Titration of Acids and Bases: An Introduction

Experiments 20 and 21 are really two parts of a single experiment having a single ultimate objective, namely, the determination of the concentration of an acid solution. This special overview has been written to point out the division of the procedure into two parts, and to furnish you with a basis for understanding how these parts are related. In brief, Experiment 21 uses a sodium hydroxide solution of *known* concentration to find the unknown concentration of the acid. The sodium hydroxide solution used in Experiment 21 is prepared, and its concentration is determined, in Experiment 20. It is therefore essential that the solution you prepare in Experiment 20 be kept for use in Experiment 21.

MOLARITY: A CONCENTRATION UNIT

In these experiments you will use **molarity** as your concentration unit. By definition, molarity is the number of moles of solute per liter of solution. So you may see clearly how molarity may be found from experimental data—so you may see what information you require to calculate molarity and how you use that information—the idea is presented here side by side with a more familiar parallel:

Rate of travel is expressed by speed, the units of which are miles per hour, or miles/hour.	Solution concentration is expressed by molarity, the units of which are moles per liter, or moles/liter.
If you were to hike 12.0 miles in 4.00 hours, you would find your average speed by dividing 12.0 miles by 4.00 hours: $\frac{12.0\ \text{miles}}{4.00\ \text{hours}} = 3.00\,\text{miles/hour}$	If you were to dissolve 12.0 moles of solute in 4.00 liters of solution, you would find your molarity by dividing 12.0 moles by 4.00 liters: $\frac{12.0\ \text{miles}}{4.00\ \text{liters}} = 3.00\,\text{moles/liter}$
Your calculation method matches the units in which speed is expressed: if you divide the number of miles traveled in a given trip by the hours taken for the same trip, the result is average speed.	Your calculation method matches the units in which molarity is expressed: if you divide the number of moles in a given sample of solution by the number of liters in the same sample, the result is the molarity of the solution.

The two essential items you require for calculation of speed are *miles traveled* and *hours in trip.*	The two essential items you require for calculation of molarity are *moles of solute* and *liters of solution.*

The last sentence in the right column sets your objective for both experiments: to find the number of moles of solute in a sample of solution and the volume of that sample. Dividing one by the other yields the required molarity.

TITRATION: A LABORATORY PROCESS

Titration is the controlled addition of a solution into a reaction vessel from a buret. By means of titration, the volume of solution used may be determined quite precisely. The titration process is used in many analytical determinations, including those involving acid–base reactions.

An **indicator** is a substance used to signal when the titration arrives at the point at which the reactants are stoichiometrically (or chemically) equal, as defined by the reaction equation. For example, in an acid–base titration between sodium hydroxide and hydrochloric acid,

$$NaOH(aq) + HCl(aq) \longrightarrow H_2O(\ell) + NaCl(aq)$$

the indicator should tell when the numbers of moles of NaOH and HCl are exactly equal, matching the 1:1 ratio in the equation. For the reaction

$$2\,NaOH(aq) + H_2SO_4(aq) \longrightarrow 2\,H_2O(\ell) + Na_2SO_4(aq)$$

the indicator should tell when the number of moles of NaOH is exactly twice the number of moles of H_2SO_4, this time reflecting the 2:1 molar ratio between the reactants. This point of chemical equality is called the **equivalence point** of the titration. Acid–base indicators send their signal by changing color at or very near the equivalence point of the titration.

A **standard solution** is a solution with a precisely determined concentration. Initially the concentration of a standard solution is determined from a weighed quantity of a **primary standard,** a highly purified reference chemical. A standard solution may be prepared in either of two ways:

1. A primary standard is carefully weighed, dissolved, and diluted accurately to a known volume. Its concentration can be calculated from the data.
2. A solution is made to an approximate concentration and then standardized by titrating an accurately weighed quantity of a primary standard.

Once a solution has been standardized in one reaction, it may be used as a standard solution in subsequent reactions. Thus the standard solution prepared in Experiment 20 will be used in the reaction of Experiment 21 to determine the concentration of an unknown acid.

