text{m}^3 \pm 0.00008\,\text{m}^3 \\ T &= 297.3\,\text{K} \pm 0.2\,\text{K}. \end{aligned}$$

Find the expected error in the amount of nitrogen.

4. The van der Waals equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

For carbon dioxide, $a = 0.3640\,\text{Pa m}^6\,\text{mol}^{-1}$ and $b = 4.267\times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$. Find the pressure of 0.500 mol of carbon dioxide if $V = 0.00256\ \text{m}^3$ and $T = 298.0$ K. Find the uncertainty in the pressure if the uncertainty in the volume is $0.00004\ \text{m}^3$ and the uncertainty in the temperature is 0.5 K. Assume that the uncertainty in n is negligible. Find the pressure predicted by the ideal gas equation of state. Compare the difference between the two pressures you calculated and the expected error in the pressure.

[19] Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., McGraw-Hill, New York, 2003, pp. 321–323.

5. The following is a set of student data on the vapor pressure of liquid ammonia, obtained in a physical chemistry laboratory course. Find the indicated enthalpy change of vaporization. Remember that the Kelvin temperature must be used.

Temperature/°C	**Pressure**/torr
−76.0	51.15
−74.0	59.40
−72.0	60.00
−70.0	75.10
−68.0	91.70
−64.0	112.75
−62.0	134.80
−60.0	154.30
−58.0	176.45
−56.0	192.90

a) Ignoring the systematic errors, find the 95% confidence interval for the enthalpy change of vaporization.

b) Assuming that the apparatus used to obtain the data in the previous problem was about like that found in most undergraduate physical chemistry laboratories, make a reasonable estimate of the systematic errors and find the 95% confidence interval for the enthalpy change of vaporization, including both systematic and random errors.

6. The vibrational contribution to the molar heat capacity of a gas of nonlinear molecules is given in statistical mechanics by the formula

$$C_m(\text{vib}) = R \sum_{i=1}^{3n-6} \frac{u_1^2 e^{-u_i}}{(1-e^{-u_i})^2},$$

where $u_i = h\nu_i / k_B T$. Here ν_i is the frequency of the ith normal mode of vibration, of which there are $3n-6$ if n is the number of nuclei in the molecule (assumed nonlinear), h is Planck's constant, k_B is Boltzmann's constant, R is the gas constant, and T is the absolute temperature. The H_2O molecule has three normal modes. If their frequencies are given by

$$\begin{aligned} \nu_1 &= 4.78 \times 10^{13}\,\text{s}^{-1} \pm 0.002 \times 10^{13}\,\text{s}^{-1} \\ \nu_2 &= 1.095 \times 10^{14}\,\text{s}^{-1} \pm 0.004 \times 10^{14}\,\text{s}^{-1} \\ \nu_3 &= 1.126 \times 10^{14}\,\text{s}^{-1} \pm 0.004 \times 10^{14}\,\text{s}^{-1} \end{aligned}$$

calculate the vibrational contribution to the heat capacity of H_2O vapor at 500 K and find the 95% confidence interval.

7. Water rises in a clean glass capillary tube to a height h given by

$$h + \frac{r}{3} = \frac{2\gamma}{\rho g r},$$

where r is the radius of the tube, ρ is the density of water, equal to 998.2 kg m^{-3} at 20 °C, g is the acceleration due to gravity, equal to 9.80 m s^{-2}, h is the height to the bottom of the meniscus, and γ is the surface tension of the water. The term $r/3$ corrects for the liquid above the bottom of the meniscus.

a) If water at 20 °C rises to a height h of 29.6 mm in a tube of radius $r = 0.500$ mm, find the value of the surface tension of water at this temperature.

b) If the height h is uncertain by 0.4 mm and the radius of the capillary tube is uncertain by 0.02 mm, find the uncertainty in the surface tension.

c) The acceleration due to gravity varies with latitude. At the poles of the earth it is equal to $9.83\,\mathrm{m\,s^{-2}}$. Find the error in the surface tension of water due to using this value rather than $9.80\,\mathrm{m\,s^{-2}}$, which applies to latitude 39 °.

8. The *nth moment of a probability distribution* is defined by

$$M_n = \int (x - \mu)^n f(x)\, dx.$$

The second moment is the variance, or square of the standard deviation. Show that for the Gaussian distribution, $M_3 = 0$, and find the value of M_4. For this distribution, the limits of integration are $-\infty$ and $+\infty$.

9. Vaughan[20] obtained the following data for the dimerization of butadiene at 326° C.

Time/min	**Partial pressure of butadiene**/atm
0	to be deduced
3.25	0.7961
8.02	0.7457
12.18	0.7057
17.30	0.6657
24.55	0.6073
33.00	0.5573
42.50	0.5087
55.08	0.4585
68.05	0.4173
90.05	0.3613
119.00	0.3073
259.50	0.1711
373.00	0.1081

Determine whether the reaction is first, second, or third order, using the least-squares method. Find the rate constant and its 95% confidence interval, ignoring systematic errors. Find the initial pressure of butadiene.

10. Make a graph of the partial pressure of butadiene as a function of time, using the data in the previous problem. Find the slope of the tangent line at 33.00 min and deduce the rate constant from it. Compare with the result from the previous problem.

[20] W. E. Vaughan, "The Homogeneous Thermal Polymerization of 1,3-Butadiene," *J. Am. Chem. Soc.* **54**, 3863 (1932).

11. The following are (contrived) data for a chemical reaction of one substances.

Time/min	Concentration/mol l^{-1}
0	0.500
2	0.349
4	0.267
6	0.217
8	0.182
10	0.157
12	0.139
14	0.124
16	0.112
18	0.102
20	0.093

a) Assume that there is no appreciable back reaction and determine the order of the reaction and the value of the rate constant.

b) If you use Excel, find the expected error in the rate constant at the 95% confidence level.

c) Smooth the data. Find the value of the derivative dc/dt at $t = 10$ min., using the first, second, and third differences. Find the value of the rate constant from this value and compare it with your value from part a.

12. Use Eq. (11.32) to "smooth" the data given in Example 11.11. Using the smoothed data and Eq. (11.34) find the derivative dc/dt at $t = 25$ min. Find the rate constant.

13. If a capacitor of capacitance C is discharged through a resistor of resistance R the voltage on the capacitor follows the formula

$$V(t) = V(0)e^{-t/RC} \tag{11.103}$$

The following are data on the voltage as a function of time for the discharge of a capacitor through a resistance of 102 kΩ.

t/s	V/s
0.00	1.00
0.020	0.819
0.040	0.670
0.060	0.549
0.080	0.449
0.100	0.368
0.120	0.301
0.140	0.247
0.160	0.202
0.180	0.165
0.200	0.135

Find the capacitance and its expected error.

14. The *Bouguer–Beer law* (sometimes called the *Lambert–Beer law*) states $A = abc$, where A is the of a solution, defined as $\log_{10}(I_0/I)$ where I_0 is the incident intensity of light at the appropriate wavelength and I is the transmitted intensity; b is the length of the cell through which the light passes; and c is the concentration of the absorbing substance. The coefficient a is called the *molar absorptivity* if the concentration is in moles per liter. The following is a set of data for the absorbance of a set of solutions of disodium fumarate at a wavelength of 250 nm. Using a linear least-squares fit with intercept set equal to zero, find the value of the absorptivity a if $b = 1.000$ cm. For comparison, carry out the fit without specifying zero intercept.

A	$c(\text{mol l}^{-1})$
0.1425	1.00×10^{-4}
0.2865	2.00×10^{-4}
0.4280	3.00×10^{-4}
0.5725	4.00×10^{-4}
0.7160	5.00×10^{-4}
0.8575	6.00×10^{-4}

Additional Reading

Here is a list of some books that are useful sources for further study in mathematics to be used in chemistry. No attempt has been made to be comprehensive. Some of the books are out of print, but should be available in college and university libraries.

Books on Mathematics for Science

- Donald A. McQuarrie, *Mathematical Methods for Scientists and Engineers*, University Science Books, New York, 2003. This is an ambitious book, with over 1000 pages. The author is well known for writing clear and useful books.
- Philip M. Morse and Herman Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York, 1953. This book comes in two parts and is a complete survey of all of the mathematics that a scientist might need. It is out of print, but should be found in almost any college or university library.
- Clifford E. Swartz, *Used Math for the First Two Years of College Science*, AAPT, College Park, MD, 1993. This book is a survey of various mathematical topics at the beginning college level.

Calculus Textbooks

- Thomas H. Barr, *Vector Calculus*, 2nd ed., Prentice Hall, Upper Saddle River, NJ, 2000. This is a textbook for a third-semester calculus course that emphasizes vector calculus.
- Wilfred Kaplan, *Advanced Calculus*, 5th ed., Addison-Wesley, Reading, MA, 2003. This is a text for a calculus course beyond the first year. It discusses infinite series and Fourier series.
- H. M. Schey, *Div, Grad, Curl, and All That: An Informal Text on Vector Calculus*, Norton, 1996
- James Stewart, *Calculus*, 5th ed., Brooks/Cole, Pacific Grove, CA, 2003. This is a calculus textbook that uses some examples from physics in its discussions. You can read about coordinate systems, vectors, and complex numbers in almost any calculus textbook, including this one.

Books on Numerical Analysis

- Richard L. Burden and J. Douglas Faires, *Numerical Analysis*, 4th ed., Brooks/Cole, 2001. This is a standard numerical analysis textbook at the advanced

undergraduate level. It contains explicit algorithms that can easily be converted into computer programs. out of print

Advanced Mathematics Books

- Dean G. Duffy, *Transform Methods for Solving Partial Differential Equations*, 2nd ed., Chapman and Hall/CRC Press, Boca Raton, 2004. This book is a textbook for engineering students and focuses on practical applications.

- J. F. James, *A Student's Guide to Fourier Transforms, with Applications to Physics and Engineering*, Cambridge Univ. Press, Cambridge, UK, 2002. This book is designed to teach the subject to a student without previous knowledge of Fourier transforms. It contains a description of the fast Fourier transform method and a computer program in BASIC to carry out the transformation.

- Erwin Kreyszig, *Advanced Engineering Mathematics*, 8th ed., Wiley, New York, 1999. This book is meant for engineers. It emphasizes applications rather than mathematical theory in a way that is useful to chemists.

- David L. Powers, *Boundary Value Problems*, Harcourt/Academic Press, New York, 1999. This book includes a 40-page chapter on Fourier series and integrals.

Books on Experimental Data Analysis

- P. R. Bevington and D. K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences*, 2nd ed., McGraw-Hill, New York, 1992. This is a very nice book, which includes a lot of useful things, including a discussion of different probability distributions, including the Gaussian distribution, and a discussion of weighted least-squares procedures.

- Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., McGraw-Hill, New York, 2003. This is a standard physical chemistry laboratory textbook and contains a good section on the treatment of experimental errors as well as most of the experiments commonly done in physical chemistry courses.

- John A. Rice, *Mathematical Statistics and Data Analysis*, 2nd ed., Duxbury Press, 1985. This is a standard textbook for mathematical statistics. It includes numerous examples from experimental chemistry and is a good reference for chemists.

Computer Books

- E. J. Billo, *Microsoft Excel for Chemists: A Comprehensive Guide*, 2nd ed., Wiley, New York, 2001. This is a much more useful guide to Excel than the manual provided by the manufacturer.

- Robert de Levie, *How to Use Excel in Analytical Chemistry and in General Scientific Data Analysis*, Cambridge University Press, 2001.

- Robert de Levie, *Advanced Excel for Scientific Data Analysis*, Oxford University Press, 2004. This book is available in both paperback and hardbound editions.

- Dermot Diamond and Venita C. A. Hanratty, *Spreadsheet Applications in Chemistry Using Microsoft Excel*, Wiley Interscience, New York, 1997. This is a comprehensive introduction to the use of Excel for chemists.

- Erwin Kreyszig and E. J. Norminton, *Mathematica Computer Manual to Accompany Advanced Engineering Mathematics*, 8th ed., Wiley, New York, 2001.

- Stephen Wolfram, *The Mathematica Book*, 5th ed., Wolfram Media, 2003. This is a textbook that provides a complete introduction to the use of Mathematica, written by its inventor.

Problem-Solving and Problem Books

- G. Polya, *How to Solve It, A New Aspect of Mathematical Method*, 2nd ed., Princeton Univ. Press, Princeton, NJ, 1957. This small book is out of print but it should be in every college or university library. It contains a detailed discussion of general methods of solving problems.

- C. R. Metz, *2000 Solved Problems in Physical Chemistry*, McGraw-Hill, New York, 1990. This is a good source of practice problems in physical chemistry.

Mathematical Tables

- Milton Abramowitz and Irene A. Stegun, Eds., *Handbook of Mathematical Functions with Formulas, Graphs and Mathematical Tables*, National Bureau of Standards Applied Mathematics Series No. 55, U.S. Government Printing Office, Washington, DC, 1964. This large but inexpensive book contains a variety of different things, including integrals and useful formulas.

- A. Erdélyi, Ed., *Tables of Integral Transforms*, Vols. I and II, McGraw-Hill, New York, 1954. This set of two volumes contains a brief introduction of several types of integral transforms, with extensive tables of transforms of specific functions.

- Herbert B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan Co., New York, 1962. This book is out of print, but if you can find a used copy, you will find that it is a very useful compilation of formulas, including trigonometric identities, derivatives, infinite series, and definite and indefinite integrals.

- I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products*, 4th ed., prepared by Yu. V. Geronimus and M. Yu. Tseytlin, translated by Alan Jeffreys, Academic Press, New York, 1965. This is a large book with lots of definite and indefinite integrals in it. It is out of print but should be available in college and university libraries.

- The *Handbook of Chemistry and Physics*, CRC Publishing Co., Boca Raton, FL, with various editors and various editions, contains various mathematical tables.