With this background, we now proceed to Experiments 20 and 21 individually.

Titration of Acids and Bases–I

Performance Goals

20–1 Given the volume of a solution of known molarity, and the volume to which it is diluted with water, calculate the molarity of the diluted solution.

20–2 Given the approximate molarity and volume of an acid or base solution to be used in a titration, calculate the number of grams of a known solid base or acid required for the reaction.

20–3 Given the volume of a base or acid solution that reacts with a weighed quantity of a primary standard acid or base, calculate the molarity of the base or acid solution.

20–4 Perform acid–base titrations reproducibly.

CHEMICAL OVERVIEW

In this experiment you will prepare a standard solution of sodium hydroxide to be used in Experiment 21. Solid sodium hydroxide has the property of absorbing moisture from the air. It is therefore not possible to weigh sodium hydroxide accurately, which makes it unsuitable as a primary standard. Consequently, you will use the second of the two methods for preparing a standard solution listed on page 268. Your primary standard will be oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\,H_2O$. The reaction between the acid and base is

$$2\,NaOH(aq) + H_2C_2O_4(aq) \longrightarrow 2\,H_2O(\ell) + Na_2C_2O_4(aq) \qquad (20.1)$$

Sodium hydroxide will be made available in the laboratory in the form of a solution that is approximately one molar (1 M) in concentration. Note that this is an *approximate* concentration, expressed in *one* significant figure. No calculation based on that concentration can be considered reliable. You will be instructed to dilute a specified quantity of that solution to a larger volume with water, and then to calculate the *approximate* concentration of the diluted solution (see Performance Goal 20-1). This is one of two preliminary calculations in this experiment, and it appears as Question 1 in the Advance Study Assignment. If you turn in your Advance Study Assignment at the beginning of the laboratory period, be sure to keep a copy of your calculation for use while performing the experiment. The diluted NaOH solution will be used in the titration.

Next it will be necessary for you to calculate the quantity of solid oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\ H_2O$, that will react with approximately 15 mL of the diluted NaOH solution. This is a solution stoichiometry problem in which the first step is to find the number of moles of NaOH in 15 mL of solution at the approximate concentration just determined. The volume of a solution times its molarity yields the number of moles:

$$\text{Volume (liter)} \times \text{molarity}\left(\frac{\text{moles}}{\text{liter}}\right) = \text{moles} \qquad (20.2)$$

The balance of the problem is set up and solved in the usual stoichiometry pattern. This is the second of the two preliminary calculations, and it corresponds to Performance Goal 20–2. This calculation appears as Question 2 in the Advance Study Assignment. Again, be sure to keep a copy for use while performing the experiment.

After carefully weighing out three samples of solid oxalic acid dihydrate, you will dissolve it and perform the titration described by Equation 20.1. From the mass of oxalic acid you will be able to determine the number of moles of acid present. From the equation you will determine the number of moles of NaOH required in the neutralization. You will then know both the volume of the NaOH solution and the number of moles of NaOH it contains. These are the ''two essential items you require for (the) calculation of molarity'' (see Introduction, p. 267): dividing moles by liters yields molarity. (See Performance Goal 20–3.)

The last of the performance goals for this experiment calls for you to perform titrations reproducibly. To meet this requirement you must come up with sodium hydroxide concentrations that are ''the same'' in separate titrations. This calls for establishing a standard of ''sameness.'' You will be instructed to conduct three titrations as a minimum. If two of these yield molarities that are within 0.007 M of each other, they will be accepted as satisfying the reproducibility requirement. If you do not reach this result, additional titrations will be required.

So far nothing has been mentioned about the *accuracy* of your work. Indeed, within Experiment 20 there is no way to judge accuracy, because each student will have his/her own sodium hydroxide solution, which will have a concentration slightly different from that of his/her neighbor. In Experiment 21, however, you will use your standard solution to determine the concentration of an acid that is unknown to you, *but known to your instructor.* At this point an accurate result will be required. It should be apparent that your result in Experiment 21 cannot be accurate unless the concentration of the solution prepared in Experiment 20 has been determined accurately. As a consequence, if your accuracy in Experiment 21 does not meet the standard established, *it may be necessary for you to repeat Experiment 20 in order to correct previously undetected errors made there.* With this in mind, you are strongly urged to retain a complete record of *all* data, of *all* volumes in the titrations, even if you think they might be incorrect. It is surprising how often ''incorrect'' data turn out to be just what is needed by the time a long experiment is completed.

SAMPLE CALCULATIONS

The following examples illustrate the calculations involved in Performance Goals 20–1 and 20–3:

Example 1

25.0 mL of a 12.0 M solution is diluted to 500 mL. Calculate the molarity of the dilute solution.

The number of moles of solute is the same in both the initial solution and the diluted solution; only water is added. This number of moles is

$$0.0250\ \text{L} \times \frac{12.0\ \text{moles}}{\text{L}} = 0.300\ \text{mole}$$

In the diluted solution the 0.300 mole of solute is dissolved in 500 mL, or 0.500 L. The concentration is therefore

$$\frac{0.300\ \text{mole}}{0.500\ \text{L}} = 0.600\,\text{mole/L}$$

Example 2

Calculate the molarity of an NaOH solution if a sample of oxalic acid weighing 1.235 g requires 42.5 mL of the base for neutralization.

First, determine the number of moles of oxalic acid present. The formula of solid oxalic acid is $H_2C_2O_4 \cdot 2\,H_2O$. Notice that, although the water of hydration is not shown in Equation 20.1, the acid is weighed as a solid, which includes the water. Accordingly, calculations must be based on the proper molar mass. Thus,

$$1.235\ \text{g}\ H_2C_2O_4 \cdot 2H_2O \times \frac{1\ \text{mole}\ H_2C_2O_4}{126\,\text{g}\ H_2C_2O_4 \cdot 2H_2O} = 0.00980\ \text{mole}\ H_2C_2O_4$$

Second, determine the number of moles of NaOH required to react with 0.00980 mole of $H_2C_2O_4$, according to the equation.

$$0.00980\ \text{mole}\ H_2C_2O_4 \times \frac{2\ \text{moles NaOH}}{1\ \text{mole}\ H_2C_2O_4} = 0.0196\ \text{mole NaOH}$$

Third, if 0.0196 mole of NaOH is present in 42.5 mL of solution, find the concentration in moles per *liter*.

$$\frac{0.0196\ \text{mole NaOH}}{0.0425\,\text{L}} = 0.461\ \text{M NaOH}$$

As a single dimensional analysis setup, this calculation would appear as:

$$1.235\ \text{g}\ H_2C_2O_4 \cdot 2H_2O \times \frac{1\ \text{mole}\ H_2C_2O_4}{126\,\text{g}\ H_2C_2O_4 \cdot 2H_2O} \times \frac{2\,\text{moles NaOH}}{1\,\text{mole}\ H_2C_2O_4} \times \frac{1}{0.0425\,\text{L}} = 0.461\text{M NaOH}$$

SAFETY PRECAUTIONS AND DISPOSAL METHODS

If some of the sodium hydroxide solution, either concentrated or dilute, comes into contact with your skin, it will have a slippery feeling, somewhat like soap. This is produced because the solution is slowly dissolving a layer of your skin. For obvious reasons, the process should not be allowed to continue. If you encounter that feeling at any time during the experiment, take time out to wash your hands thoroughly until the slippery feeling is gone.

Both the acid and base used in this experiment are corrosive and harmful over prolonged exposure. Avoid all unnecessary contact, and keep them off your clothing too. Both solutions are harmful to the eyes; be sure to wear goggles when working with all chemicals, either solid or in solution, during this experiment. The goggle requirement extends to cleaning-up operations, as well.