Appendixes

A

Values of Physical Constants[1]

Avogadro's constant,

$$N_{\mathrm{Av}} = 6.02214 \times 10^{23}\ \mathrm{mol}^{-1}\,.$$

Molar ideal gas constant,

$$\begin{aligned} R &= 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}} = 0.082056\ \mathrm{liter\ atm\ K^{-1}\ mol^{-1}} \\ &= 1.9872\ \mathrm{cal\,K^{-1}\,mol^{-1}}\,. \end{aligned}$$

The magnitude of an electron's charge,

$$e = 1.602177 \times 10^{-19}\,\mathrm{C}\,.$$

Planck's constant,

$$h = 6.62608 \times 10^{-34}\ \mathrm{J\,s}.$$

Boltzmann's constant,

$$k_B = 1.38066 \times 10^{-23}\ \mathrm{J\,K^{-1}}.$$

The rest-mass of an electron,

$$m_e = 9.10939 \times 10^{-31}\ \mathrm{kg}.$$

The rest-mass of a proton,

$$m_p = 1.672623 \times 10^{-27}\ \mathrm{kg}.$$

The rest-mass of a neutron,

$$m_n = 1.674929 \times 10^{-27}\ \mathrm{kg}.$$

The speed of light (exact value, used to define the standard meter),

$$c = 2.99792458 \times 10^{8}\ \mathrm{m\,s^{-1}} = 2.99792458 \times 10^{10}\,\mathrm{cm\,s^{-1}}\,.$$

[1] From E. G. Cohen and B. N. Taylor, The 1986 Adjustment of the Fundamental Physical Constants, CODATA Bulletin, Number 63, November 1986.

The acceleration due to gravity near the earth's surface (varies slightly with latitude. This value applies near the latitude of Washington, DC, USA, or Madrid, Spain),

$$g = 9.80 \text{ m s}^{-7}.$$

The gravitational constant,

$$\text{G} = 6.673 \times 10^{-11} \text{ m}^3\text{s}^{-2} \text{ kg}^{-1}.$$

The permittivity of a vacuum,

$$\epsilon_0 = 8.8545187817 \times 10^{-12}\text{C}^2\text{N}^{-1}\text{m}^{-2}.$$

The permeability of a vacuum (exact value, by definition),

$$\mu_0 = 4\pi \times 10^{-7} \text{ NA}^{-2}.$$

Some Conversion Factors

1 pound = 1lb = 0.4535924 kg
1 inch = 1 in = 0.0254 m (exact value by definition)
1 calorie = 1 cal = 4.184 J (exact value by definition)
1 electron volt = 1 eV = 1.60219×10^{-19}J
1 erg = 10^{-7} J (exact value by definition)
1 atm = 760 torr = $101,325$ N m^{-2} = $101,325$ pascal (Pa) (exact values by definition)
1 atomic mass unit = 1 u = 1.66054×10^{-27} kg
1 horsepower = 1 hp = 745.700 watt = 745.700 J s^{-1}

B

Some Mathematical Formulas and Identities

1. The arithmetic progression of the first order to n terms,

$$a + (a + d) + (a + 2d) + \cdots + [a + (n - 1)d] = na + \frac{1}{2}n(n - 1)d$$
$$= \frac{n}{2}(\text{1st term} + n\text{th term}).$$

2. The geometric progression to n terms,

$$a + ar + ar^2 + \cdots + ar^{n-1} = \frac{a(1 - r^n)}{1 - r}.$$

3. The definition of the arithmetic mean of $a_1, a_2, \ldots, a_n$,

$$\frac{1}{n}(a_1 + a_2 + \cdots + a_n).$$

4. The definition of the geometric mean of $a_1, a_2, \ldots, a_n$,

$$\bar{a}_G = (a_1 a_2 \ldots a_n)^{1/n}.$$

5. The definition of the harmonic mean of $a_1, a_2, \ldots, a_n$: If $\bar{a}_{\mathrm{H}}$ is the harmonic mean, then

$$\frac{1}{\bar{a}_H} = \frac{1}{n}\left(\frac{1}{a_1} + \frac{1}{a_2} + \frac{1}{a_3} + \cdots + \frac{1}{a_n}\right).$$

6. If

$$a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \cdots + a_n x^n = b_0 + b_1 x + b_2 x^2 + b_3 x^3 + \cdots + b_n x^n$$

for all values of x, then

$$a_0 = b_0, \qquad a_1 = b_1 \qquad a_2 = b_2, \cdots, a_n = b_n.$$

Trigonometric Identities

7. $\sin^2(x) + \cos^2(x) = 1.$

8. $\tan(x) = \dfrac{\sin(x)}{\cos(x)}.$

9. $\operatorname{ctn}(x) = \dfrac{1}{\tan(x)}.$

10. $\sec(x) = \dfrac{1}{\cos(x)}.$

11. $\csc(x) = \dfrac{1}{\sin(x)}.$

12. $\sec^2(x) - \tan^2(x) = 1.$

13. $\csc^2(x) - \operatorname{ctn}^2(x) = 1.$

14. $\sin(x + y) = \sin(x)\cos(y) + \cos(x)\sin(y).$

15. $\cos(x + y) = \cos(x)\cos(y) - \sin(x)\sin(y).$ 16.

16. $\sin(2x) = 2\sin(x)\cos(x).$

17. $\cos(2x) = \cos^2(x) - \sin^2(x) = 1 - 2\sin^2(x).$

18. $\tan(x + y) = \dfrac{\tan(x) + \tan(y)}{1 - \tan(x)\tan(y)},$

19. $\tan(2x) = \dfrac{2\tan(x)}{1 - \tan^2(x)}.$

20. $\sin(x) = \dfrac{1}{2i}(e^{ix} - e^{-ix}).$

21. $\cos(x) = \dfrac{1}{2}(e^{ix} + e^{-ix}).$

22. $\sin(x) = -\sin(-x).$

23. $\cos(x) = \cos(-x).$

24. $\tan(x) = -\tan(-x).$

25. $\sin(ix) = i\sinh(x).$

26. $\cos(ix) = \cosh(x).$

27. $\tan(ix) = i\tanh(x).$

28. $\sin(x \pm iy) = \sin(x)\cosh(y) \pm i\cos(x)\sinh(y).$

29. $\cos(x \pm iy) = \cos(x)\cosh(y) \mp i\sin(x)\sinh(y).$

30. $\cosh(x) = \frac{1}{2}(e^x + e^{-x}).$

31. $\sinh(x) = \frac{1}{2}(e^x - e^{-x}).$

32. $\tanh(x) = \dfrac{\sinh(x)}{\cosh(x)}$.

33. $\operatorname{sech}(x) = \dfrac{1}{\cosh(x)}$.

34. $\operatorname{csch}(x) = \dfrac{1}{\sinh(x)}$.

35. $\operatorname{ctnh}(x) = \dfrac{1}{\tanh(x)}$.

36. $\cosh^2(x) - \sinh^2(x) = 1$.

37. $\tanh^2(x) + \operatorname{sech}^2(x) = 1$.

38. $\operatorname{ctnh}^2(x) - \operatorname{scsh}^2(x) = 1$.

39. $\sinh(x) = -\sinh(-x)$.

40. $\cosh(x) = \cosh(-x)$.

41. $\tanh(-x) = -\tanh(-x)$.