After you have finished the titrations, SAVE your NaOH solution for Experiment 21. The content of the Erlenmeyer flasks can be poured down the drain.

PROCEDURE

NOTE: Record all mass measurements in grams to the nearest 0.001 g. Record all volume measurements from the buret in milliliters to the nearest 0.1 mL.

Preparation of NaOH Solution

A. Using a graduated cylinder, transfer about 100 mL of 1 M NaOH to a large beaker (600 mL or larger). With continuous stirring, dilute with deionized water until the total volume is about 500 mL.

NOTE: Thorough mixing is essential at this point. If you determine the ''concentration'' of an unmixed solution, you determine the concentration of only that part of the solution that you use. If you then use another part of the solution, with a different concentration, you will have no accuracy in your second application.

B. Transfer your solution to a stoppered or capped storage bottle. (Always keep your standard solution covered, because any evaporation loss or CO_2 absorption will change its concentration.) Label the bottle with your name, so it does not become lost among the bottles of your laboratory neighbors.

C. Calculate the approximate molarity of your solution. (This is Question 1 in the Advance Study Assignment.)

Preparation of Oxalic Acid Solutions

A. From the approximate molarity of the diluted NaOH solution, calculate the mass of oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\,H_2O$, needed to neutralize 15 mL of the base. Don't forget the water of hydration in the solid acid, because it will be present in what you weigh out. Have your instructor approve your calculation before proceeding. (This is Question 2 in the Advance Study Assignment.)

B. Make identifying marks on three 250-mL Erlenmeyer flasks.

NOTE: The next step is extremely critical. Your purpose is to transfer into each of the above Erlenmeyer flasks an amount of oxalic acid dihydrate that is approximately equal to what was calculated in Step 2A, but whose actual mass is known to the closest milligram. The care with which this step is performed will determine both the accuracy and precision with which your sodium hydroxide solution is standardized, and the accuracy of your result in Experiment 21. Be particularly careful that no oxalic acid is spilled. If that happens, begin again.

C. Label three **dry** Erlenmeyer flasks. Using a milligram balance, weigh the first flask to the milligram and record the mass of the empty flask. From a beaker, using a spatula, transfer some oxalic acid crystals into the flask, being very careful not to spill any. The mass of the acid in each flask should be approximately equal to the amount you calculated in Step 2A. The amount of acid transferred can be calculated by taking the mass of the flask plus acid and subtracting the mass of the empty flask. Repeat the procedure with the other flasks.

If you do not have dry flasks available, use a weighing paper instead. Weigh the empty paper first, then add the oxalic acid. Be very careful when you transfer the solid into the labeled Erlenmeyer flasks not to lose any crystals.

D. Add about 75 mL of deionized water to each flask. Swirl or use a magnetic stirrer to *completely* dissolve the crystals.

Titration of Oxalic Acid with NaOH

A. Rinse your buret with deionized water. Now, rinse the buret with about 10 mL of *your dilute* NaOH solution. Make sure the tip of the buret has also been rinsed. Drain and discard the rinse and repeat the rinsing with a second portion of NaOH. Fill the buret with NaOH, using a funnel. Drain the solution into the calibrated portion of the buret, letting the liquid flow through the tip. Make sure there is no bubble present under the stopcock. Set the bottom of the meniscus on a whole line—never start between lines! Record the buret reading as the initial buret reading on the work page.

B. Add 3 to 5 drops of phenolphthalein to each oxalic acid solution.

C. If you have a magnetic stirring apparatus available, carefully add a stirring bar to the flask containing the completely dissolved acid. Position the flask such that the tip of the buret is inside the neck of the flask. Start stirring at a moderate speed. If you do not have such apparatus available, you will have to swirl the flask manually throughout the titration (see Figure 20.1).

Start the addition of NaOH. At the beginning of the titration you may add the base in larger portions, slowing down as the time required for the pink color to disappear gets longer. It is essential that you mix (or swirl) the contents of the flask throughout the titration to ensure complete mixing of the solutions. The end of the titration is reached when the pink color persists for 30 seconds. Record the final buret reading on the work page.