42. Relations obeyed by any triangle with angle A opposite side a, angle B opposite side b, and angle C opposite side c:

a) $A + B + C = 180^\circ = \pi$ rad

b) $c^2 = a^2 + b^2 - 2ab\cos(C)$

c) $\dfrac{a}{\sin(A)} = \dfrac{b}{\sin(B)} = \dfrac{c}{\sin(C)}$.

C

Infinite Series

C.1 Series with Constant Terms

1. $1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} + \cdots = \infty.$

2. $1 + \frac{1}{2^2} + \frac{1}{3^2} + \frac{1}{4^2} + \cdots = \frac{\pi^2}{6}.$

3. $1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \cdots = \frac{\pi^4}{90}.$

4. $1 + \frac{1}{2^p} + \frac{1}{3^p} + \frac{1}{4^p} + \cdots = \zeta(p).$
The function $\zeta(p)$ is called the *Riemann zeta function.*[1]

5. $1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots = \ln(2).$

6. $1 - \frac{1}{2^p} + \frac{1}{3^p} + \frac{1}{4^p} + \cdots = (1 - \frac{2}{2^p})\zeta(p).$

C.2 Power Series

7. Maclaurin's series. If there is a power series in x for $f(x)$, it is

$$f(x) = f(0) + \left.\frac{df}{dx}\right|_{x=0} x = \frac{1}{2!}\left.\frac{d^2f}{dx^2}\right|_{x=0} x^2 = \frac{1}{3!}\left.\frac{d^3f}{dx^3}\right|_{x=0} x^3 + \cdots .$$

8. Taylor's series. If there is a power series in $x - a$ for $f(x)$, it is

$$f(x) = f(a) + \left.\frac{df}{dx}\right|_{x=a} (x-a) + \frac{1}{2!}\left.\frac{d^2f}{dx^2}\right|_{x=a} (x - a^2) + \cdots .$$

In Eqs. (7) and (8), $\left.\frac{df}{dx}\right|_{x=a}$ means the value of the derivative df/dx evaluated at $x = a$.

[1] See H. B. Dwight, *Tables of Elementary and Some Higher Mathematical Functions*, 2nd ed., Dover, New York, 1958, for tables of values of this function.

9. If, for all values of x,

$$a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots = b_0 + b_1x + b_2x^2 + b_3x^3 + \cdots$$

then $a_0 = b_0$, $a_1 = b_1$, $a_2 = b_2$, etc.

10. The reversion of a series. If

$$y = ax + bx^2 + cx^3 + \cdots$$

and

$$x = Ay + By^2 + Cy^3 + \cdots,$$

then

$$\begin{aligned} A &= \frac{1}{a}, \quad B = -\frac{b}{a^3}, \quad C = \frac{1}{a^5}(2b^2 - ac), \\ D &= \frac{1}{a^7}(5abc - a^2d - 5b^3), \quad \text{etc.} \end{aligned}$$

See Dwight, *Table of Integrals and Other Mathematical Data* (cited above), for more coefficients.

11. Powers of a series. If

$$S = a + bx + cx^2 + dx^3 + \cdots,$$

then

$$\begin{aligned} S^2 &= a^2 + 2abx + (b^2 + 2ac)x^2 + 2(ad + bc)x^3 \\ &\quad + (c^2 + 2ae + 2bd)x^4 + 2(af + be + cd)x^5 + \cdots \\ S^{1/2} &= a^{1/2}\left[1 + \frac{b}{2a}x + (\frac{2}{2a} - \frac{b^2}{8a^2})x^2 + \cdots\right] \\ S^{-1} &= a^{-1}\left[1 - \frac{b}{a}x + (\frac{b^2}{a^2} - \frac{c}{a})x^2 + (\frac{2bc}{a^2} - \frac{d}{a} - \frac{b^3}{a^3})x^3 + \cdots\right]. \end{aligned}$$

12. $\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$.

13. $\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$.

14. $\sin(\theta + x) = \sin(\theta) + x\cos(\theta) - \dfrac{x^2}{2!}\sin(\theta) - \dfrac{x^3}{3!}\cos(\theta) + \cdots$.

15. $\cos(\theta + x) = \cos(\theta) - x\sin(\theta) - \dfrac{x^2}{2!}\cos(\theta) + \dfrac{x^3}{3!}\sin(\theta) + \cdots$.

16. $\sin^{-1}(x) = x + \dfrac{x^3}{2\cdot 3}\cdot + \dfrac{1\cdot 3x^5}{2\cdot 4\cdot 5} + \dfrac{1\cdot 3\cdot 5x^7}{2\cdot 4\cdot 6\cdot 7} + \cdots$, where $x^2 < 1$. The series gives the principal value, $-\pi/2 < \sin^{-1}(x) < \pi/2$.

17. $\cos^{-1}(x) = \dfrac{\pi}{2} - \left(x + \dfrac{x^3}{2\cdot 3} + \dfrac{1\cdot 3x^5}{2\cdot 4\cdot 5} + \cdots\right)$, where $x^2 < 1$. The series gives the principal value, $0 < \cos^{-1}(x) < \pi$.

18. $e^x = 1 + x + \dfrac{x^2}{2!} + \dfrac{x^3}{3!} + \dfrac{x^4}{4!} + \cdots (x^2 < \infty).$

19. $a^x = e^{x\ln(a)} = 1 + x\ln(a) + \dfrac{(x\ln(a))^2}{2!} + \cdots.$

20. $\ln(1+x) = x - \dfrac{x^2}{2} + \dfrac{x^3}{3} - \dfrac{x^4}{4} \cdots \ (x^2 < 1 \text{ and } x = 1).$

21. $\ln(1-x) = -\left(x + \dfrac{x^2}{2} + \dfrac{x^3}{3} + \dfrac{x^4}{4} + \cdots\right)(x^2 < 1 \text{ and } x = -1).$

22. $\sinh(x) = x + \dfrac{x^3}{3!} + \dfrac{x^5}{5!} + \dfrac{x^7}{7!} + \cdots (x^2 < \infty).$

23. $\cosh(x) = 1 + \dfrac{x^2}{2!} + \dfrac{x^4}{4!} + \dfrac{x^6}{6!} + \cdots (x^2 < \infty).$

D

A Short Table of Derivatives

In the following list, a, b, and c are constants, and e is the base of natural logarithms.

1. $\dfrac{d}{dx}(au) = a\dfrac{du}{dx}$.

2. $\dfrac{d}{dx}(uv) = u\dfrac{dv}{dx} + v\dfrac{du}{dx}$.

3. $\dfrac{d}{dx}(uvw) = uv\dfrac{dw}{dx} + uw\dfrac{dv}{dx} + vw\dfrac{du}{dx}$.

4. $\dfrac{d(x^n)}{dx} = nx^{n-1}$.

5. $\dfrac{d}{dx}(\dfrac{u}{v}) = \dfrac{1}{v}\dfrac{du}{dx} - \dfrac{u}{v^2}\dfrac{dv}{dx} = \dfrac{1}{v^2}\left(v\dfrac{du}{dx} - u\dfrac{dv}{dx}\right)$.

6. $\dfrac{d}{dx}f(u) = \dfrac{df}{du}\dfrac{du}{dx}$, where f is some differentiable function of u and u is some differentiable function of x (the *chain rule*).

7. $\dfrac{d^2}{dx^2}f(u) = \dfrac{df}{du}\dfrac{d^2u}{dx^2} + \dfrac{d^2f}{du^2}\left(\dfrac{du}{dx}\right)^2$.

8. $\dfrac{d}{dx}\sin(ax) = a\cos(ax)$.

9. $\dfrac{d}{dx}\cos(ax) = -a\sin(ax)$.

10. $\dfrac{d}{dx}\tan(ax) = a\sec^2(ax)$.

11. $\dfrac{d}{dx}\mathrm{ctn}(ax) = -a\csc^2(ax)$.

12. $\dfrac{d}{dx}\sec(ax) = a\sec(ax)\tan(ax)$.

13. $\dfrac{d}{dx}\csc(ax) = -a\csc(ax)\mathrm{ctn}(ax).$

14. $\dfrac{d}{dx}\sin^{-1}\left(\dfrac{x}{a}\right) = \dfrac{1}{\sqrt{a^2 - x^2}}$ *if* x/a is in the first or fourth quadrant

$= \dfrac{-1}{\sqrt{a^2 - x^2}}$ *if* x/a is in the second or third quadrant.

15. $\dfrac{d}{dx}\cos^{-1}\left(\dfrac{x}{a}\right) = \dfrac{-1}{\sqrt{a^2 - x^2}}$ *if* x/a is in the first or second quadrant

$= \dfrac{1}{\sqrt{a^2 - x^2}}$ *if* x/a is in the third or fourth quadrant.

16. $\dfrac{d}{dx}\tan^{-1}\left(\dfrac{x}{a}\right) = \dfrac{a}{a^2 + x^2}.$

17. $\dfrac{d}{dx}\mathrm{ctn}^{-1}\left(\dfrac{x}{a}\right) = \dfrac{-a}{a^2 + x^2}.$

18. $\dfrac{d}{dx}e^{ax} = ae^{ax}.$

19. $\dfrac{d}{dx}a^x = a^x \ln(a).$

20. $\dfrac{d}{dx}a^{cx} = ca^{cx}\ln(a).$

21. $\dfrac{d}{dx}u^y = yu^{y-1}\dfrac{d}{dx} + u^y \ln(u)\dfrac{d}{dx}.$

22. $\dfrac{d}{dx}x^x = x^x[1 + \ln(x)].$

23. $\dfrac{d}{dx}\ln(ax) = \dfrac{1}{x}.$

24. $\dfrac{d}{dx}\log_a(x) = \dfrac{\log_a(a)}{x}.$

25. $\dfrac{d}{dq}\displaystyle\int_p^q f(x)\,dx = f(q)$ if p is independent of q.

26. $\dfrac{d}{dq}\displaystyle\int_p^q f(x)\,dx = -f(p)$ if q is independent of p.

E

A Short Table of Indefinite Integrals

In the following, an arbitrary constant of integration is to be added to each equation. a, b, c, g, and n are constants.

1. $\int dx = x.$

2. $\int x\,dx = \frac{x^2}{2}.$

3. $\int \frac{1}{x}\,dx = \ln(|x|)$ Do not integrate from negative to positive values of x.

4. $\int x^n\,dx = \frac{x^{n+1}}{n+1}$, where $n \neq -1.$

5. $\int (a+bx)^n\,dx = \frac{(a+bx)^{n+1}}{b(n+1)}.$

6. $\int \frac{1}{(a+bx)}\,dx = \frac{1}{b}\ln(|a+bx|).$

7. $\int \frac{1}{(a+bx)^n}\,dx = \frac{-1}{(n-1)b(a+bx)^{n-1}}.$

8. $\int \frac{x}{(a+bx)}\,dx = \frac{1}{b^2}\left[(a+bx) - a\ln(|a+bx|)\right].$

9. $\int \frac{a+bx}{c+gx}\,dx = \frac{bx}{g} + \frac{ag-bc}{g^2}\ln(|c+gx|).$

10. $\int \frac{1}{(a+bx)(c+gx)}\,dx = \frac{1}{ag-bc}\ln\left(\left|\frac{c+gx}{cx+bx}\right|\right).$

11. $\int \frac{1}{a^2+x^2}\,dx = \frac{1}{a}\tan^{-1}(\tfrac{x}{a}).$

12. $\displaystyle\int \frac{x}{(a^2+x^2)^2}\,dx = \frac{-1}{2(a^2+x^2)}.$

13. $\displaystyle\int \frac{x}{(a^2+x^2)}\,dx = \frac{1}{2}\ln(a^2+x^2).$

14. $\displaystyle\int \frac{1}{(a^2-b^2x^2)}\,dx = \frac{1}{2ab}\ln\left(\left|\frac{a+bx}{a-bx}\right|\right).$

15. $\displaystyle\int \frac{x}{(a^2-x^2)}\,dx = -\frac{1}{2}\ln(|a^2-x^2|).$

16. $\displaystyle\int \frac{x^{1/2}}{(a^2+b^2x)}\,dx = \frac{2x^{1/2}}{b^2} - \frac{2a}{b^3}\tan^{-1}\left(\frac{bx^{1/2}}{a}\right).$

17. $\displaystyle\int \frac{1}{(a+bx^2)^{\rho/2}}\,dx = \frac{-2}{(p-2)b(a+bx)^{(\rho-2)/2}}.$

18. $\displaystyle\int \frac{1}{(x^2+a^2)^{1/2}}\,dx = \ln(x+(x^2+a^2)^{1/2}).$

19. $\displaystyle\int \frac{x}{(x^2+a^2)^{1/2}}\,dx = (x^2+a^2)^{1/2}.$

20. $\displaystyle\int \frac{1}{(x^2-a^2)^{1/2}}\,dx = \ln(x+(x^2-a^2)^{1/2}).$

21. $\displaystyle\int \frac{x}{(x^2-a^2)^{1/2}}\,dx = (x^2-a^2)^{1/2}.$

22. $\displaystyle\int \sin(ax)\,dx = -\frac{1}{a}\cos(ax).$

23. $\displaystyle\int \sin(a+bx)\,dx = -\tfrac{1}{b}\cos(a+bx).$

24. $\displaystyle\int x\sin(x)\,dx = \sin(x) - x\cos(x).$

25. $\displaystyle\int x^2\sin(x)\,dx = 2x\sin(x) - (x^2-2)\cos(x).$

26. $\displaystyle\int \sin^2(x)\,dx = \frac{x}{2} - \frac{\sin(2x)}{4} = \frac{x}{2} - \frac{\sin(x)\cos(x)}{2}.$

27. $\displaystyle\int x\sin^2(x)\,dx = \frac{x^2}{4} - \frac{x\sin(2x)}{4} - \frac{\cos(2x)}{8}.$

28. $\displaystyle\int \frac{1}{1+\sin(x)}\,dx = -\tan\left(\frac{\pi}{4} - \frac{x}{2}\right).$

29. $\displaystyle\int \cos(ax)\,dx = \frac{1}{a}\sin(ax).$

30. $\displaystyle\int \cos(a+bx)\,dx = \frac{1}{b}\sin(a+bx).$

31. $\int x\cos(x)\,dx = \cos(x) + x\sin(x).$

32. $\int x^2\cos(x)\,dx = 2x\cos(x) + (x^2-2)\sin(x).$

33. $\int \cos^2(x)\,dx = \frac{x}{2} + \frac{\sin(2x)}{4} = \frac{x}{2} + \frac{\sin(x)\cos(x)}{2}.$

34. $\int x\cos^2(x)\,dx = \frac{x^2}{4} + \frac{x\sin(2x)}{4} + \frac{\cos(2x)}{8}.$

35. $\int \frac{1}{1+\cos(x)}\,dx = \tan\left(\frac{x}{2}\right).$

36. $\int \sin(x)\cos(x)\,dx = \frac{\sin^2(x)}{2}.$

37. $\int \sin^2(x)\cos^2(x)\,dx = \frac{1}{8}\left[x - \frac{\sin(4x)}{4}\right].$

38. $\int \sin^{-1}\left(\frac{x}{a}\right)\,dx = x\sin^{-1}\left(\frac{x}{a}\right) + (a^2-x^2)^{1/2}.$

39. $\int [\sin^{-1}\left(\frac{x}{a}\right)]^2\,dx = x[\sin^{-1}\left(\frac{x}{a}\right)]^2 - 2x + 2(a^2-x^2)^{1/2}\sin^{-1}\left(\frac{x}{a}\right).$

40. $\int \cos^{-1}\left(\frac{x}{a}\right)\,dx = x\cos^{-1}\left(\frac{x}{a}\right) - (a^2-x^2)^{1/2}.$

41. $\int [\cos^{-1}\left(\frac{x}{a}\right)]^2\,dx = x[\cos^{-1}\left(\frac{x}{a}\right)]^2 - 2x - 2(a^2-x^2)^{1/2}\cos^{-1}\left(\frac{x}{a}\right).$

42. $\int \tan^{-1}\left(\frac{x}{a}\right)\,dx = x\tan^{-1}\left(\frac{x}{a}\right) - \frac{a}{2}\ln(a^2+x^2).$

43. $\int x\tan^{-1}\left(\frac{x}{a}\right)\,dx = \frac{1}{2}(x^2+a^2)\tan^{-1}\left(\frac{x}{a}\right) - \frac{ax}{2}.$

44. $\int e^{ax}\,dx = \frac{1}{a}e^{ax}.$

45. $\int a^r\,dx = \frac{a^x}{\ln(a)}.$

46. $\int xe^{ax}\,dx = e^{ax}\left(\frac{x}{a} - \frac{1}{a^2}\right).$

47. $\int x^2e^{ax}\,dx = e^{ax}\left[\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right].$

48. $\int e^{ax}\sin(x)\,dx = \frac{e^{ax}}{a^2+1}[a\sin(x) - \cos(x)].$

49. $\int e^{ax}\cos(x)\,dx = \frac{e^{ax}}{a^2+1}[a\sin(x) + \sin(x)].$

50. $\displaystyle\int e^{ax}\sin^2(x)\,dx = \frac{e^{ax}}{a^2+4}\left[a\sin^2(x) - 2\sin(x)\cos(x) + \frac{2}{a}\right].$

51. $\displaystyle\int \ln(ax)\,dx = x\ln(ax) - x.$

52. $\displaystyle\int x\ln(x)\,dx = \frac{x^2}{2}\ln(x) - \frac{x^2}{4}.$

53. $\displaystyle\int \frac{\ln(ax)}{x}\,dx = \frac{1}{2}[\ln(ax)]^2.$

54. $\displaystyle\int \frac{1}{x\ln(x)}\,dx = \ln(|\ln(x)|).$

55. $\displaystyle\int \tan(ax)\,dx = \frac{1}{a}\ln(|\sec(ax)|) = -\frac{1}{a}\ln(|\cos(ax)|).$

56. $\displaystyle\int \cot(ax)\,dx = \frac{1}{a}\ln(|\sin(ax)|).$

F

A Short Table of Definite Integrals

In the following list, a, b, m, n, p, and r are constants.

1. $\displaystyle\int_0^\infty x^{n-1}e^{-x}\,dx = \int_0^1 \left[\ln\left(\frac{1}{x}\right)\right]^{-1} dx = \Gamma(n) \quad (n > 0).$

The function $\Gamma(n)$ is called the *gamma function.* It has the following properties: for any $n > 0$,

$$\Gamma(n+1) = n\Gamma(n).$$

for any integral value of $n > 0$,

$$\Gamma(n) = (n-1)!$$

for n not an integer,

$$\Gamma(n)\Gamma(1-n) = \frac{\pi}{\sin(n\pi)}$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}.$$

2. $\displaystyle\int_0^\infty \frac{1}{1+x+x^2}\,dx = \frac{\pi}{3\sqrt{3}}.$

3. $\displaystyle\int_0^\infty \frac{x^{p-1}}{(1+x)^\rho}\,dx = \frac{\pi}{\sin(p\pi)} \quad (0 < p < 1).$

4. $\displaystyle\int_0^\infty \frac{x^{p-1}}{a+x}\,dx = \frac{\pi a^{p-1}}{\sin(p\pi)} \quad (0 < p < 1).$

5. $\displaystyle\int_0^\infty \frac{x^p}{(1+ax)^2}\,dx = \frac{p\pi}{a^{\rho+1}\sin(p\pi)}.$

6. $\displaystyle\int_0^\infty \frac{1}{1+x^p}\,dx = \frac{\pi}{p\sin(\pi/p)}.$

7. $\displaystyle\int_0^{\pi/2} \sin^2(mx)\,dx = \int_0^{\pi/2} \cos^2(mx)\,dx = \frac{\pi}{4}\ (m = 1, 2, \ldots).$

8. $\displaystyle\int_0^{\pi} \sin^2(mx)\,dx = \int_0^{\pi} \cos^2(mx)\,dx = \frac{\pi}{2}$ $(m = 1, 2, \ldots)$.

9. $\displaystyle\int_0^{\pi/2} \tan^p(x)\,dx = \int_0^{\pi/2} \operatorname{ctn}^p(x)\,dx = \frac{\pi}{2\cos(p\pi/2)}$ $(p^2 < 1)$.

10. $\displaystyle\int_0^{\pi/2} \frac{x}{\tan(x)}\,dx = \frac{\pi}{2}\ln(2)$.

11. $\displaystyle\int_0^{\pi/2} \sin^p(x)\cos^p(x)\,dx = \frac{\Gamma\left((p+1)/2\right)\Gamma\left((q+1)/2\right)}{2\Gamma((p+q)/2+1)}$ $(p+1 > 0, q+1 > 0)$.

12. $\displaystyle\int_0^{\pi} \sin(mx)\sin(nx)\,dx = \begin{cases} 0 & \text{if } m \neq n \\ \frac{\pi}{2} & \text{if } m = n \end{cases}$ $(m, n \text{ integers})$.

13. $\displaystyle\int_0^{\pi} \cos(mx)\cos(nx)\,dx = \begin{cases} 0 & \text{if } m \neq n \\ \frac{\pi}{2} & \text{if } m = n \end{cases}$ $(m, n \text{ integers})$.

14. $\displaystyle\int_0^{\pi} \sin(mx)\sin(nx)\,dx$

$$= \begin{cases} 0 & \text{if } m = n \\ 0 & \text{if } m \neq n \text{ and } m+n \text{ is even} \\ \frac{2m}{m^2-n^2} & \text{if } m \neq n \text{ and } m+n \text{ is odd } (m, n \text{ integers}). \end{cases}$$

15. $\displaystyle\int_0^{\infty} \sin\left(\frac{\pi x^2}{2}\right)dx = \int_0^{\infty} \cos\left(\frac{\pi x^2}{2}\right)dx = 1/2$.

16. $\displaystyle\int_0^{\infty} \sin(x^p)\,dx = \Gamma\left(1+\frac{1}{p}\right)\sin\left(\frac{\pi}{2p}\right) \quad (p > 1)$.

17. $\displaystyle\int_0^{\infty} \cos(x^p)\,dx = \Gamma\left(1+\frac{1}{p}\right)\cos\left(\frac{\pi}{2p}\right) \quad (p > 1)$.

18. $\displaystyle\int_0^{\infty} \frac{\sin(mx)}{x}\,dx = \begin{cases} \frac{\pi}{2} & \text{if } m > 0 \\ 0 & \text{if } m = 0 \\ -\frac{\pi}{2} & \text{if } m < 0 \end{cases}$.

19. $\displaystyle\int_0^{\infty} \frac{\sin(mx)}{x^{\rho}}\,dx = \frac{\pi m^{p-1}}{2\sin(p\pi/2)\Gamma(p)} \quad (0 < p < 2, m > 0)$.

20. $\displaystyle\int_0^{\infty} e^{-ax}\,dx = \frac{1}{a} \quad (a > 0)$.

21. $\displaystyle\int_0^{\infty} xe^{-ax}\,dx = \frac{1}{a^2} \quad (a > 0)$.

22. $\displaystyle\int_0^{\infty} x^2e^{-ax}\,dx = \frac{2}{a^3} \quad (a > 0)$.

23. $\displaystyle\int_0^\infty x^{1/2}e^{-ax}\,dx = \frac{\sqrt{\pi}}{2a^{3/2}} \quad (a > 0).$

24. $\displaystyle\int_0^\infty e^{-r^2x^2}\,dx = \frac{\sqrt{\pi}}{2r} \quad (r > 0).$

25. $\displaystyle\int_0^\infty xe^{-r^2x^2}\,dx = \frac{1}{2r^2} \quad (r > 0).$

26. $\displaystyle\int_0^\infty x^2e^{-r^2x^2}\,dx = \frac{\sqrt{\pi}}{4r^3} \quad (r > 0).$

27. $\displaystyle\int_0^\infty r^{2n+1}e^{-r^2x^2}\,dx = \frac{n!}{2r^{2n+2}} \quad (r > 0,\ n = 1, 2, \ldots).$

28. $\displaystyle\int_0^\infty x^{2n}e^{-r^2x^2}\,dx = \frac{(1)(3)(5)\cdots(2n-1)}{2^{n+1}r^{2n+1}}\sqrt{\pi} \quad (r > 0,\ n = 1, 2, \ldots).$

29. $\displaystyle\int_0^\infty x^a e^{-(rx)^b}\,dx = \frac{1}{br^{a+1}}\Gamma\left(\frac{a+1}{b}\right) \quad (a + 1 > 0,\ r > 0,\ b > 0).$

30. $\displaystyle\int_0^\infty \frac{e^{-ax} - e^{-bx}}{x}\,dx = \ln\left(\frac{b}{a}\right).$

31. $\displaystyle\int_0^\infty e^{-ax}\sin(mx)\,dx = \frac{m}{a^2 + m^2} \quad (a > 0).$

32. $\displaystyle\int_0^\infty xe^{-ax}\sin(mx)\,dx = \frac{2am}{(a^2 + m^2)^2} \quad (a > 0).$

33. $\displaystyle\int_0^\infty x^{p-1}e^{-ax}\sin(mx)\,dx = \frac{\Gamma(p)\sin(p\theta)}{(a^2 + m^2)^{p/2}} \quad (a > 0,\ p > 0,\ m > 0)$, where $\sin(\theta) = m/r$, $\cos(\theta) = a/r$, $r = (a^2 + m^2)^{1/2}$.

34. $\displaystyle\int_0^\infty e^{-ax}\cos(mx)\,dx = \frac{a}{a^2 + m^2} \quad (a > 0).$

35. $\displaystyle\int_0^\infty xe^{-ax}\cos(mx)\,dx = \frac{a^2 - m^2}{(a^2 + m^2)^2} \quad (a > 0).$

36. $\displaystyle\int_0^\infty x^{p-1}e^{-ax}\cos(mx)\,dx = \frac{\Gamma(p)\cos(p\theta)}{(a^2 + m^2)^{\rho/2}} \quad (a > 0,\ p > 0)$, where θ is the same as given in Eq. (33).

37. $\displaystyle\int_0^\infty \frac{e^{-ax}}{x}\sin(mx)\,dx = \tan^{-1}\left(\frac{m}{a}\right) \quad (a > 0).$

38. $\displaystyle\int_0^\infty \frac{e^{-ax}}{x}[\cos(mx) - \cos(nx)]\,dx = \frac{1}{2}\ln\left(\frac{a^2 + n^2}{a^2 + m^2}\right) \quad (a > 0).$

39. $\displaystyle\int_0^\infty e^{-ax}\cos^2(mx)\,dx = \frac{a^2 + 2m^2}{a(a^2 + 4m^2)} \quad (a > 0).$

40. $\displaystyle\int_0^\infty e^{-ax}\sin^2(mx)\,dx = \frac{2m^2}{a(a^2 + 4m^2)} \quad (a > 0).$

41. $\displaystyle\int_0^1 \left[\ln\left(\frac{1}{x}\right)\right]^q dx = \Gamma(q+1) \quad (q+1>0).$

42. $\displaystyle\int_0^1 x^p \ln\left(\frac{1}{x}\right) dx = \frac{1}{(p+1)^2} \quad (p+1>0).$

43. $\displaystyle\int_0^1 x^p \left[\ln\left(\frac{1}{x}\right)\right]^q dx = \frac{\Gamma(q+1)}{(p+1)^{q+1}} \quad (p+1>0,\, q+1>0).$

44. $\displaystyle\int_0^1 \ln(1-x)\, dx = -1.$

45. $\displaystyle\int_0^1 x\ln(1-x)\, dx = \frac{-3}{4}.$

46. $\displaystyle\int_0^1 \ln(1+x)\, dx = 2\ln(2) - 1.$

47. $\displaystyle\int_0^\infty e^{-ax^2}\cos(kx)\, dx = \frac{\sqrt{\pi}}{2\sqrt{a}} e^{-k^2/(4a)}.$

G

Some Integrals with Exponentials in the Integrands: The Error Function

We begin with the integral

$$\int_0^\infty e^{-x^2}\,dx = 1.$$

We compute the value of this integral by a trick, squaring the integral and changing variables:

$$I^2 = \left[\int_0^\infty e^{-x^2}\,dx\right]^2 = \int_0^\infty e^{-x^2}\,dx \int_0^\infty e^{-y^2}dy = \int_0^\infty\int_0^\infty e^{-(x^2+y^2)}\,dx\,dy.$$

We now change to polar coordinates,

$$\begin{aligned} I^2 &= \int_0^{\pi/2}\int_0^\infty e^{-\rho^2}\rho\,d\rho\,d\phi = \frac{\pi}{2}\int_0^\infty e^{-\rho^2}\rho\,d\rho \\ &= \frac{\pi}{2}\int_0^\infty \frac{1}{2}e^{-z}\,dz = \frac{\pi}{4}. \end{aligned}$$

Therefore,

$$I = \int_0^\infty e^{-x^2}\,dx = \frac{\sqrt{\pi}}{2}$$

and

$$\boxed{\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}} \tag{A.1}$$

Another trick can be used to obtain the integral,

$$\int_0^\infty x^{2n} e^{-ax^2}\, dx,$$

where n is an integer. For $n = 1$,

$$\begin{aligned}\int_0^\infty x^2 e^{-ax^2}\, dx &= -\int_0^\infty \frac{d}{da}\left[e^{-ax^2}\right] dx = -\frac{d}{da}\int_0^\infty e^{-ax^2}\, dx \\ &= -\frac{d}{da}\left[\frac{1}{2}\sqrt{\frac{\pi}{a}}\right] = \frac{1}{4a}\sqrt{\frac{\pi}{a}} = \frac{\pi^{1/2}}{4a^{3/2}}. \end{aligned} \tag{A.2}$$

For n an integer greater than unity,

$$\int_0^\infty x^{2n} e^{-ax^2}\, dx = (-1)^n - \frac{d^n}{da^n}\left[\frac{1}{2}\sqrt{\frac{\pi}{a}}\right]. \tag{A.3}$$

Equations (A.2) and (A.3) depend on the interchange of the order of differentiation and integration. This can be done if an improper integral is uniformly convergent. The integral in Eq. (A.1) is uniformly convergent for all real values of a greater than zero. Similar integrals with odd powers of x are easier. By the method of substitution,

$$\int_0^\infty x e^{-ax^2}\, dx = \frac{1}{2a}\int_0^\infty e^{-y}\, dy = \frac{1}{2a}. \tag{A.4}$$

We can apply the trick of differentiating under the integral sign just as in Eq. (A.3) to obtain

$$\int_0^\infty x^{2n+1} e^{-ax^2}\, dx = (-1)^n \frac{d^n}{da^n}\left(\frac{1}{2a}\right). \tag{A.5}$$

The integrals with odd powers of x are related to the gamma function, defined in Appendix G. For example,

$$\int_0^\infty x^{2n+1} e^{-x^2}\, dx = \frac{1}{2}\int_0^\infty y^n e^{-y}\, dy = \frac{1}{2}\Gamma(n+1). \tag{A.6}$$

The Error Function

The indefinite integral

$$\int e^{-x^2}\, dx$$

has never been expressed as a closed form (a formula not involving an infinite series or something equivalent). The definite integral for limits other than 0 and ∞ is not obtainable in closed form. Because of the frequent occurrence of such

definite integrals, tables of numerical approximations have been generated.[1] One form in which the tabulation is done is as the *error function*, denoted by $\text{erf}(x)$ and defined by

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-t^2}\, dt.$$

As you can see from Eq. (A.1),

$$\lim_{x \to \infty} \text{erf}(x) = 1.$$

The name "error function" is chosen because of its frequent use in probability calculations involving the Gaussian probability distribution. Another form giving the same information is the *normal probability integral*[2]

$$\frac{1}{\sqrt{2\pi}} \int_{-x}^{x} e^{-t^2/2}\, dt.$$

Values of the Error Function

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt^*$$

x		0	1	2	3	4	5	6	7	8	9
0.0	0.0	000	113	226	338	451	564	676	789	901	*013
0.1	0.1	125	236	348	459	569	680	790	900	*009	*118
0.2	0.2	227	335	443	550	657	763	869	974	*079	*183
0.3	0.3	286	389	491	593	694	794	893	992	*090	*187
0.4	0.4	284	380	475	569	662	755	847	937	*027	*117
0.5	0.5	205	292	379	465	549	633	716	798	879	959
0.6	0.6	039	117	194	270	346	420	494	566	638	708
0.7		778	847	914	981	*047	*112	*175	*238	*300	*361
0.8	0.7	421	480	538	595	651	707	761	814	867	918
0.9		969	*019	*068	*116	*163	*209	*254	*299	*342	*385
1.0	0.8	427	468	508	548	586	624	661	698	733	768
1.1		802	835	868	900	931	961	991	*020	*048	*076
1.2	0.9	103	130	155	181	205	229	252	275	297	319
1.3		340	361	381	400	419	438	456	473	490	507
1.4	0.95	23	39	54	69	83	97	*11	*24	*37	*49
1.5	0.96	61	73	84	95	*06	*16	*26	*36	*45	*55
1.6	0.97	63	72	80	88	96	*04	*11	*18	*25	*32

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[1] Two commonly available sources are Eugene Jahnke and Fritz Emde, *Tables of Functions*. Dover, New York, 1945, and Milton Abramowitz and Irene A. Stegun, Eds., *Handbook of Mathematical Functions with Formulas, Graph and Mathematical Tables*, U.S. Government Printing Office, Washington, DC, 1964.

[2] See for example Herbert B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan, New York, 1961.

x		0	1	2	3	4	5	6	7	8	9
1.7	0.98	38	44	50	56	61	67	72	77	82	86
1.8		91	95	99	*03	*07	*11	*15	*18	*22	*25
1.9	0.99	28	31	34	37	39	42	44	47	49	51
2.0	0.995	32	52	72	91	*09	*26	*42	*58	*73	*88
2.1	0.997	02	15	28	41	53	64	75	85	95	*05
2.2	0.998	14	22	31	39	46	54	61	67	74	80
2.3		86	91	97	*02	*06	*11	*15	*20	*24	*28
2.4	0.999	31	35	38	41	44	47	50	52	55	57
2.5		59	61	63	65	67	69	71	72	74	75
2.6		76	78	79	80	81	82	83	84	85	86
2.7		87	87	88	89	89	90	91	91	92	92
2.8	0.9999	25	29	33	37	41	44	48	51	54	56
2.9		59	61	64	66	68	70	72	73	75	77

* From Eugene Jahnke and Fritz Emde, *Tables of Functions*, Dover Publications, New York, 1945, p. 24.

To use this table, obtain the first digits of $\text{erf}(x)$ from column 2 and the remaining digits from the appropriate column. Entries marked with * correspond to the value in the next lower row of column 2.

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