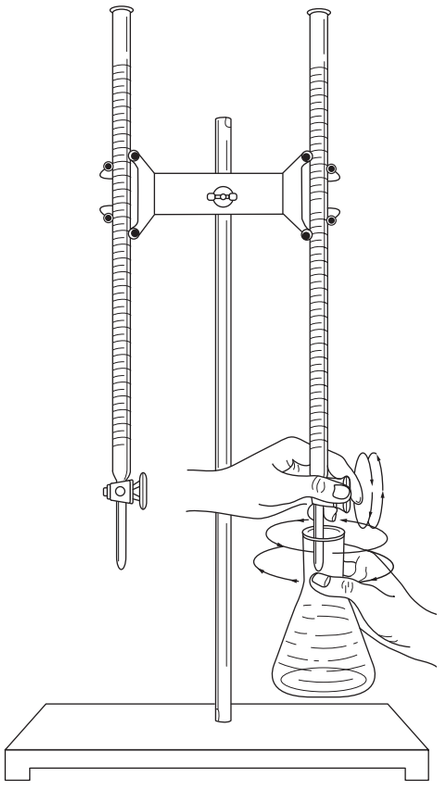

Figure 20.1
Titration from a buret into a flask.

D. Adjust the volume so that the bottom of the meniscus is on a whole line. Do not start from the final volume of the previous run if this volume was between lines! Be sure there is sufficient volume of NaOH left to complete the second titration. Remember, the bottom portion of the buret is not calibrated! If this is not the case, fill up the buret (using a funnel), adjust the liquid level, record the initial reading, and proceed with the second titration as described above.

E. Calculate the results of the first three runs immediately. If the range of the molarity values is greater than 0.007, repeat the process with two more samples. *Keep all titration data.*

If you satisfy the reproducibility requirement, proceed to Experiment 21. If that experiment is to be done at another time, store your NaOH solution in an upright position (see Step 1B). Clean all glassware thoroughly and rinse it with deionized water before putting it away or returning it to the stockroom.

Name _____ Date _____ Section _____

Experiment 20

Advance Study Assignment

1. Read Part 1 for the preparation of your NaOH solution. Calculate the approximate molarity of the solution (Step 1C). Use three significant figures.

2. Using your result from Question 1, calculate the mass of oxalic acid dihydrate, $H_2C_2O_4 \cdot 2\,H_2O$, required to react with 15 mL of your NaOH solution (Step 2A in the procedure). Round off your answer to three significant figures. It is this result that must be approved by your instructor before you go beyond Step 2A in the procedure.

3. If 0.628 g of $H_2C_2O_4 \cdot 2\,H_2O$ requires 24.7 mL of NaOH(aq) in a titration, calculate the molarity of the solution.

4. Why must you save your NaOH solution at the end of Experiment 20?

5. If your fingers feel slippery at any time during this experiment, what does that indicate and what should you do about it?

Name *Date* *Section*

Experiment 20

Work Page

TABLE OF DATA AND RESULTS
(Beneath the table show the full calculation setup for at least one valid titration run)

Sample	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Mass of flask + acid (g)								
Mass of flask (g)								
Mass of oxalic acid (g)								
Initial buret reading (mL)								
Final buret reading (mL)								
Volume of NaOH (mL)								
Molarity of NaOH								

Average molarity———

Calculation setup for at least one valid titration run:

Name _____ Date _____ Section _____

Experiment 20

Report Sheet

TABLE OF DATA AND RESULTS
(Beneath the table show the full calculation setup for at least one valid titration run)

Sample	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Mass of flask + acid (g)								
Mass of flask (g)								
Mass of oxalic acid (g)								
Initial buret reading (mL)								
Final buret reading (mL)								
Volume of NaOH (mL)								
Molarity of NaOH								

Average molarity ——

Calculation setup for at least one valid titration run: