CHAPTER 1

1.Introduction to Analytical Chemistry

Chemistry is the study of matter, including its composition and structure, its physical properties, and its reactivity. There are many ways to study chemistry, but, we traditionally divide it into five fields: organic chemistry, inorganic chemistry, biochemistry, physical chemistry, and analytical chemistry.

Analytical chemistry is often described as the area of chemistry responsible for **1.** Characterizing the composition of matter, both qualitatively and quantitatively,

2. Improving established analytical methods, **3.** Extending existing analytical methods to new types of samples, and **4.** Developing new analytical methods for measuring chemical phenomena.

2. Measurements in Analytical Chemistry

Units of Measurement

A measurement usually consists of a unit and a number expressing the quantity of that unit. We may express the same physical measurement with different units, which can create confusion.

To ensure consistency, and to avoid problems, scientists use a common set of fundamental units. These units are called SI units after the Système International d'Unités. Sometimes it is preferable to express measurements without the exponential term, replacing it with a prefix (Table 1.1). A mass of 1×10^{-15} g, for example, is the same as 1 fg, or femtogram.

Table 1.1 Common Prefix for Exponential Notation

Prefix	Symbol	Factor	Prefix	Symbol	Factor	Prefix	Symbol	Factor
yotta	Y	10^{24}	kilo	k	10^{3}	micro	μ	10^{-6}
zetta	Z	10^{21}	hecto	h	10^{2}	nano	n	10^{-9}
eta	E	10^{18}	deka	da	10^{1}	pico	p	10^{-12}
peta	P	10^{15}	-	-	10^{0}	femto	f	10^{-15}
tera	T	10^{12}	deci	d	10^{-1}	atto	a	10^{-18}
giga	G	10^{9}	centi	c	10^{-2}	zepto	z	10^{-21}
mega	M	10^{6}	milli	m	10^{-3}	yocto	y	10^{-24}

Question: What Is a Mole and Why Are Moles Used?

Answer: A mole is simply a unit of measurement. Units are invented when existing units are inadequate. Chemical reactions often take place at levels where using grams wouldn't make sense, yet using absolute numbers of atoms/molecules/ions would be confusing, too.

Like all units, a mole has to be based on something reproducible قابل للإعادة. A mole is the quantity of anything that has the same number of particles found in 12.000 grams of carbon-12.

That number of particles is Avogadro's Number, which is roughly 6.02×10^{23}. A mole of carbon atoms is 6.02×10^{23} carbon atoms. A mole of chemistry teachers is 6.02×10^{23} chemistry teachers. It's a lot easier to write the word 'mole' than to write '6.02×10^{23}' anytime you want to refer to a large number of things! Basically, that's why this particular unit was invented.

Why don't we simply stick with units like grams (and nanograms and kilograms, etc.)? The answer is that moles give us a consistent method to convert between atoms/molecules and grams. It's simply a convenient unit to use when performing calculations.

The number of grams in a mole is different from substance to substance. If you're like most students, it's this that's confusing you. Picture it this way: a dozen elephants have a different weight than a dozen rabbits- but in each case, you have a

dozen animals. Similarly, a mole of oxygen gas has a different weight than a mole of water- but in each case, you have 6.02×10^{23} molecules.

Weight g /molecular wt. g/mol.= moles

2.1 Uncertainty in Measurements

A measurement provides information about its magnitude and its uncertainty. Consider, for example, the balance in Figure 1.1, which is recording the mass of a cylinder. When weighing an object on a balance, the measurement fluctuates in the final decimal place. We record this cylinder's mass as 1.2637 g ± 0.0001 g. mass as 1.2637 g ± 0.0001 g, indicating both its magnitude and its absolute uncertainty.

Suppose you weigh a sample on a balance that measures mass to the nearest ±0.1 mg. reporting the sample's mass as 1.762 g instead of 1.7623 g is incorrect because it does not properly convey the measurement's uncertainty. Reporting the sample's mass as 1.76231 g also is incorrect because it falsely suggest an uncertainty of ±0.01 mg or ±0.00001g.

2.2 Accuracy

The closeness of an experimental measurement or result to the true or accepted value.

2.3 Precision

The random or indeterminate error associated with a measurement or result. Sometimes called the variability, it can be represented statistically by the standard deviation or relative standard deviation (coefficient of variation)

2.4 Concentration

Concentration is a general measurement unit stating the amount of solute present in a known amount of solution: or (The ratio of the amount of solute to the amount of solution.) Although we associate the terms "solute" and "solution" with liquid samples, we can extend their use to gas-phase and solid-phase samples as well.

The following table shows examples of solution in liquid, gaseous, and solid states of matter.

Table 1.2 Solution of Different States of Matter.

State of Matter	Solvent	Solute	Solution
Liquid	Water	Acetic Acid	Vinegar
Gas	Nitrogen	Oxygen	Air
Solid	Copper	Tin	Bronze

2.5 Solution

A homogenous mixture of molecules or ions.

2.6 Solvent

The medium in which the molecules or ions are dissolved.

2.7 Solute

Any substance dissolved in a solvent.

2.8 Analyte

Constituent of the sample which is to be studied by quantitative measurements or identified qualitatively.

2.9 Molarity

Molarity express concentration as moles of solute per liter of solution (number of moles of solute in one litre of solution). Molarity is the concentration of a particular chemical species.

Molarity is used so frequently that we use a symbolic notation to simplify its expression in equations and in writing. Square brackets around a species indicate that we are referring to molarity. Thus, [Na+] is read as "the molarity of sodium ions.

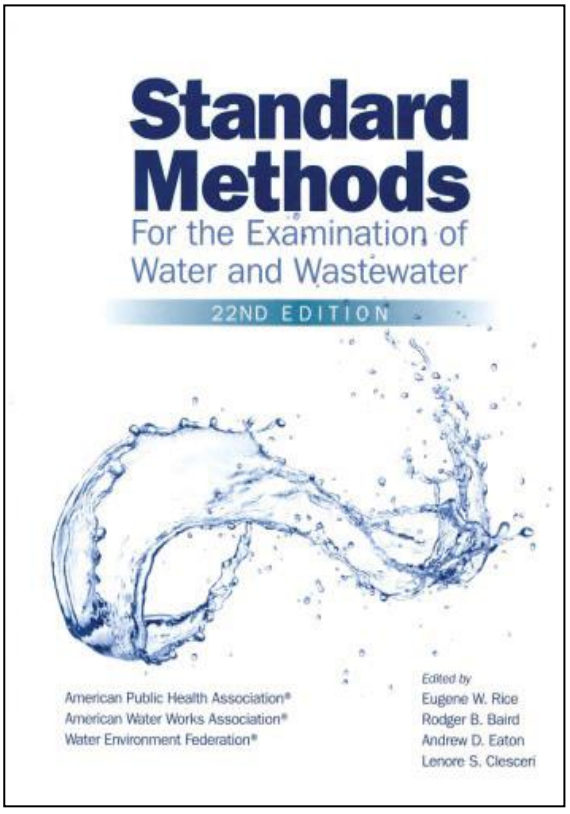
2.10 Normality

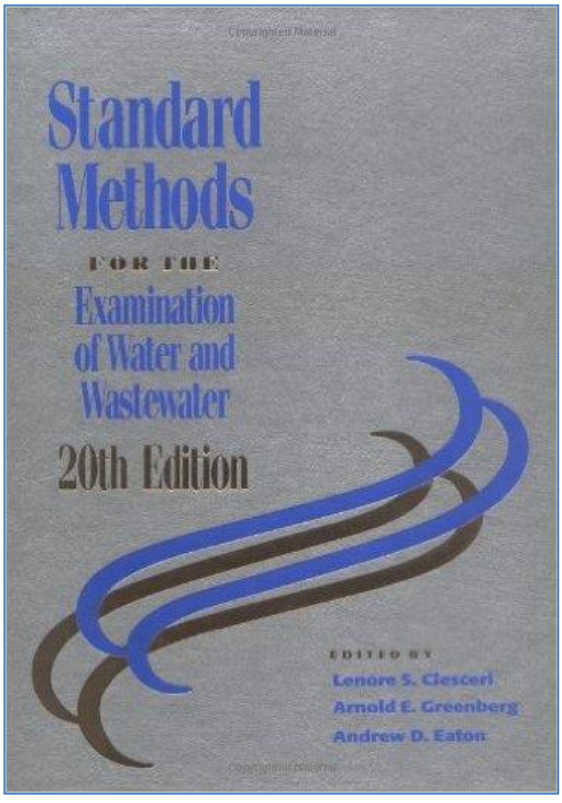
Normality is a concentration unit that is no longer in common use. Normality defines concentration in terms of an equivalent, in one litre of solution, which is the

amount of one chemical species reacting stoichiometrically with another chemical species.

One handbook that still uses normality is Standard Methods for the Examination of Water and Wastewater, a joint publication of the American Public Health Association APHA, the American Water Works Association AWWA, and the Water environment Federation WEF. This handbook is one of the primary resources for the environmental analysis of water and wastewater.

Standard Methods for examination of water and wastewater. 22nd ed. Washington: American Public Health Association; 2012. The first edition of Standard Methods was published in 1905. Since then it has been considered to be the best available guidance of water analysts, which covers all aspects of water and wastewater analysis techniques and categorizes the analytical methods based on the constituent and not on the type of water.





2.11 Molality

Molarity is based on the volume of solution containing the solute. Since density is a temperature dependent property on a solution's volume, and thus its molar concentration, changes with temperature. By using the solvent's mass (1 kg) in place of the solution's volume, the resulting concentration becomes independent of temperature.

Molality = no. of moles / weight of solvent (kg)

2.12 Weight, Volume, and Weight-to-Volume Ratios

Weight percent (w/w %), volume percent (% v/v) and weight-to-volume percent

1.(w/w %)= $\frac{Wt\ of\ solute\ g}{Wt\ of\ solution\ g}\ x\ 100$

Example (a):

What is the weight percent of 25 g of sodium sulphate dissolved in 200 g of solution?

(w/w %)= $\frac{25g}{200\ g}\ x\ 100$ = 0.125 x 100 =12.5%

Example (b):

Calculate the wt% for a solution prepared by dissolving 5 g of AgNO3 in 100 ml water

Water density = 1g/ml

100 ml of water=100 g of water = weight of solvent

(w/w %)= $\frac{Wt\ of\ solute\ g}{Wt\ of\ solution\ g}\ x\ 100$

Weight of solution = solute + solvent = 5+100= 105 g

(w/w %)= $\frac{5\ g}{105\ g}\ x\ 100$ =4.76%

2. (v/v %)= $\frac{v\ of\ solute\ ml}{v\ of\ solution\ ml}\ x\ 100$

Example:

Calculate v/v% of a solution that was prepared by adding 50 ml of methanol to 200 ml water.

Volume of solution = volume of solute + volume of solvent

Vol. of solution= 50+ 200= 250 ml

(v/v %)= $\frac{50\ ml}{250\ ml}$ $x\ 100$ = 20%

3. (wt/v %)= $\frac{wt\ of\ solute\ g}{v\ of\ solution\ ml}$ $x\ 100$

Example (a):

Calculate wt/v % for 4g of NaOH dissolved in 500 ml solution.

wt/v%= $\frac{4\ g}{500\ ml}$ $x\ 100$**=0.8%**

Example (b)

Calculate the molarity of 4 g of NaOH dissolved in 500 ml solution (NaOH Molecular wt.= 40 g/mole

No. of NaOH moles= 4 g/ 40 g/mol)= 0.1 mol

$$M = \frac{no.\ of\ moles}{litre\ solution}$$

$$M = \frac{0.1\ mol}{\frac{500ml}{1000ml/l}} = \frac{0.1\ molx\ 1000\ ml\ x\ l}{500\ ml} = 0.2\ M$$

2.13 Parts per Million and Parts per Billion

Part per million (ppm) and ***parts per billion*** (ppb) are ratios giving the grams of solute to, respectively, one million or one billion grams of sample. For example, 450 ppm Mn in steel that is =steel contains 450 μg of Mn for every gram of steel.

If we approximate the density of an aqueous solution as 1.00 g/mL, or 1000 kg/M^3 then solution concentrations can be express in ppm or ppb using the following relationships.

Ppm = mg/ L = mg/1000 ml = mg/1000g = mg/kg or =1mg/1000000mg = ppm

ppb= µg/L = µg/1000ml= µg/1000g = µg/kg= 1 µg /1000000000 µg

For gases a part per million usually is a volume ratio. Thus, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 µL of He.=1µL/L=ppm

2.14 Constituent

A component of a sample; it may be further classified as:
Major > 10%
Minor 0.01–10%
Trace 1–100 ppm (0.0001–0.01%)
Ultratrace < 1 ppm

2.15 Detection Limit

The smallest amount or concentration of an analyte that can be detected by a given procedure and with a given degree of confidence

3. CONVERTING BETWEEN CONCENTRATION UNITS

The most common ways to express concentration in analytical chemistry are molarity, weight percent, volume percent, weight-to-volume percent, and parts per million and parts per billion.

Example 2.2

A concentrated solution of ammonia is 28.0% w/w NH_3 and has a density of 0.899 g/mL. What is the molar concentration of NH_3 in this solution?

SOLUTION

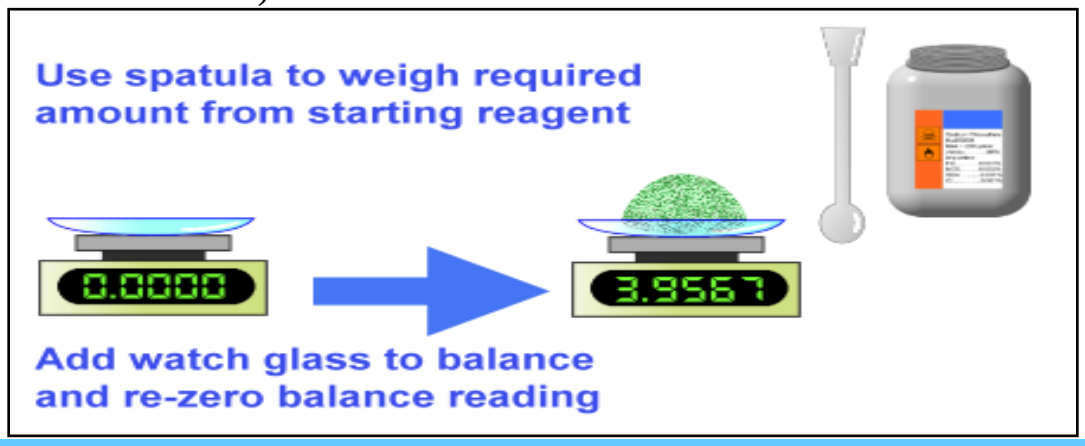
$$\frac{28.0\ \text{g NH}_3}{100\ \text{g solution}} \times \frac{0.899\ \text{g solution}}{\text{mL solution}} \times \frac{1\ \text{mol NH}_3}{17.04\ \text{g NH}_3} \times \frac{1000\ \text{mL}}{\text{L}} = 14.8\ \text{M}$$

4. PREPARING STOCK SOLUTIONS

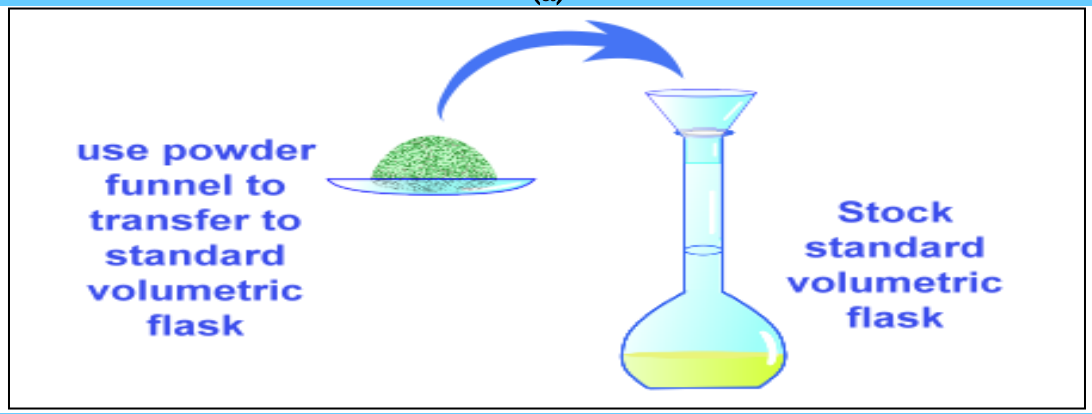
A stock solution is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid and diluting to a known volume. Exactly how this is done depends on the required concentration unit. For example, to prepare a solution with a desired molarity you weigh out an appropriate mass of the reagent, dissolve it in a portion of solvent, and bring to the desired volume. To prepare a solution where the solute's concentration is a volume percent, you measure out an appropriate volume of solute and add sufficient solvent to obtain the desired total volume.

Example 4

Describe how to prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu^{2+} using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid (99.8% w/w acetic acid).



(a)



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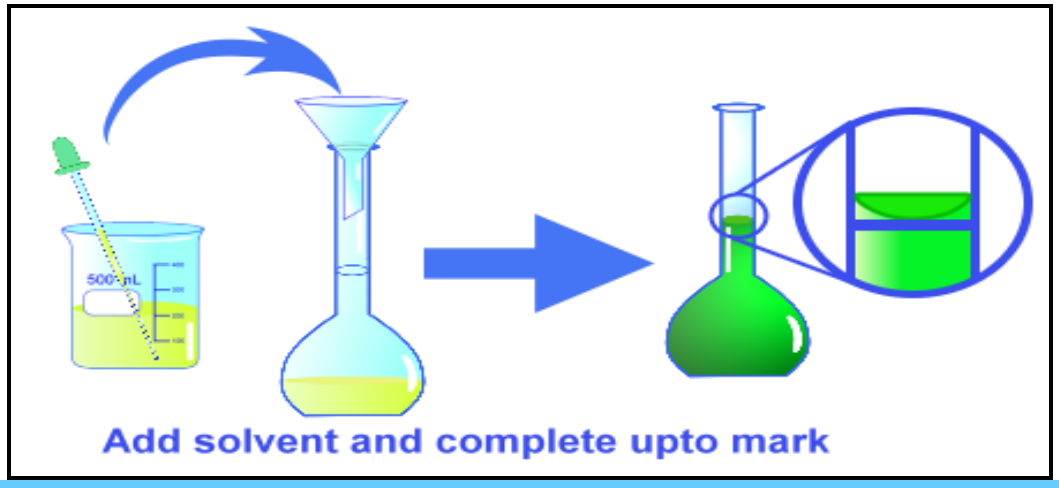

(c)

Figure 1.1: Preparing a stock solution of known molarity. (a) A measured number of moles of solute is weighed using analytical balance. (b) Solute is transferred in a volumetric flask. (c) Enough solvent is added to dissolve the solute by swirling and further solvent is carefully added until the calibration mark on the neck of the flask is reached, and the solution is then shaken until uniform.

$$\frac{0.20\ \text{mol NaOH}}{\text{L}} \times \frac{40.0\ \text{g NaOH}}{\text{mol NaOH}} \times 0.50\ \text{L} = 4.0\ \text{g}$$

To prepare the solution, place 4.0 grams of NaOH, weighed to the nearest tenth of a gram, in a bottle or beaker and add approximately 500 mL of water.

$$\frac{150.0\ \text{mg Cu}}{\text{L}} \times 1.000\ \text{L} = 150.0\ \text{mg Cu} = 0.1500\ \text{g Cu}$$

To prepare the solution we measure out exactly 0.1500 g of Cu into a small beaker and dissolve using small portion of concentrated HNO_3. The resulting solution is transferred into a 1-L volumetric flask. Rinse the beaker several times with small portions of water, adding each rinse to the volumetric flask. This process, which is called a quantitative transfer, ensures that the complete transfer of Cu^{2+} to the

volumetric flask. Finally, additional water is added to the volumetric flask's calibration mark.

c.

$$\frac{4\ \text{mL}\ CH_3COOH}{100\ \text{mL}} \times 2000\ \text{mL} = 80\ \text{mL}\ CH_3COOH$$

To prepare the solution, use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L and add sufficient water to bring the solution to the desired volume.

NOTE: What is the difference between acetic acid and glacial acetic acid?

There is technically no difference between the two but the acetic acid you buy in shops (vinegar) is usually 5-6% acetic acid in water and glacial acetic acid is basically 100% and gets its name from its tendency to freeze when it's cold. Glacial acetic acid can be purchased from chemical suppliers such as Sigma Aldrich.

Practice Exercise 2.5

Provide instructions for preparing 500 mL of 0.1250 M $KBrO_3$.

$KBrO_3$=167.0 g/mol. Ans. =10.44 g $KBrO_3$

5. PREPARING SOLUTIONS BY DILUTION

Solutions are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume. The resulting new concentration can be calculated using:

C1 V1 = C2V2

CHAPTER 1

Example (dilution)

If 25.0 mL of a 2.19 M solution are diluted to 72.8 mL, what is the final concentration?

Solution

Using the dilution equation, we have

(2.19 M) (25.0 mL) = M_2 (72.8 mL) M =mol/L= mmol/ml L

Solving for the second concentration (noting that the milliliter units cancel),

M_2 = 0.752 M

Example (dilution)

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, determine how much stock solution to use

(10%) $V1$ = (0.50%)(100 mL) 0.5= .5

$V1$ = 5 mL

Exercises

1. What is the difference between dilution and concentration?

   Dilution is a decrease in a solution's concentration, whereas concentration is an increase in a solution's concentration.

2. What quantity remains constant when you dilute a solution?
3. A 1.88 M solution of NaCl has an initial volume of 34.5 mL. What is the final concentration of the solution if it is diluted to 134 mL?

   Ans. 0.484 M

4. A 0.664 M solution of NaCl has an initial volume of 2.55 L. What is the final concentration of the solution if it is diluted to 3.88 L?
5. If 1.00 mL of a 2.25 M H_2SO_4 solution needs to be diluted to 1.00 M, what will be its final volume?

   Ans. 2.25 mL

6. If 12.00 L of a 6.00 M HNO_3 solution needs to be diluted to 0.750 M, what will be its final volume?
7. If 665 mL of a 0.875 M KBr solution are boiled gently to concentrate the solute to 1.45 M, what will be its final volume?

   Ans. 401.0 ml
8. If 1.00 L of an LiOH solution is boiled down to 164 mL and its initial concentration is 0.00555 M, what is its final concentration?
9. How much water must be added to 75.0 mL of 0.332 M $FeCl_3$(aq) to reduce its concentration to 0.250 M?

   Ans 24.6 ml
10. How much water must be added to 1.55 L of 1.65 M $Sc(NO_3)_3$(aq) to reduce its concentration to 1.00 M?

How to Convert between Percent & Parts per Million (ppm) Concentrations

Suppose we are given a parts per million measurement (ppm of X in Y) and we want to convert that to a percent concentration of X in Y.

% Concentration = ppm / 10,000

= ppm concentration divided by 10,000

The number 10000 is always used in these conversion.

Example 1

The air we breathe is 0.9% argon. Convert this value to ppm=1/1000000

$0.9\% = \frac{0.9}{100} \times \frac{10000}{10000} = 9{,}000$ ppm

Example 2

The air we breathe is about 0.036% carbon dioxide CO2. Convert this value to ppm.

$0.036\% = \frac{0.036}{100} \; x \; \frac{10000}{10000} = 360$ ppm

To change ppm values to percentages $\frac{1}{10000}$

Example 3

Whole milk is around 48000 ppm convert this value to %

48000 ppm= $\frac{48000}{100\ 00\ 00}$x $\frac{\frac{1}{10000}}{\frac{1}{10000}}$ = 4.8%

Example 4

A solution of Salt (NaCl) in water contains 520 ppm Sodium ions Na^+. **Convert** this value to percentage.%

520 ppm = $\frac{520}{100\ 00\ 00}$x $\frac{\frac{1}{10000}}{\frac{1}{10000}}$ = 0.052%

Molarity and parts per million (ppm)

Molarity and parts per million (ppm) are two units of measurement used to describe the concentration of a chemical solution. One mole is equivalent to the molecular or atomic mass of the solute. Parts per million, of course, refers to the number of molecules of solute per million parts of a solution. Since both of these units of measurement are commonly referred to in chemistry, it's helpful to understand how to convert from one to the other.

Example 1

A solution contains Cu^{2+} ions at a concentration of 3 x 10^{-4} M. What is the Cu^{2+} concentration in ppm?

Solution

Convert moles to mg.
From the periodic table, the atomic mass of Cu = 63.55 g/mol.
moles/L of Cu2+= (3 x 10^{-4} mol x 63.55 g/mol)/L
moles/L of Cu2+ = 1.9 x 10^{-2} g/L

moles/L of Cu^{2+} = 1.9 x 10^{-2} g/L x 1000 mg/1 g

moles/L of Cu^{2+}= 19 mg/L = 19 ppm

Example 2

Find the ppm concentration of chloride ions in a 0.1 M NaCl solution. **Knowing that** Cl atomic weight is 35.5 g/mol.

0.1 M NaCl solution= (0.1 mol./L) x 35.5 g/mol. x 1000 mg/g

= 3550 mg/L

Since 1 mg/L is about 1 ppm:

A 0.1 M solution of NaCl has a concentration of about 3550 ppm Cl ions.

Calculation of pH of a single solution containing specific masses of acid or base

Q1. What is the pH of a 1.5 liter solution containing .03 g Sulfuric acid H_2SO_4?

$$\frac{.03\ g}{98\ g/mol} \mathbf{x} \frac{1}{1.5\ l} \mathbf{x} \frac{2\ moles\ of\ H}{1\ mole\ of\ H2SO4} = 4.1 \times 10^{-4} \text{ mol/l} = M$$

pH= - log [4.1 x 10^{-4} mol/l] = pH= 3.4

Q2. What is the pH of a 0.75 L solution containing .025 g Calcium hydroxide $Ca(OH)_2$?

Molecular weight Ca=40+ (O=16 +H=1)2=74 g/mol,

$$\frac{.025\ g}{0.75\ l} \text{x} \frac{mol}{74\ g} \text{x} \frac{2\ moles\ of\ OH}{Mole\ of\ CaOH} = \text{OH} = 9 \times 10^{-4} \text{ mol/l} = M$$

P OH=-Log [9 x 10^{-4}**]= 3.1**
pH= 14-3.1= 11

Q3. What is the pH of a 1.75 liter solution containing .035 g Phosphoric acid? Knowing that (m. wt H_3PO_4 = 98g/mol)
Ans. H= 6.1 x10^{-4} mol/l) pH= 3.2

Q4. What is the pH of 0.5L solution that is .005 molar in H+ when it is added to a 0.5 L solution that is 0.004 molar in OH^- .

Ans:
The total volume of the new solution is 0.5+ 0.5= 1 L
The 0.004 moles of OH will neutralize 0.004 moles of H+ leaving 0.00l mole of H+
pH= -Log [0.001]= -Log [$1x10^{-3}$] , pH= 3.

Q5. Calculate the pH of 1 L solution containing 0.001g HCl and 0.001g NaOH

$\frac{.001\ gNaOH}{}x\frac{mol.}{40\ g}$= 2.5 $x10^{-5}$ mol. of NaOH

$\frac{.001\ gHCl}{}x\frac{mol}{36.5\ g}$= 2.7 $x10^{-5}$ mol of HCl

0.2 $x10^{-5}$ mol of extra H+, 0.2 $x10^{-5}$ mol/1L= 0.2 $x10^{-5}$ M
pH= -Log [2 $x10^{-6}$]= 5.7

Q6. Find the pH of a 1 liter solution of 0.04 molar hydrochloric acid to which .02 g sodium hydroxide has been added?
Ans: pH= 1.4

Q7. Calculate the pH of a 2 L aqueous solution to which were added .025g lithium hydroxide (Li OH) and 0.018 g nitric acid (HNO_3), m.wt (LiOH)=23.9 g/mol., (HNO_3) = 63 g/mol
Ans: pH =10.6

Q8. Calculate the pH of a 0.02 molar solution of HCl acid. Ans: 1.7

Q9. Calculate the concentration of H+ ions in .010 M NaOH.
Ans: [H+] =1.0 x 10^{-12}

[H] x [OH]= 1x10^{-14}

Q10. Calculate the pH of a 1.5 L aqueous solution to which were added .035 g Calcium hydroxide ($Ca(OH)_2$) and .047 g sulfuric acid H_2SO_4 m.wt $Ca(OH)_2$=74 gmol, H_2SO_4=98g/mol, Ans: pH= 5

$$\frac{0.035g}{} \text{x} \frac{mol.}{74\ Ca(OH)2g} \text{x} \frac{2\ moles\ of\ OH}{1\ mole\ of\ Ca(OH)2} = \quad 9.4 \text{ x} 10^{-4} \qquad \text{mol of OH-}$$

$$\frac{0.047g}{} \text{x} \frac{mol}{98g\ of\ H2SO4} \text{x} \frac{2\ moles\ of\ H}{1\ mole\ of\ H2SO4} = \qquad \text{mol of H+}$$

mol/1.5L= M

pH= -log[mol/1.5L]= 5

Analytical Chemistry

pH problems

Q1. What is the pH of a 1.5 liter solution containing .03 g Sulfuric acid?
Ans: [4.1 x 10^{-4} mol/l] pH= 3.4

Q2. What is the pH of a 0.75 L solution containing .025 g Calcium hydroxide?
Ans: [Molecular weight Ca=40+ (O=16 +H=1)2=74 g/mol], OH=9 x 10^{-4} mol/l pH=11

Q3. What is the pH of a 1.75 liter solution containing .035 g Phosphoric acid?
Ans: [m. wt H3PO4 = 98g/mol] H= 6.1 x10^{-4} mol/l) pH= 3.2

Q4. What is the pH of 0.5L solution that is .005 molar in H+ when it is added to a 0.5 L solution that is 0.004 molar in OH^- .
Ans: 1x10^{-3}(pH= 3).

Q5. Calculate the pH of 1 L solution containing 0.001gHCl and 0.001g NaOH
Ans: H+= 0.2X10^{-5} } pH= 5.7

Q6. the pH of a 1 liter solution of 0.04 molar hydrochloric acid to which .02 g sodium hydroxide has been added?
Ans: pH= 1.4

Q7. Calculate the pH of a 2 L aqueous solution to which were added .025g lithium hydroxide (Li OH) and 0.018 g nitric acid (HNO_3), m.wt (LiOH)=23.9 g/mol., (HNO_3) = 63 g/mol
Ans: pH =10.6

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Q9. Calculate the concentration of H+ ions in .010 M NaOH.
Ans: [H+] =1.0 x 10^{-12}

Q10. Calculate the pH of a 1.5 L aqueous solution to which were added .035 g Calcium hydroxide ($Ca(OH)_2$) and .047 g sulfuric acid H_2SO_4.mwt $Ca(OH)_2$)=74 gmol, H_2SO_4=98g/mol, Ans: 5

Q11. Calculate the concentration of H^+ ions in:

a. 0.75M solution of nitric acid(HNO_3)=
b. 2 M solution of potassium hydroxide (KOH)
c. 0.05 M solution of sulfuric acid(H_2SO_4)
d. 0.002 M solution of calcium hydroxide($Ca(OH)_2$)

Chapter Two
BASIC TOOLS AND OPERATIONS OF ANALYTICAL CHEMISTRY

Chapter 2 URLs

"Get your facts first, and then you can distort them as much as you please"
—Mark Twain

Learning Objectives

WHAT ARE SOME OF THE KEY THINGS WE WILL LEARN FROM THIS CHAPTER?

- Keep a good notebook, p. 20
- Use reagent-grade chemicals, p. 23
- How to use the analytical balance, p. 23
- Volumetric glassware and how to use it, pp. 30, 35
- How to calibrate glassware, p. 39
- How to prepare standard acid and base solutions, p. 42
- Common laboratory apparatus for handling and treating samples, p. 43
- How to filter and prepare precipitates for gravimetric analysis, p. 46
- How to sample solids, liquids, and gases, p. 49
- How to prepare a solution of the analyte, p. 51

Read this chapter before performing experiments.

Textbook Companion Site **www.wiley.com/college/christian**. Select the textbook, 7th edition, and then Instructor Companion Site. This will require an assigned username and password. This site is designed to contain a variety of helpful materials to supplement this textbook, including additional problems, presentations, worksheets, and experiments.

Analytical chemistry requires measurements in order to get the facts. Throughout the text, specific analytical equipment and instrumentation available to the analyst are discussed as they pertain to specific measuring techniques. Several standard items, however, are common to most analyses and will be required when performing the experiments. These are described in this chapter. They include the analytical balance and volumetric glassware and items such as drying ovens and filters. Detailed explanation of the physical manipulation and use of this equipment is best done by your laboratory instructor, when you can see and practice with the actual equipment, particularly since the type and operation of equipment will vary from one laboratory to another. Some of the general procedures of good laboratory technique will be mentioned as we go along.

See the **website** for this textbook for pictures of commonly used glassware and apparatus in the analytical laboratory.

2.1 The Laboratory Notebook—Your Critical Record

A well-kept laboratory record will help assure reliable analyses.

You should first realize that in the analytical laboratory, more than anywhere else, cleanliness and neatness are of the utmost importance. This also applies to the keeping of an orderly notebook. All data should be recorded permanently in ink *when they are collected*. When you go into the analytical laboratory, you will find that this orderliness is to your advantage. First of all, there is a saving of time in not having to reorganize and rewrite the data. There is probably an additional saving of time since you will be more organized in carrying out the operations of the analysis if you have trained yourself to put the data down in an orderly fashion. Chances for a mistake are reduced.

Second, if you make an immediate record, you will be able to detect possible errors in measurements or calculations. Data will not be lost or transferred incorrectly if they are recorded directly in a notebook instead of collected on scraps of paper.

For practicing analytical chemists and on-the-job applications, it is especially important to use the lab notebooks for entering observations and measurements directly. Complete documentation is essential for forensic or industrial laboratories for legal or patent considerations. In industrial research labs, the notebook must generally be signed (witnessed) and dated by another person familiar with the work to assure legal patent priority if applicable.

An example of a well-kept notebook with properly recorded data is illustrated next for the volumetric analysis of a soda ash unknown in your laboratory. This example is an abbreviated version in which actual calculation or numerical setups are omitted. For complete record keeping, you should include the computational setups in your notebook so an error can be tracked down later, if necessary.

Date: 7 September, 2013
Analysis of soda ash unknown
Principle: The soda ash is dissolved in water and titrated to a bromcresol green end point with standard hydrochloric acid. The hydrochloric acid is standardized against primary standard sodium carbonate. Weigh sodium carbonate and soda ash unknown by difference.
Reference: Experiment 8
Titration Reaction $CO_3^{2-} + 2H^+ = H_2CO_3$
Standardization

$$M(\text{HCl}) = \frac{\text{mg } Na_2CO_3}{\text{f wt } Na_2CO_3(\text{mg/mmol}) \times \frac{1}{2}(\text{mmol } Na_2CO_3/\text{mmol HCl}) \times \text{mL HCl}}$$

$$= \frac{\text{mg } Na_2CO_3}{105.99\ (\text{mg/mmol}) \times \frac{1}{2} \times \text{mL HCl}}$$

	#1	#2	#3
Bottle + sample	24.2689 g	24.0522 g	23.8597 g
Less sample	24.0522 g	23.8597 g	23.6269 g
g Na_2CO_3	0.2167 g	0.1925 g	0.2328 g
mg Na_2CO_3	216.7 mg	192.5 mg	232.8 mg
Buret reading	40.26 mL	35.68 mL	43.29 mL
Initial reading	0.03 mL	0.00 mL	0.02 mL
Net volume	40.23 mL	35.68 mL	43.27 mL
Molarity:	0.1016_4 *M*	0.1018_0 *M*	0.1015_2 *M*

Mean: 0.1016_5
Std. devn: 1.6 ppt
Range: 2.8 ppt

Soda Ash

$$\%\ Na_2CO_3 = \frac{M \times \text{mL} \times \text{f wt } Na_2CO_3 \times \frac{1}{2}\ (\text{mmol } Na_2CO_3/\text{mmol HCl})}{\text{mg sample}} \times 100$$

$$= \frac{0.1016_5\ (\text{mmol/mL}) \times \text{mL} \times 105.99\ (\text{mg/mmol}) \times \frac{1}{2}}{\text{mg sample}} \times 100$$

Bottle + sample	25.6728 g	25.4673 g	25.2371 g
Less sample	25.4673 g	25.2371 g	25.0027 g
g sample	0.2055 g	0.2302 g	0.2344 g
mg sample	205.5 mg	230.2 mg	234.4 mg
Buret reading	35.67 mL	40.00 mL	40.70 mL
Initial reading	0.00 mL	0.01 mL	0.05 mL
Net volume	35.67 mL	39.99 mL	40.65 mL
% Na_2CO_3	93.50%	93.58%	93.42%

Mean: 93.50
Std. devn: 0.9 ppt
Range: 1.7 ppt

The correct number of significant figures in measurements and calculations is critical in giving the proper significance to an analysis. See Chapter 3.

Rather than fill all the space in the laboratory notebook, it is recommended you leave alternate pages for scratch pages (e.g., the left page, leaving the right page for computations and summarizing data). It is also important that you record your data to the proper number of significant figures. Significant figures are discussed in Chapter 3, and you should review this material before beginning in the laboratory.

Laboratory Notebook Documentation

The laboratory notebook is a record of your job as an analytical chemist. It documents everything you do. It is the source for reports, publications, and regulatory submissions. The success or failure of a company's product or service may depend on how well you do that documentation. The notebook becomes a legal document for patent issues, government regulation issues (validation, inspections, legal actions), and the like. Remember, "if it isn't written down, it wasn't done." The notebook is where you record your original ideas that may form the basis of a patent, and so it is important to record what went into those ideas and when.

What are the features of a well-maintained notebook? They will vary with individual preferences. but here are some good rules:

- Use a hardcover notebook (no loose leafs).
- Number pages consecutively.
- Record only in ink.
- Never tear out pages. If not used, put a line through the page.
- Date each page, sign it, and have it signed and dated (soon after you complete your report) by someone else, stating "Read and Understood by."
- Record the name of the project, why it is being done, and any literature references.
- Record all data on the day you obtain it.

Modern instrument software allows the analyst to collect, store, and process data directly from the instrument signal, based on appropriate calibration. It is important that the software and calibration be validated, as for the remainder of the analysis, as a part of

good laboratory practice, discussed in Chapter 4. A variety of electronic notebooks and organizational tools are commercially available, many of which have very good functionality for storing and organizing notebook data in a variety of formats, for example, data files and spreadsheets. In addition, there are software-based laboratory information management systems (LIMS) to manage data, which ultimately aims at the complete elimination of paper notebooks. See http://en.wikipedia.org/wiki/Laboratory_information_management_system.

2.2 Laboratory Materials and Reagents

Table 2.1 lists the properties of materials used in the manufacture of common laboratory apparatus. Borosilicate glass (brand names: Pyrex, Kimax) is the most commonly used material for laboratory apparatus such as beakers, flasks, pipets, and burets. It is stable to hot solutions and to rapid changes in temperature. For more specific applications, there are several other materials employed that may possess advantage with respect to chemical resistance, thermal stability, and so forth.

Reagent-grade chemicals are almost always used in analyses. Primary standards are used for preparing volumetric standard solutions.

The different grades of chemicals are listed on the inside *back cover* of the text. In general, only *American Chemical Society* (*ACS*) *reagent-grade* or *primary standard* chemicals should be used in the analytical laboratory.

The American Chemical Society publishes a compendium of tests for evaluating the purity and quality of basic laboratory chemicals. Reagent chemicals that do not reference the ACS meet the manufacturer's own reagent specifications, which vary among suppliers.

The reagent-grade chemicals, besides meeting minimum requirements of purity, may be supplied with a report of analysis of the impurities (printed on the label). Primary standard chemicals are generally at least 99.95% pure. They are analyzed and the results are printed on the label. They are more expensive than reagent-grade chemicals and are used only for the preparation of standard solutions or for the standardization of a solution by reaction (titration) with it. Not all chemicals are available in primary standard grade. There are special grades of solvents for special purposes, for example, spectroscopy or liquid chromatography/mass spectrometry grades. These are specifically purified to remove impurities that might interfere in the particular application. Likewise, there are "semiconductor grade" acids that are specially refined and tested in greater detail for trace elemental impurities, typically in the parts per billion range.

In addition to commercial producers, the National Institute of Standards and Technology supplies primary standard chemicals. *NIST Special Publication 260* catalogs standard reference materials. (See http://ts.nist.gov/ts/htdocs/230/232/232.htm for information on the SRM program and lists of reference standards.) Reference standards are complex materials, such as alloys that have been carefully analyzed for the ingredients and are used to check or calibrate an analytical procedure.

The concentrations of commercially available acids and bases are listed on the inside *back cover*.

2.3 The Analytical Balance—The Indispensible Tool

Weighing is a required part of almost any analysis, both for measuring the sample and for preparing standard solutions. In analytical chemistry we deal with rather small weights, on the order of a few grams to a few milligrams or less. Standard laboratory weighings are typically made to three or four significant figures, and so the weighing

Table 2.1
Properties of Laboratory Materials

Material	Max. Working Temperature (°C)	Sensitivity to Thermal Shock	Chemical Inertness	Notes
Borosilicate glass	200	150°C change OK	Attacked somewhat by alkali solutions on heating	Trademarks: Pyrex (Corning Glass Works); Kimax (Owens-Illinois)
Soft glass		Poor	Attacked by alkali solutions	Boron-free. Trademark: Corning
Alkali-resistant glass		More sensitive than borosilicate		
Fused quartz	1050	Excellent	Resistant to most acids, halogens	Quartz crucibles used for fusions
High-silica glass	1000	Excellent	More resistant to alkalis than borosilicate	Similar to fused quartz Trademark: Vycor (Corning)
Porcelain	1100 (glazed)	Good	Excellent	
Porcelain	1400 (unglazed)			
Platinum	ca. 1500		Resistant to most acids, molten salts. Attacks by aqua regia, fused nitrates, cyanides, chlorides at > 1000°C. Alloys with gold, silver, and other metals	Usually alloyed with iridium or rhodium to increase hardness. Platinum crucibles for fusions and treatment with HF
Nickel and iron			Fused samples contaminated with the metal	Ni and Fe crucibles used for peroxide fusions
Stainless steel	400–500	Excellent	Not attacked by alkalis and acids except conc. HCl, dil. H_2SO_4, and boiling conc. HNO_3	
Polyethylene	115		Not attacked by alkali solutions or HF. Attacked by many organic solvents (acetone, ethanol OK)	Flexible plastic
Polypropylene	120	Excellent Susceptible to attack by strong oxidizing agents	Translucent. Has replaced polyethylene for many purposes	
Polystyrene	70		Not attacked by HF. Attacked by many organic solvents	Somewhat brittle
Teflon	250		Inert to most chemicals	Useful for storage of solutions and reagents for trace metal analysis. Is permeable to oxygen

The balance measures mass.

device must be both accurate and sensitive. There are various sophisticated ways of achieving this, but the most useful and versatile device used is the **analytical balance**.

Most analytical balances used today are electronic balances. The mechanical single-pan balance is seldom used in the modern analytical laboratory anymore. The calibration of electronic or digital balances is based on comparison of one weight against another. Factors such as zero-point drift and air buoyancy must be considered for all balance types. We really deal with masses rather than weights. The **weight** of an object is the force exerted on it by the gravitational attraction. This force will differ at different locations on Earth. **Mass**, on the other hand, is the quantity of matter of which the object is composed and is invariant.

Modern electronic balances offer convenience in weighing and are subject to fewer errors or mechanical failures than are mechanical balances, which have become largely obsolete. The operation of dialing weights, turning and reading micrometers, and beam and pan arrest of mechanical balances are eliminated, greatly speeding the measurement. A digital-display electronic balance is shown in Figure 2.1, and the operating principle of an electronic balance is illustrated in Figure 2.2. There are no weights or knife edges as with mechanical balances. The pan sits on the arm of a movable hanger (2), and this movable system is compensated by a constant electromagnetic force. The position of the hanger is monitored by an electrical position scanner (1), which brings the weighing system back to the zero position. The compensation current is proportional to the mass placed on the pan. This is sent in digital form to a microprocessor that converts it into the corresponding weight value, which appears as a digital display. The weight of the container can be automatically subtracted.

These balances use the principle of electromagnetic force compensation first described by Angstrom in 1895. But they still use the principle of comparing one weight with another. The balance is "zeroed," or calibrated, with a known weight. When the sample is placed on the pan, its weight is electronically compared with the known. This is a form of self-calibration. Modern balances may have such features as compensating for wandering from true zero and averaging variations due to building vibrations.

A single control bar is used to switch the balance on and off, to set the display to zero, and to automatically tare a container on the pan. Since results are available as an electrical signal, they can be readily processed by a personal computer and stored. Weighing statistics can be automatically calculated.

Greater precision equals greater cost. A balance readable to 0.1 mg costs <~ $2000 whereas microbalances can cost ~> $10,000.

Electronic analytical balances can be purchased with different weighing ranges and readabilities. A standard analytical balance typically has a maximum capacity of 160–300 g and a readability of 0.1 mg. Semimicro balances (readability 0.01 mg, capacity up to 200 g), microbalances (readability 1 µg, capacity up to 30 g) and ultramicro balances (readability 0.1 µg, capacity up to 2 g) are currently commercially available.

Electrochemical quartz balances are available with 100-µg range that can detect 1 ng (10^{-9} g) changes! The balance utilizes a thin quartz crystal disk oscillating at,

Fig. 2.1. Electronic analytical balance. (Courtesy of Denver Instrument Co. Denver Instrument Company owns all images.)

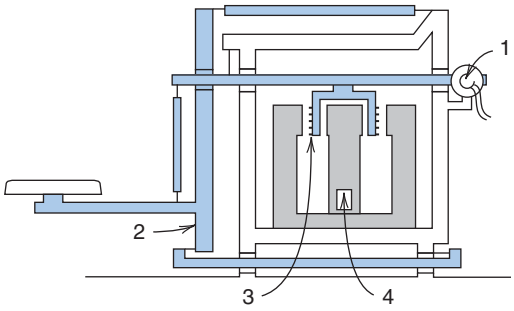


Fig. 2.2. Operating principle of electronic balance: 1, position scanner; 2, hanger; 3, coil; 4, temperature sensor. (From K. M. Lang, *American Laboratory*, March, 1983, p. 72. Reproduced by permission of American Laboratory, Inc.)

for example, 10 MHz. The frequency of oscillation changes with any change in mass, and the frequency change measured by the instrument is converted to mass units. A film of gold is evaporated on the quartz, and the gold substrate can be coated with the material of interest. Mass changes as small as a few percent of a monolayer coverage of atoms or molecules on the gold surface can be measured. Mass changes with time can be recorded. Such balances are incorporated in air particle mass monitors, see for example, http://www.kanomax-usa.com/dust/3521/3521.html.

Older mechanical balances used the lever principle: $M_1L_1 = M_2L_2$, where L_1 and L_2 are the lengths of the two arms of the lever and M_1 and M_2 are the corresponding masses. If L_1 and L_2 are constructed to be as nearly equal as possible then at balance, $M_1 = M_2$.

SINGLE-PAN MECHANICAL BALANCE

Electronic balances have largely replaced mechanical balances. But they are still used some, so we have placed on the Chapter 2 text website a description of the single-pan mechanical balance.

Such balances are based on the first-class lever, like a teeter totter, that compares two masses at each end of the lever, one the unknown and the other standard weights, and the relationship $M_1L_1 = M_2L_2$ holds. The single-pan balance actually has unequal lever lengths, and the operation is based on removing weights from the lever end on which the unknown is placed, equal in value to the unknown mass. See the **website** for details.

Burns' Hog Weighing Method: "1) Get a perfectly straight plank and balance it across a sawhorse. 2) Put the hog on one end of the plank. 3) Pile rocks on the other end until the plank is again perfectly balanced. 4) Carefully guess the weight of the rocks."—Robert Burns

SEMIMICRO- AND MICROBALANCES

We make most quantitative weighings to 0.1 mg.

The discussion thus far has been limited to conventional macro or analytical balances. These perform weighings to the nearest 0.1 mg, and loads of up to 160-300 g can be handled. These are satisfactory for most routine analytical weighings. All of the above classes of balances can be made more sensitive by changing the parameters affecting the sensitivity, such as decreasing the mass of the beam (for mechanical balances) and pans, increasing the length of the beam, and changing the center of gravity of the beam. Lighter material can be used for the beam since it need not be as sturdy as the beam of a conventional balance.

The *semimicrobalance* is sensitive to about 0.01 mg, and the *microbalance* is sensitive to about 0.001 mg (1 μg). The load limits of these balances are correspondingly less than the conventional balance, and greater care must be taken in their use.

ZERO-POINT DRIFT

The zero setting of a balance is not a constant that can be determined or set and forgotten. It will drift for a number of reasons, including temperature changes, humidity, and static electricity. The zero setting should therefore be checked at least once every half-hour during the period of using the balance.

WEIGHT IN A VACUUM—THIS IS THE ULTIMATE ACCURACY

An object of 1-mL volume will be buoyed up by 1.2 mg!

The weighings that are made on a balance will, of course, give the weight in air. When an object displaces its volume in air, it will be buoyed up by the weight of air displaced (**Archimedes' principle**—see the box in Chapter 1 on how analytical chemistry originated). The density of air is 0.0012 g (1.2 mg) per milliliter. If the density of the weights and the density of the object being weighed are the same, then they will be buoyed up by the same amount, and the recorded weight will be equal to the weight in a vacuum, where there is no buoyancy. If the densities are markedly different, the differences in the buoyancies will lead to a small error in the weighing: One will be buoyed up more than the other, and an unbalance will result. Such a situation arises in the weighing of very dense objects [e.g., platinum vessels (density = 21.4)

or mercury (density = 13.6)] or light, bulky objects [e.g., water (density ≈ 1)]; and in very careful work, a correction should be made for this error. For comparison, the density of weights used in balances is about 8. See Reference 14 for air buoyancy corrections with a single-pan balance. (Reference 10 describes the calibration of the weights in a single-pan balance.)

The buoyancy of the weighing vessel is ignored, since it is subtracted.

Note that in most cases, a correction is not necessary because the error resulting from the buoyancy will cancel out in percent composition calculations. The same error will occur in the numerator (as the concentration of a standard solution or weight of a gravimetric precipitate) and in the denominator (as the weight of the sample). Of course, all weighings must be made with the materials in the same type of container (same density) to keep the error constant.

Buoyancy corrections are usually significant in glassware calibration.

An example where correction in vacuum is used is in the calibration of glassware. The mass of water or mercury delivered or contained by the glassware is measured. From a knowledge of the density of the liquid at the specified temperature, its volume can be calculated from the mass. Even in these cases, the buoyancy correction is only about one part per thousand. For most objects weighed, buoyancy errors can be neglected.

Weights of objects in air can be corrected to the weight in vacuum by

$$W_{\text{vac}} = W_{\text{air}} + W_{\text{air}}\left(\frac{0.0012}{D_o} - \frac{0.0012}{D_w}\right) \tag{2.1}$$

where

W_{vac} = weight in vacuum, g
W_{air} = observed weight in air, g
D_o = density of object
D_w = density of standard weights
0.0012 = density of air

The density of brass weights is 8.4 and that of stainless steel weights is 7.8. A calculation with water as the object will convince you that even here the correction will amount to only about one part per thousand.

Example 2.1

The same buoyancy corrections apply for mechanical or electronic balances (which are calibrated with weights of known density).

A convenient way to calibrate pipets is to weigh water delivered from them. From the exact density of water at the given temperature, the volume delivered can then be calculated. Suppose a 20-mL pipet is to be calibrated. A stoppered flask when empty weighs 29.278 g. Water is delivered into it from the pipet, and it now weighs 49.272 g. If brass weights are used, what is the weight of water delivered, corrected to weight in vacuum?

Solution

The increase in weight is the weight of water in air:

$$49.272 - 29.278 = 19.994 \text{ g}$$

The density of water is 1.0 g/mL (to 2 significant figures from 10 to 30°C—see Table 2.4). Therefore,

$$W_{\text{vac}} = 19.994 + 19.994\left(\frac{0.0012}{1.0} - \frac{0.0012}{8.4}\right) = 20.015 \text{ g}$$

■

Example 2.2

Recalculate the weight of the water delivered by the pipet in Example 2.1, using stainless steel weights at density 7.8 g/cm^3.

Solution

Do not round off until the end of the calculation. Then the same value results:

$$W_{vac} = 19.994 + 19.994\left(\frac{0.0012}{1.0} - \frac{0.0012}{7.8}\right) = 20.015 \text{ g}$$

This illustrates that the buoyancy corrections in Table 2.4 are valid for either type of weight (see Calibration of Glassware below). ■

SOURCES OF ERROR IN WEIGHING

Several possible sources of error have been mentioned, including zero-point drift and buoyancy. Changes in ambient temperature or temperature of the object being weighed are probably the biggest sources of error, causing a drift in the zero or rest point due to convection-driven air currents. Hot or cold objects must be brought to ambient temperature before being weighed. Hygroscopic samples may pick up moisture, particularly in a high-humidity atmosphere. Exposure of the sample to air, prior to and during weighing, must be minimized.

GENERAL RULES FOR WEIGHING

Learn these rules!

The specific operation of your particular balance will be explained by your instructor. The main objectives are to protect all parts from dust and corrosion, avoid contamination or change in load (of sample or container), and avoid draft (air convection) errors. Some general rules you should familiarize yourself with before weighing with any type of analytical balance are:

1. Never handle objects to be weighed with the fingers. A piece of clean paper or tongs should be used.
2. Weigh at room temperature, and thereby avoid air convection currents.
3. Never place chemicals directly on the pan, but weigh them in a vessel (weighing bottle, weighing dish) or on powder paper. Always brush spilled chemicals off immediately with a soft brush.
4. Always close the balance case door before making the weighing. Air currents will cause the balance to be unsteady.

Although modern digital balances do not have user-manipulable weights, corrosion can still cause problems. Volatile corrosive substances (e.g., iodine or conc. HCl) should never be weighed in open containers in a balance.

WEIGHING OF SOLIDS

Weighing by difference is required for hygroscopic samples.

Solid chemical (nonmetal) materials are usually weighed and dried in a **weighing bottle**. Some of these are shown in Figure 2.3. They have standard tapered ground-glass joints, and hygroscopic samples (which take on water from the air) can be weighed with the bottle kept tightly capped. Replicate weighings can be conveniently carried out by **difference**. The sample in the weighing bottle is weighed, and then a portion is removed (e.g., by tapping) and quantitatively transferred to a vessel appropriate for dissolving the sample. The weighing bottle and sample are reweighed, and from the difference in weight, the weight of sample is calculated. The next sample is removed and the weight is repeated to get its weight by difference, and so on. This is illustrated in the Laboratory Notebook example for the soda ash experiment.

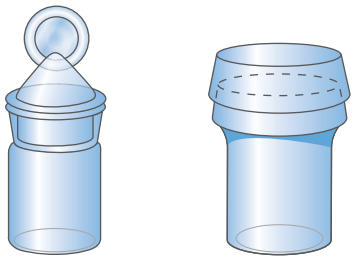


Fig. 2.3. Weighing bottles.

It is apparent that by this technique an average of only one weighing for each sample, plus one additional weighing for the first sample, is required. However, each weight represents the difference between two weighings, so that the total experimental error is given by the combined error of both weighings. Weighing by difference *with the bottle capped* must be used if the sample is hygroscopic or cannot otherwise be exposed to the atmosphere before weighing. If there are no effects from atmospheric exposure, the bottles need not be capped.

For **direct weighing**, a **weighing dish**, weighing paper, or a weighing boat (all typically disposable) is used. The dish, paper, or boat is weighed empty and then with the added sample. This requires two weighings for each sample. The weighed sample is transferred by tapping. Direct weighing is satisfactory only if the sample is nonhygroscopic.

When making very careful weighings (e.g., to a few tenths of a milligram or less), you must take care not to contaminate the weighing vessel with extraneous material that may affect its weight. Special care should be taken not to get perspiration from the hands on the vessel because this can be quite significant. It is best to handle the vessel with a piece of paper. Alternatively, finger cots may be used. These are similar to just the fingertip region of protective gloves. Solid samples must frequently be dried to a constant weight (e.g., ± 0.5 mg for a 0.5 g sample). Highly insulating material, for example laboratory ware made from fluorocarbons, easily acquire static charge that affect weigh readings. Brushes with a built in source of ionizing radiation (http://www.amstat.com/solutions/staticmaster.html) that help dissipate such charges are recommended for gently swiping such objects before weighing.

WEIGHING OF LIQUIDS

Weighing of liquids is usually done by direct weighing. The liquid is transferred to a weighed vessel (e.g., a weighing bottle), which is capped to prevent evaporation during weighing, and is then weighed. If a liquid sample is weighed by difference by pipetting out an aliquot from the weighing bottle, the inside of the pipet must be rinsed several times after transferring. Care should be taken not to lose any sample from the tip of the pipet during transfer.

TYPES OF WEIGHING—WHAT ACCURACY DO YOU NEED?

Only some weighings have to be done on an analytical balance, those involved in the quantitative calculations.

There are two types of weighing done in analytical chemistry, **rough** or **accurate**. Rough weighings to two or three significant figures are normally used when the amount of substance to be weighed need only be known to within a few percent. Examples are reagents to be dissolved and standardized later against a known standard, or the apportioning of reagents that are to be dried and then later weighed accurately, or simply added as is, as for adjusting solution conditions. That is, only rough weighings

are needed when the weight is not involved in the computation of the analytical result. Rough weighings need not be done on analytical balances but may be completed on a top-loading balance.

Accurate weighings are reserved for obtaining the weight of a sample to be analyzed, the weight of the dried product in gravimetric procedures, or the weight of a dried reagent being used as a standard in a determination, all of which must generally be known to four significant figures or better to be used in calculating the analytical result. **These are performed only on an analytical balance**, **usually to the nearest 0.1 mg**. An exact predetermined amount of reagent is rarely weighed (e.g., 0.5000 g), but rather an approximate amount (about 0.5 g) is weighed accurately (e.g., to give 0.5129 g). Some chemicals are never weighed on an analytical balance. Sodium hydroxide pellets, for example, are so hygroscopic that they continually absorb moisture. The weight of a given amount of sodium hydroxide is not reproducible (and its purity is not known). To obtain a solution of known sodium hydroxide concentration, the sodium hydroxide is weighed on a rough balance and dissolved, and the solution is standardized against a standard acid solution.

2.4 Volumetric Glassware—Also Indispensible

Although accurate volume measurements of solutions can be avoided in gravimetric methods of analysis, they are required for almost any other type of analysis involving solutions.

VOLUMETRIC FLASKS

Volumetric flasks contain an accurate volume.

Volumetric flasks are used for the dilution of solutions to a certain volume. They come in a variety of sizes, from 1 mL to 2 L or more. A typical flask is shown in Figure 2.4. These flasks are designed **to contain** an accurate volume at the specified temperature (20 or 25°C) when the bottom of the meniscus (the concave curvature of the upper surface of water in a column caused by capillary action—see Figure 2.10) just touches the etched "fill" line across the neck of the glass. The coefficient of expansion of glass is small, and for ambient temperature fluctuations the volume can be considered constant. These flasks are marked with "**TC**" to indicate "to contain." Other, less accurate containers, such as graduated cylinders, are also marked "TC." Many of these are directly marked on the face by the manufacturer as to the uncertainty of the container measurement; for example, a 250 mL volumetric flask is "±0.24 mL," or roughly a 0.1% error.

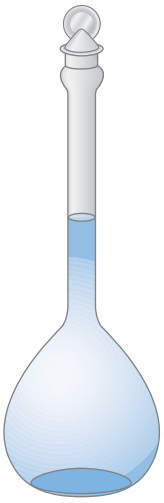


Fig. 2.4. Volumetric flask.

Initially, a small amount of diluent (usually distilled water) is added to the empty flask. Reagent chemicals should never be added directly to a dry glass surface, as glass is highly absorbant. When using a volumetric flask, a solution should be prepared stepwise. The desired reagent chemical (either solid or liquid) to be diluted is added to the flask, and then diluent is added to fill the flask about two-thirds (taking care to rinse down any reagent on the ground glass lip). It helps to swirl the solution before diluent is added to the neck of the flask to obtain most of the mixing (or dissolving in the case of a solid). Finally, diluent is added so that the bottom of the meniscus is even with the middle of the calibration mark (at eye level). If there are any droplets of water on the neck of the flask above the meniscus, take a piece of tissue and blot these out. Also, dry the ground-glass stopper joint.

The solution is finally thoroughly mixed as follows. Keeping the stopper on securely by using the thumb or palm of the hand, invert the flask and swirl or shake it *vigorously* for 5 to 10 s. Turn right side up and allow the solution to drain from the neck of the flask. Repeat at least 10 times.

Note. When preparing the solution of an expensive chemical, should the volume of liquid go over the calibration mark, it is still possible to save the solution as follows. Paste against the neck of the flask a thin strip of paper and mark on it with a sharp pencil the position of the meniscus, avoiding parallax error. After removing the thoroughly mixed solution from the flask, fill the flask with water to the calibration mark. Then by means of a buret or small volume graduated pipet, add water to the flask until the meniscus is raised to the mark on the strip of paper. Note and record the volume so added and use it to mathematically correct the concentration calculation. For an inexpensive chemical, start over. If the volume goes over the mark, you cannot accurately calculate concentration without determining how far over the mark you went. Be very careful and patient when filling volumetric flasks, especially when the components in the flask are irreplaceable or expensive.

PIPETS

The pipet is used to transfer a particular volume of solution. As such, it is often used to deliver a certain fraction (**aliquot**) of a solution. To ascertain the fraction, the original volume of solution from which the aliquot is taken must be known, but it need not all be present, so long as it has not evaporated or been diluted. There are two common types of pipets, the **volumetric**, or **transfer**, **pipet** and the **measuring** or **graduated pipet** (see Figures 2.5 and 2.6). Variations of the latter are also called **clinical**, or **serological**, **pipets**.

Pipets are designed **to deliver** a specified volume at a given temperature, and they are marked "**TD**." Again, the volume can be considered to be constant with small changes in temperature. Pipets are calibrated to account for the drainage film remaining on the glass walls. This drainage film will vary somewhat with the time taken to deliver, and usually the solution is allowed to drain under the force of gravity and the pipet is removed shortly after the solution is delivered. A uniform drainage time should be adopted.

The volumetric pipet is used for accurate measurements since it is designed to deliver only one volume and is calibrated at that volume. Accuracy to four significant figures is generally achieved, although with proper calibration, five figures may be obtained if necessary. See the table on the *back cover* for tolerances of class A transfer pipets. Measuring pipets are straight-bore pipets that are marked at different volume intervals. These are not as accurate because nonuniformity of the internal diameter of the device will have a relatively larger effect on total volume than is the case for pipets with a bulb shape. Also, the drainage film will vary with the volume delivered. At best, accuracy to three significant figures can be expected from these pipets, unless you make the effort to calibrate the pipet for a given volume delivered.

Most volumetric pipets are calibrated to deliver with a certain small volume remaining in the tip. This should not be shaken or blown out. In delivering, the pipet is held vertically and the tip is touched on the side of the vessel to allow smooth delivery without splashing and so that the proper volume will be left in the tip. The forces of attraction of the liquid on the wall of the vessel will draw out a part of this.

Some pipets are **blowout** types (including measuring pipets calibrated to the entire tip volume). The final volume of solution must be blown out from the tip to deliver the calibrated amount. These pipets are easy to identify, as they will always have one or two **ground bands or rings** around the top. (These are not to be confused with a colored ring that is used only as a color coding for the volume of the pipet.) The solution is not blown out until it has been completely drained by gravity. Blowing to increase the rate of delivery will change the volume of the drainage film.

Volumetric pipets are available in sizes of 100 to 0.5 mL or less. Measuring and serological pipets range from a total capacity of 25 to 0.1 mL. Measuring pipets can be

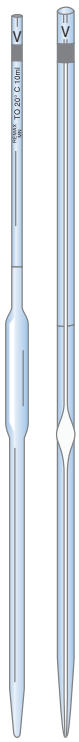


Fig. 2.5. Transfer or volumetric pipets.

Volumetric pipets deliver an accurate volume.

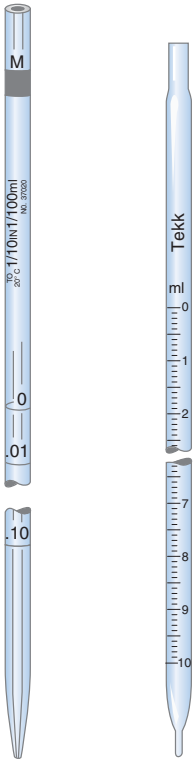


Fig. 2.6. Measuring pipets.

used for accurate measurements, especially for small volumes, if they are calibrated at the particular volume wanted. The larger measuring pipets usually deliver too quickly to allow drainage as fast as the delivery, and they have too large a bore for accurate reading.

In using a pipet, one should always wipe the outside of the tip dry after filling. If a solvent other than water is used, or if the solution is viscous, pipets must be recalibrated for the new solvent or solution to account for difference in drainage rate.

Pipets are filled by suction, using a rubber pipet bulb, a pipet pump, or other such pipetting device. Before using a pipet, practice filling and dispensing with water. **No solution should be pipetted by mouth**.

SYRINGE PIPETS

Syringe pipets are useful for delivering microliter volumes.

These can be used for both macro and micro volume measurements. The calibration marks on the syringes may not be very accurate, but the reproducibility can be excellent if automatic delivery is used, such as a spring-loaded device that draws the plunger up to the same preset level each time. The volume delivered in this manner is free from drainage errors because the solution is forced out by the plunger. The volume delivered can be accurately calibrated. Microliter syringe pipets are used for introduction of samples into gas chromatographs. A typical syringe is illustrated in Figure 2.7. They are fitted with a needle tip, and the tolerances are as good as those found for other micropipets. In addition, any desired volume throughout the range of the syringe can be delivered. Syringes are available with a total volume as small as 0.5 µL, in which a wire plunger travels within the needle and so the entire syringe volume is within the needle.

The above syringe pipets are useful for accurate delivery of viscous solutions or volatile solvents; with these materials the drainage film would be a problem in conventional pipets. Syringe pipets are well suited to rapid delivery and also for thorough mixing of the delivered solution with another solution as a result of the rapid delivery.

A second type of syringe pipet is that shown in Figure 2.8. This type is convenient for rapid, one-hand dispensing of fixed (or variable) volumes in routine procedures and is widely used in the analytical chemistry laboratory. It contains a disposable nonwetting plastic tip (e.g., polypropylene) to reduce both film error and contamination. A thumb button operates a spring-loaded plunger, which stops at an intake or a discharge stop; the latter stop is beyond the former to ensure complete delivery. The sample never contacts the plunger and is contained entirely in the plastic tip. These pipets are available in volumes of 0.1 to 5000 µL and are reproducible to 1 to 2% or better, depending on the volume. Variable volume pipettes of this type typically deliver volumes across a defined range, such as 0.1 to 10 µL, 20 to 200 µL, 100 to 1000 µL, and 500 to 5000 µL. It is important to be consistent in your use of different pipettes for related procedures (e.g., always use a single draw from the 20 to 200 µL pipette to dispense 100 µL) to maintain consistency.

The volume may not be accurately known, but it is reproducible.

Sometimes, the actual volume delivered by these and other micropipets does not need to be known because they are used in relative measurements. For example, the same pipet may be used to deliver a sample and an equal volume of a standard solution for calibrating the instrument used for the measurement. Precision in delivery is usually more important than the absolute volume delivered. The European standard for pipet calibration in Europe is the German DIN 126650 (or a similar international standard ISO 8655). Calibrations are based on gravimetric testing (weighing of water). The DIN standard does not give separate limits for accuracy and precision, but rather uses a combined error limit equal to percent accuracy plus 2 times the standard deviation, that is, it gives a range in which we are 95% confident the delivery will fall (see

Joseph Gay-Lussac (1778–1850) designed the first buret and named the buret and pipet.

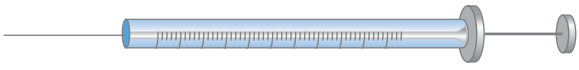


Fig. 2.7. Hamilton microliter syringe.

Fig. 2.8. Single-channel and multichannel digital displacement pipets and microwell plates. (Courtesy of Thermo Fisher Scientific.)

Chapter 3 for a discussion of standard deviation and confidence limits). Table 2.2 lists the DIN error limits for single-channel displacement pipets. Table 2.3 lists accuracies and precisions for a typical variable volume single-channel pipet.

Besides the manually operated syringes, there are electronically controlled and variable-volume motor-driven syringes available for automated repetitive deliveries. When syringes are used in electrically driven syringe pumps for very slow infusion of solution, there can be stick–slip behavior, resulting in pulsed flow. Inexpensive

Table 2.2

DIN 12650 Error Limits for Single-Channel Fixed-Volume Air Displacement Pipets[a]

Nominal Volume (µL)	Maximum Error (µL)	Relative Error (%)
1	±0.15	±15.0
2	±0.20	±10.0
5	±0.30	±6.0
10	±0.30	±3.0
20	±0.40	±2.0
50	±0.80	±1.6
100	±1.50	±1.5
200	±2.00	±1.0
500	±5.00	±1.0
1000	±10.00	±1.0
2000	±20.00	±1.0
5000	±50.00	±1.0
10000	±100.00	±1.0

[a]These limits apply to manufacturers with a controlled environment. If the tests are performed by a user in a normal laboratory environment, the limits in the table may be doubled.
Courtesy of Thermo Labsystems Oy, Finland.

Table 2.3

Accuracy and Precision Limits for Single-Channel Variable-Volume Finnpipettes Model F1

Range (μL)	Increment (μL)	Volume (μL)	Accuracy		Precision[a]	
			(μL)	(%)	s.d. (μL)	CV (%)
0.2–2 μL	0.002 μL	2	±0.050	±2.50	0.040	2.00
		1	±0.040	±4.00	0.040	3.50
		0.2	±0.024	±12.00	0.020	10.00
0.5–5 μL	0.01 μL	5	±0.080	±1.50	0.050	1.00
		2.5	±0.0625	±2.50	0.0375	1.50
		0.5	±0.030	±6.00	0.025	5.00
1–10 μL	0.02 μL	10	±0.100	±1.00	0.050	0.50
		5	±0.080	±1.50	0.040	0.80
		1	±0.025	±2.50	0.020	2.00
1–10 μL	0.02 μL	10	±0.100	±1.00	0.080	0.80
		5	±0.080	±1.50	0.040	0.80
		1	±0.035	±3.50	0.030	3.00
2–20 μL	0.02 μL	20	±0.20	±1.00	0.08	0.40
		10	±0.15	±1.50	0.06	0.60
		2	±0.06	±3.00	0.05	2.50
2–20 μL	0.02 μL	20	±0.20	±1.00	0.08	0.40
		10	±0.15	±1.50	0.06	0.60
		2	±0.06	±3.00	0.05	2.50
5–50 μL	0.1 μL	50	±0.30	±0.60	0.15	0.30
		25	±0.25	±1.00	0.13	0.50
		5	±0.15	±3.00	0.125	2.50
5–50 μL	0.1 μL	50	±0.30	±0.60	0.15	0.30
		25	±0.25	±1.00	0.13	0.50
		5	±0.15	±3.00	0.125	2.50
10–100 μL	0.2 μL	100	±0.80	±0.80	0.20	0.20
		50	±0.60	±1.20	0.20	0.40
		10	±0.30	±3.00	0.10	1.00
20–200 μL	0.2 μL	200	±1.2	±0.60	0.4	0.20
		100	±1.0	±1.00	0.4	0.40
		20	±0.36	±1.80	0.14	0.70
30–300 μL	1 μL	300	±1.8	±0.60	0.6	0.20
		150	±1.5	±1.00	0.6	0.40
		30	±0.45	±1.50	0.18	0.60
100–1000 μL	1 μL	1000	±6.0	±0.60	2.0	0.20
		500	±4.0	±0.80	1.5	0.30
		100	±1.0	±1.00	0.6	0.60
0.5–5 ml	0.01 ml	5000	±25.0	±0.50	10.0	0.20
		2500	±17.5	±0.70	7.5	0.30
		500	±10.0	±2.00	4.0	0.80
1–10 ml	0.02 ml	10000	±50.0	±0.50	20.0	0.20
		5000	±40.0	±0.80	15.0	0.30
		1000	±20.0	±2.00	8.0	0.80

[a]s.d. = standard deviation, CV = coefficient of variation.
From https://fscimage.fishersci.com/images/D11178~.pdf

automated dispensers can be laboratory made from syringes [see for example, "Inexpensive Automated Electropneumatic Syringe Dispenser", P. K. Dasgupta and J. R. Hall, *Anal. Chim. Acta* 221 (1989) 189.] Also, you may purchase pipets with multiple syringes for simultaneous delivery, with for example, 12 or 16 channels. These are useful for delivering solutions into microwell plates used in biotechnology

or clinical chemistry laboratories that process thousands of samples (Figure 2.8). You may find more information on displacement pipets from representative manufacturers, for example, www.thermoscientific.com/finnpipette or www.eppendorf.com.

BURETS

A buret is used for the accurate delivery of a variable amount of solution. Its principal use is in **titrations**, where a standard solution is added to the sample solution until the **end point** (the detection of the completion of the reaction) is reached. The conventional buret for macrotitrations is marked in 0.1-mL increments from 0 to 50 mL; one is illustrated in Figure 2.9. The volume delivered can be read to the nearest 0.01 mL by interpolation actually (good to about ±0.02 or ±0.03 mL). Burets are also obtainable in 10-, 25-, and 100-mL capacities, and microburets are available in capacities of down to 2 mL, where the volume is marked in 0.01-mL increments and can be estimated to the nearest 0.001 mL. Ultramicroburets of 0.1-mL capacity graduated in 0.001-mL (1-μL) intervals are used for microliter titrations.

Drainage film is a factor with conventional burets, as with pipets, and this can be a variable if the delivery rate is not constant. The usual practice is to deliver at a fairly slow rate, about 15 to 20 mL per minute, and then to wait several seconds after delivery to allow the drainage to "catch up." In actual practice, the rate of delivery is only a few drops per minute near the end point, and there will be no time lag between the flow rate and the drainage rate. As the end point is approached, fractions of a drop are delivered by just opening, or "cracking," the stopcock and then touching the tip of the buret to the wall of the titration vessel. The fraction of the drop is then washed down into the solution with distilled water.

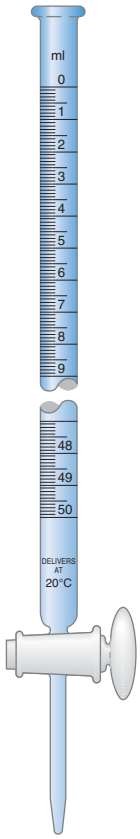


Fig. 2.9. Typical buret.

CARE AND USE OF VOLUMETRIC GLASSWARE

We have mentioned a few precautions in the use of volumetric flasks, pipets, and burets. Your laboratory instructor will supply you with detailed instructions in the use of each of these tools. A discussion of some general precautions and good laboratory technique follows.

Cleanliness of glassware is of the utmost importance. If films of dirt or grease are present, liquids will not drain uniformly and will leave water breaks or droplets on the walls. Under such conditions the calibration will be in error. Initial cleaning should be by repeated rinses with laboratory detergent and then water. Then try cleaning with dilute nitric acid and rinse with more water. Use of a buret or test tube brush aids the cleaning of burets and necks of volumetric flasks—but be careful of scratching the interior walls. Pipets should be rotated to coat the entire surface with detergent. There are commercial cleaning solutions available that are very effective.

Rinse pipets and burets with the solution to be measured.

Pipets and burets should be rinsed at least twice with the solution with which they are to be filled. If they are wet, they should be rinsed first with water, if they have not been already, and then a minimum of *three* times with the solution to be used; about one-fifth the volume of the pipet or buret is adequate for each rinsing. A volumetric flask, if it is wet from a previously contained solution, is rinsed with three portions of water only since later it will be filled to the mark with water. It need not be dry.

Note that analytical glassware should not be subjected to the common practice employed in organic chemistry laboratories of drying either in an oven (this can affect the volume of calibrated glassware) or by drying with a towel or by rinsing with a volatile organic solvent such as acetone (which can cause contamination). The glassware usually does not have to be dried. The preferred procedure is to rinse it with the solution that will fill it.

Avoid parallax error in reading buret or pipet volumes.

Care in reading the volume will avoid parallax error, that is, error due to incorrect alignment of the observer's eye, the meniscus, and the scale. Correct position is with your eye at the same level as the menicus. If the eye level is above the

meniscus, the volume read will be smaller than that taken; the opposite will be true if the eye level is too low.

After glassware is used, it can usually be cleaned sufficiently by immediate rinsing with water. If the glassware has been allowed to dry, it should be cleaned with detergent. Volumetric flasks should be stored with the stopper inserted, and preferably filled with distilled water. Burets should be filled with distilled water and stoppered with a rubber stopper when not in use.

There are commercial glassware washing machines to automate the cleaning of glassware. These use detergents and deionized water for cleaning and rinsing. See, for example, L. Choplo, "The Benefits of Machine Washing Laboratory Glassware Versus Hand Washing," *Amer. Lab*. October (2008) 6 (http://new.americanlaboratory.com/914-Application-Notes/34683-The-Benefits-of-Machine-Washing-Laboratory-Glassware-Versus-Hand-Washing/), and M. J. Felton, "Labware Washers," *Today's Chemist at Work*, November (2004) 43 (http://pubs.acs.org/subscribe/archive/tcaw/13/i11/pdf/1104prodprofile.pdf).

GENERAL TIPS FOR ACCURATE AND PRECISE TITRATING

If the buret contains a Teflon stopcock, it does not require lubrication.

Your buret probably has a Teflon stopcock, and this will not require lubrication. Make sure it is secured tightly enough to prevent leakage, but not so tight as to make rotation hard. If your buret has a ground-glass stopcock, you may have to grease the stopcock. A thin layer of stopcock grease (not silicone lubricant) is applied uniformly to the stopcock, using very little near the hole and taking care not to get any grease in the hole. The stopcock is inserted and rotated. There should be a uniform and transparent layer of grease, and the stopcock should not leak. If there is too much lubricant, it will be forced into the barrel or may work into the buret tip and clog it. Grease can be removed from the buret tip and the hole of the stopcock by using a fine wire.

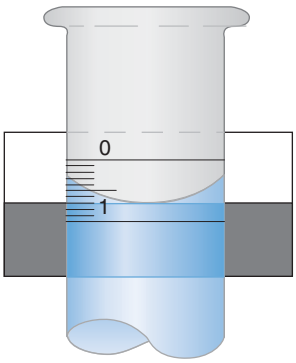


Fig. 2.10. Meniscus illuminator for buret.

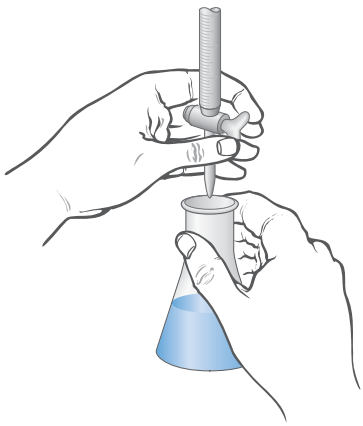


Fig. 2.11. Proper technique for titration.

Next, we fill the buret with the solution it will deliver. The buret is filled above the zero mark and the stopcock is opened to fill the tip. Check the tip for air bubbles. If any are present, they may work out of the tip during the titration, causing an error in reading. Work air bubbles out by rapid opening and closing of the stopcock to squirt the titrant through the tip or tapping the tip while solution is flowing. No bubbles should be in the barrel of the buret. If there are, the buret is probably dirty.

The initial reading of the buret is taken by allowing it to drain slowly to the zero mark. Wait a few seconds to make certain the drainage film has caught up to the meniscus. Read the buret to the nearest 0.01 mL (for a 50-mL buret). The initial reading may be 0.00 mL or greater. The reading is best taken by placing your finger just in back of the meniscus or by using a meniscus illuminator (Figure 2.10). The meniscus illuminator has a white and a black field, and the black field is positioned just below the meniscus. Avoid parallax error by making the reading at eye level.

The titration is performed with the sample solution in an Erlenmeyer flask. The flask is placed on a white background, and the buret tip is positioned within the neck of the flask. The flask is swirled with the right hand while the stopcock is manipulated with the left hand (Figure 2.11), or whatever is comfortable. This grip on the buret maintains a slight inward pressure on the stopcock to ensure that leakage will not occur. The solution can be more efficiently stirred by means of a magnetic stirrer and stirring bar.

As the titration proceeds, the indicator changes color in the vicinity where the titrant is added, owing to local excesses; but it rapidly reverts to the original color as the titrant is dispersed through the solution to react with the sample. As the end point is approached, the return to the original color occurs more slowly, since the dilute solution must be mixed more thoroughly to consume all the titrant. At this point, the titration should be stopped and the sides of the flask washed down with distilled water from the wash bottle. A drop from the buret is about 0.02 to 0.05 mL, and the volume

is read to the nearest 0.02 mL. It is therefore necessary to split drops near the end point. This can be done by slowly turning the stopcock until a fraction of a drop emerges from the buret tip and then closing it. The fraction of drop is touched off onto the wall of the flask and is washed into the flask with the wash bottle, or it is transferred with a glass stirring rod. There will be a sudden and "permanent" (lasting at least 30 s) change in the color at the end point when a fraction of a drop is added.

The titration is usually performed in triplicate. After performing the first titration, you can calculate the approximate volume for the replicate titrations from the weights of the samples and the molarity of the titrant. This will save time in the titrations. The volume should not be calculated to nearer than 0.1 mL in order to avoid bias in the reading.

Subsequent titrations can be speeded up by using the first to *approximate* the end-point volumes.

After a titration is complete, unused titrant should never be returned to the original bottle but should be discarded. If the titrant isn't between pH 4 and 8 and on the short list of substances cleared to go down the drain, it should be disposed of in a recycle container.

If a physical property of the solution, such as potential, is measured to detect the end point, the titration is performed in a beaker with magnetic stirring so electrodes can be placed in the solution.

TOLERANCES AND PRECISION OF GLASSWARE

The National Institute of Standards and Technology (NIST) has prescribed certain *tolerances*, or absolute errors, for different volumetric glassware, and some of these are listed on the *back cover* of the text. For volumes greater than about 25 mL, the tolerance is within 1 part per thousand relative, but it is larger for smaller volumes. The letter "A" stamped on the side of a volumetric flask, buret, or pipet indicates that it complies with class A tolerances. This says nothing about the precision of delivery. Volumetric glassware that meets NIST specifications or that is certified by NIST can be purchased, but at a significantly higher price than uncertified glassware. Less expensive glassware may have tolerances double those specified by NIST. It is a simple matter, however, to calibrate this glassware to an accuracy as good as or exceeding the NIST specifications (see Experiment 2).

Class A glassware is accurate enough for most analyses. It can be calibrated to NIST specifications.

The precision of reading a 50-mL buret is about ±0.02 mL. Since a buret is always read twice, the total absolute uncertainty may be as much as ±0.04 mL. The relative uncertainty will vary inversely with the total volume delivered. It becomes apparent that a titration with a 50-mL buret should involve about 40 mL titrant to achieve a precision of 1 ppt. Smaller burets can be used for increased precision at smaller volumes. Pipets will also have a certain precision of reading, but only one reading is required for volumetric pipets.

The variances or the uncertainties in each reading are additive. See propagation of error, Chapter 3.

CALIBRATION OF GLASSWARE—FOR THE ULTIMATE ACCURACY

Example 2.1 illustrated how Equation 2.1 may be used in the calibration of glassware, to correct for buoyancy of the water used for calibration, that is, to correct to weight in vacuum. Dividing the weight of the water in vacuum by its density at the given temperature will convert it to volume.

Table 2.4 lists the calculated volumes for a gram of water in air at atmospheric pressure for different temperatures, corrected for buoyancy with stainless steel weights of density 7.8 g/cm^3. These are used to give the volume of the glassware being calibrated, from the weight of water contained or delivered by the glassware. (The values are not significantly different for brass weights of 8.4 g/cm^3 density. See Example 2.2.) The glass volumes calculated for the standard temperature of 20°C include slight adjustments for borosilicate glass (Pyrex or Kimax) container expansion or contraction with temperature changes (volumetric glassware has a cubical coefficient of expansion of about 0.000025 per degree centigrade, resulting in changes of about

Table 2.4

Glassware Calibration

	A	B	C	D	E	F	G	H
1	**Table 2.4 Glassware Calibration**							
2	Weight in vacuum assuming stainless steel weights, density 7.8 g/mL.							
3	Glass expansion for borosilicate glass, 0.000025 mL/mL/ °C.							
4	The actual spreadsheet is available on the website (Table 2.4).							
5	Save it to your desktop, and use it to calculate calibrated volumes of glassware.							
6	Substitute into the appropriate Cell B, at temperature t, the weight of water							
7	in air, obtained from the glassware at the temperature of the measurement (Cell A).							
8	The calibration volume at the temperature, t (Cell D), and at 20 °C (Cell F), is calculated.							
9	Round the calculated values to the appropriate number of significant figures, usually							
10	four or five.							
11								
12	**t, °C**	**Wt. H_2O**	**Wt. in**	**Vol. at t,**	**Glass expansion,**	**Vol. at 20°C**	**Density,**	
13		**in air, g**	**vacuum, g**	**mL**	**at 20°C, mL**	**mL**	**g/mL**	
14	10	1.0000	**1.0010**	**1.0013**	**-0.000250**	**1.0016**	0.9997026	
15	11	1.0000	1.0010	1.0014	-0.000225	1.0017	0.9996081	
16	12	1.0000	1.0010	1.0015	-0.000200	1.0017	0.9995004	
17	13	1.0000	1.0010	1.0017	-0.000175	1.0018	0.9993801	
18	14	1.0000	1.0010	1.0018	-0.000150	1.0020	0.9992474	
19	15	1.0000	1.0010	1.0019	-0.000125	1.0021	0.9991026	
20	16	1.0000	1.0010	1.0021	-0.000100	1.0022	0.9989460	
21	17	1.0000	1.0010	1.0023	-0.000075	1.0023	0.9987779	
22	18	1.0000	1.0010	1.0025	-0.000050	1.0025	0.9985896	
23	19	1.0000	1.0010	1.0026	-0.000025	1.0027	0.9984082	
24	20	1.0000	1.0010	1.0028	0.000000	1.0028	0.9982071	
25	21	1.0000	1.0010	1.0031	0.000025	1.0030	0.9979955	
26	22	1.0000	1.0010	1.0033	0.000050	1.0032	0.9977735	
27	23	1.0000	1.0010	1.0035	0.000075	1.0034	0.9975415	
28	24	1.0000	1.0010	1.0038	0.000100	1.0037	0.9972995	
29	25	1.0000	1.0010	1.0040	0.000126	1.0039	0.9970479	
30	26	1.0000	1.0010	1.0043	0.000151	1.0041	0.9967867	
31	27	1.0000	1.0010	1.0045	0.000176	1.0044	0.9965162	
32	28	1.0000	1.0010	1.0048	0.000201	1.0046	0.9962365	
33	29	1.0000	1.0010	1.0051	0.000226	1.0049	0.9959478	
34	30	1.0000	1.0010	1.0054	0.000251	1.0052	0.9956502	
35								
36	Formulas are entered into the boldface cells above as indicated below. They are							
37	copied down for all temperatures. See Chapter 3 for setting up a spreadsheet.							
38	**Cell C14:** $W_{vac} = W_{air} + W_{air}(0.0012/D_o - 0.0012/D_w) = W_{air}(0.0012/1.0 + 0.0012/7.8)$							
39		=	B14+B14*(0.0012/1.0-0.0012/7.8)			Copy down		
40	**Cell D14:** V_t (mL)= $W_{vac,t}$ (g)/D_t (g/mL)							
41		=	C14/G14			Copy down		
42	**Cell E14:** Glass expans. = (t – 20) (deg) x 0.000025 (mL/mL/deg) x Vt (mL)							
43		=	(A14-20)*0.000025*D14			Copy down		
44	**Cell F14:** $V_{20o} = V_t - Glass_{exp}$ =			D14-E14		Copy down		

0.0025% per degree; for 1 mL, this is 0.000025 mL per degree). Water expands about 0.02% per degree around 20°C. Volume (concentration) corrections may be made using the water density data in Table 2.4, taking the ratios of the relative densities.

In the textbook **website**, the Table 2.4 spreadsheet is available, with formulas as indicated in the table. You can substitute specific weights of water in air, obtained from a flask, pipet, or buret, in cell B at the temperature of measurement to obtain the calculated calibration volume at temperature, *t*, and for 20°C. We describe the use of spreadsheets in Chapter 3. The book **website** also has a table and figure of the percent error for weight in vacuum as a function of sample density.

For those of you who live at high elevations, the density of air is slightly less than 0.0012 g/mL (at sea level), for example, about 0.0010 g/mL at 5,000 feet elevation. You may, in your downloaded spreadsheet of Table 2.4, substitute the appropriate value in the the formula in cell C14, and copy the new formula down the column.

Example 2.3

(a) Use Table 2.4 to calculate the volume of the 20-mL pipet in Example 2.2 (steel weights), from its weight in air. Assume the temperature is 23°C. (b) Give the corresponding volume at 20°C as a result of glass contraction. (c) Compare with the volume calculated using the weight in air with that calculated using the weight in vacuum and the density in water (Example 2.2).

Solution

(a) From Table 2.4, the volume per gram in air is 1.0035 mL at 23°C:

$$19.994 \text{ g} \times 1.0035 \text{ mL/g} = 20.064 \text{ mL}$$

(b) The glass contraction at 20°C relative to 23°C is 0.0015 mL (0.000025 mL/mL/°C × 20 mL × 3°C), so the pipet volume at 20°C is 20.062 mL.

(c) The density of water at 23°C is 0.99754 g/mL, so from the weight in vacuum:

$$20.015 \text{ g}/0.99754 \text{ g/mL} = 20.064 \text{ mL}$$

The same value is obtained. ■

Example 2.4

You prepared a solution of hydrochloric acid and standardized it by titration of primary standard sodium carbonate. The temperature during the standardization was 23°C, and the concentration was determined to be 0.1127_2 *M*. The heating system in the laboratory malfunctioned when you used the acid to titrate an unknown, and the temperature of the solution was 18°C. What was the concentration of the titrant?

Solution

$$\begin{aligned} M_{18^\circ} &= M_{23^\circ} \times (D_{18^\circ}/D_{23^\circ}) \\ &= 0.1127_2 \times (0.99859/0.99754) \\ &= 0.1128_4 \, M \end{aligned}$$

(See Chapter 3 for significant figures and the meaning of the subscript numbers.) ■

TECHNIQUES FOR CALIBRATING GLASSWARE

You generally calibrate glassware to five significant figures, the maximum precision you are likely to attain in filling or delivering solutions. Hence, your net weight of water needs to be five figures. If the glassware exceeds 10 mL, this means weighing to 1 mg is all that is needed. This can be readily and conveniently accomplished using a top-loading balance, rather than a more sensitive analytical balance. [Note: If the volume number is large without regard to the decimal, e.g., 99, then four figures will suffice—see Chapter 3 discussion on significant figures. For example, a 10-mL pipette may be calibrated and shown to actually deliver 9.997 mL. This is as accurate as if the pipette was determined to deliver 10.003 mL (the last significant figure in both cases is one part in 10,000)].

1. Volumetric Flask Calibration. To calibrate a volumetric flask, first weigh the clean, dry flask and stopper. Then fill it to the mark with distilled water. There should be no droplets on the neck. If there are, blot them with tissue paper. The flask and

water should be equilibrated to room temperature. Weigh the filled flask, and then record the temperature of the water to 0.1°C. The increase in weight represents the weight in air of the water contained by the flask.

2. Pipet Calibration. To calibrate a pipet, weigh a dry Erlenmeyer flask with a rubber stopper or a weighing bottle with a glass stopper or cap, depending on the volume of water to be weighed. Fill the pipet with distilled water (whose temperature you have recorded) and deliver the water into the flask or bottle, using proper pipetting technique, and quickly stopper the container to avoid evaporation loss. Reweigh to obtain the weight in air of water delivered by the pipet.

3. Buret Calibration. Calibrating a buret is similar to the procedure for a pipet, except that several volumes will be delivered. The internal bore of the buret is not perfectly cylindrical, and it will be a bit "wavy," so the actual volume delivered will vary both plus and minus from the nominal volumes marked on the buret, as increased volumes are delivered. You will ascertain the volume at 20% full-volume increments (e.g., each 10 mL, for a 50-mL buret) by filling the buret each time and then delivering the nominal volume into a dry flask. (The buret is filled each time to minimize evaporation errors. You may also make successive deliveries into the same flask, i.e., fill the buret only once. Make rapid deliveries.) Since the delivered volume does not have to be exact, but close to the nominal volume, you can make fairly fast deliveries, but wait about 10 to 20 s for film drainage. Prepare a plot of volume correction versus nominal volume and draw straight lines between each point. Interpolation is made at intermediate volumes from the lines. Typical volume corrections for a 50-mL buret may range up to ca. 0.05 mL, plus or minus.

Professor's Favorite Experiment

Contributed by Professor Alex Scheeline, University of Illinois

This illustrates a possibly more precise alternative to buret calibration, as described here, or determines the optimal approach.

Place a beaker of water in the weighing compartment of the balance so that the air becomes saturated with water vapor. Fill the buret. Place it through the top of the balance housing so the effluent will enter a beaker on the weighing table. Tare the balance and record the reading on the buret.

Now drain a few tenths of a milliliter from the buret. Record the volume, and once the balance has settled, record the mass. Continue to do this so that one has ca. 100 points from the drainage of the buret. Repeat three times. Compute the volume delivered for each reading. Plot. Now answer these questions:

- Which is more precise: the fiducial marking of the buret, as manufactured, or your attempt to calibrate the buret?
- Is there a smooth curve through the data, or is there significant variation from a smooth curve?
- Is there any indication as to what the appropriate measurement interval should be to obtain calibration to ±0.01 mL while minimizing the number of calibration points?
- How does the calibration of your buret compare with that of two other students?
- What is the best precision one can get if one ignores the results of buret calibaration?

Example 2.5

You calibrate a 50-mL buret at 10-mL increments, filling the buret each time and delivering the nominal volume, with the following results:

Buret Reading (mL)	*Weight H_2O Delivered (g)*
10.02	10.03
20.08	20.03
29.99	29.85
40.06	39.90
49.98	49.86

Construct a plot of volume correction versus volume delivered. The temperature of the water is 20°C and stainless steel weights are used.

Solution

From Table 2.4 (or use Table 2.4 from the website for automatic calculation of volumes):

$$W_{vac} = 10.03 + 10.03(0.00105) = 10.03 + 0.01 = 10.04 \text{ g}$$

$$\text{Vol.} = 10.04 \text{ g}/0.9982 \text{ g/mL} = 10.06 \text{ mL}$$

Likewise, for the others, we construct the table:

Nominal Volume (mL)	*Actual Volume (mL)*	*Correction (mL)*
10.02	10.06	+0.04
20.08	20.09	+0.01
29.99	29.93	−0.06
40.06	40.01	−0.05
49.98	50.00	+0.02

Prepare a graph of nominal volume (y axis) versus correction volume. Use 10, 20, 30, 40, and 50 mL as the nominal volumes. ■

SELECTION OF GLASSWARE—HOW ACCURATE DOES IT HAVE TO BE?

Only certain volumes need to be measured accurately, those involved in the quantitative calculations.

As in weighing operations, there will be situations where you need to accurately know volumes of reagents or samples measured or transferred (accurate measurements), and others in which only approximate measurements are required (rough measurements). If you wish to prepare a standard solution of 0.1 *M* hydrochloric acid, it can't be done by measuring an accurate volume of concentrated acid and diluting to a known volume because the concentration of the commercial acid is not known adequately. Hence, an approximate solution is prepared that is then standardized. We see in the table on the inside *back cover* that the commercial acid is about 12.4 *M*. To prepare 1 L of a 0.1 *M* solution, about 8.1 mL needs to be taken and diluted. It would be a waste of time to measure this (or the water used for dilution) accurately. A 10-mL graduated cylinder or 10-mL measuring pipet will suffice, and the acid can be diluted in an ungraduated 1-L bottle. If, on the other hand, you wish to dilute a stock standard solution accurately, then a transfer pipet must be used and the dilution must be done in a volumetric flask. Any volumetric measurement that is a part of the actual analytical measurement must be done with the accuracy and precision required of the analytical measurement. This generally means four-significant-figure accuracy, and transfer pipets and volumetric flasks are required. This includes taking an accurate portion of a sample, preparation of

a standard solution from an accurately weighed reagent, and accurate dilutions. Burets are used for accurate measurement of variable volumes, as in a titration. Preparation of reagents that are to be used in an analysis just to provide proper solution conditions (e.g., buffers for pH control) need not be prepared highly accurately, and less accurate glassware can be used, for example, graduated cylinders.

2.5 Preparation of Standard Base Solutions

Sodium hydroxide is usually used as the titrant when a base is required. It contains significant amounts of water and sodium carbonate, and so it cannot be used as a primary standard. For accurate work, the sodium carbonate must be removed from the NaOH because it reacts to form a buffer that decreases the sharpness of the end point. In addition, an error will result if the NaOH is standardized using a phenolphthalein end point (in which case the CO_3^{2-} is titrated only to HCO_3^-), and then a methyl orange end point is used in the titration of a sample (in which case the CO_3^{2-} is titrated to CO_2). In other words, the effective molarity of the base has been increased, owing to further reaction of the HCO_3^-.

Remove Na_2CO_3 by preparing a saturated solution of NaOH.

Sodium carbonate is essentially insoluble in nearly saturated sodium hydroxide. It is conveniently removed by dissolving the weighed NaOH in a volume (milliliters) of water equal to its weight in grams. The insoluble Na_2CO_3 can be allowed to settle for several days, and then the clear supernatant liquid can be carefully decanted,[1] or it can be filtered in a Gooch crucible with a quartz fiber filter mat (do not wash the filtered Na_2CO_3). This procedure does not work with KOH because K_2CO_3 remains soluble.

See Experiment 7 for preparing and standardizing sodium hydroxide.

Water dissolves CO_2 from the air. In many routine determinations not requiring the highest degree of accuracy, carbonate or CO_2 impurities in the water will result in an error that is small enough to be considered negligible. For the highest accuracy, however, CO_2 should be removed from all water used to prepare solutions for acid–base titrations, particularly the alkaline solutions. This is conveniently done by boiling the water and then cooling it under a cold-water tap.

Sodium hydroxide is usually standardized by titrating a weighed quantity of primary standard potassium acid phthalate (KHP), which is a moderately weak acid ($K_a = 4 \times 10^{-6}$), approximately like acetic acid; a phenolphthalein end point is used. The sodium hydroxide solution should be stored in a plastic-lined glass bottle to prevent absorption of CO_2 from the air. If the bottle must be open (e.g., a siphon bottle), the opening is protected with an **Ascarite** II (fibrous silicate impregnated with NaOH) or soda-lime [$Ca(OH)_2$ and NaOH] tube.

2.6 Preparation of Standard Acid Solutions

Hydrochloric acid is the usual titrant for the titration of bases. Most chlorides are soluble, and few possible side reactions with this acid. It is convenient to handle. It is not a primary standard (although constant-boiling HCl, which is a primary standard, can be prepared), and an approximate concentration is prepared simply by diluting the concentrated acid. For most accurate work, the water used to prepare the solution should be boiled, although use of boiled water is not so critical as with NaOH; CO_2 will have a low solubility in strongly acidic solutions and will tend to escape during shaking of the solution.

[1] Concentrated alkali attacks glass whereas carbon dioxide can permeate through most organic polymers. One solution out of this dilemma is to insert a polyethylene bag inside a glass bottle and use a rubber stopper.

Primary standard sodium carbonate is usually used to standardize HCl solutions. The disadvantage is that the end point is not sharp unless an indicator such as methyl red or methyl purple is used and the solution is boiled at the end point. A modified methyl orange end point may be used without boiling, but this is not so sharp. Another disadvantage is the low formula weight of Na_2CO_3. Tris-(hydroxymethyl)aminomethane (THAM), $(HOCH_2)_3CNH_2$, is another primary standard that is more convenient to use. It is nonhygroscopic, but it is still a fairly weak base ($K_b = 1.3 \times 10^{-6}$) with a low molecular weight. The end point is not complicated by released CO_2, and it is recommended as the primary standard unless the HCl is being used to titrate carbonate samples.

See Experiment 8 for preparing and standardizing hydrochloric acid.

If a standardized NaOH solution is available, the HCl can be standardized by titrating an aliquot with the NaOH. The end point is sharp and the titration is more rapid. The NaOH solution is a **secondary standard**. Any error in standardizing this will be reflected in the accuracy of the HCl solution. The HCl is titrated with the base, rather than the other way around, to minimize absorption of CO_2 in the titration flask. Phenolphthalein or bromothymol blue can be used as indicator.

A secondary standard is less accurate than a primary standard.

2.7 Other Apparatus—Handling and Treating Samples

Besides apparatus for measuring mass and volume, there are a number of other items of equipment commonly used in analytical procedures.

BLOOD SAMPLERS

Syringes/needles are used to collect blood samples typically into evacuated glass vials, (**Vacutainers**).[2] Stainless steel needles are generally used with glass or plastic syringes. These usually present no problem of contamination, although special precautions may be required for analysis of trace elements (e.g., metals) in the sample. Vacutainers are evacuated test tubes with a rubber cap. The needle is pushed through the cap after the other end has been inserted into the vein, and the blood is drawn into the evacuated tube. The tube may contain an anticoagulating agent to prevent clotting of the blood if plasma or whole blood samples are to be analyzed.

A finger puncture, instead of a venipuncture, is used when small quantities of blood are to be collected for microprocedures. As much as ~0.5 mL blood can be squeezed from the finger into a small collection tube by puncturing the finger with a sterilized sharp-pointed knifelike object. Finger puncture is commonly used in conjunction with sampling for glucose monitoring devices.

DESICCATORS

A **desiccator** is used to keep samples dry while they are cooling and before they are weighed and, in some cases, to dry a wet sample. Dried or ignited samples and vessels are cooled in the desiccator. A typical glass desiccator is shown in Figure 2.12. A desiccator is an airtight container that maintains an atmosphere of low humidity. A desiccant such as calcium chloride is placed in the bottom to absorb the moisture. This desiccant will have to be changed periodically as it becomes "spent." It will usually become wet in appearance or caked from the moisture when it is time to be changed. A porcelain plate is usually placed in the desiccator to support weighing bottles, crucibles, and other vessels. An airtight seal is made by application of stopcock grease to the ground-glass rim on the top of the desiccator. A **vacuum desiccator** has a side arm on the top for evacuation so that the contents can be kept in a vacuum rather than just an atmosphere of dry air.

Oven-dried samples or reagents are cooled in a desiccator before weighing.

[2] You should *not* attempt to collect a blood sample unless you have been specifically trained to do so. A trained technician will generally be assigned to this job.

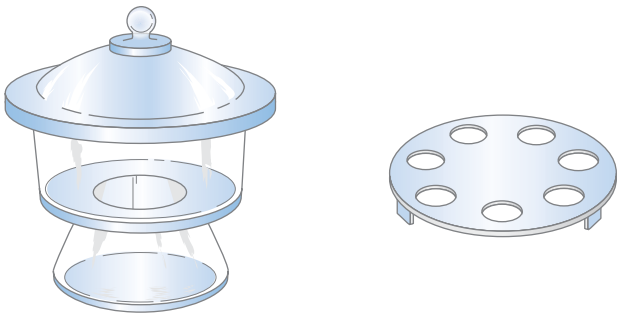


Fig. 2.12. Desiccator and desiccator plate.

Fig. 2.13. Muffle furnace. (Courtesy of Arthur H. Thomas Company.)

The top of a desiccator should not be removed any more than necessary since the removal of moisture from the air introduced is rather slow, and continued exposure will limit the lifetime of the desiccant. A red-hot crucible or other vessel should be allowed to cool in the air about 60 s before it is placed in the desiccator. Otherwise, the air in the desiccator will be heated appreciably before the desiccator is closed, and as the air cools, a partial vacuum will be created. This will result in a rapid inrush of air when the desiccator is opened and in possible spilling or loss of sample as a consequence. A hot weighing bottle should not be stoppered when placed in a desiccator because on cooling, a partial vacuum is created and the stopper may seize. The stopper should be placed in the desiccator with the weighing bottle.

Table 2.5 lists some commonly used desiccants and their properties. Aluminum oxide, magnesium perchlorate, calcium oxide, calcium chloride, and silica gel can be regenerated by heating at 150, 240, 500, 275, and 150°C, respectively.

FURNACES AND OVENS

A **muffle furnace** (Figure 2.13) is used to ignite samples to high temperatures, either to convert precipitates to a weighable form or to burn organic materials prior to inorganic analysis. There should be some means of regulating the temperature since losses of some metals may occur at temperatures in excess of 500°C. Temperatures up to about 1200°C can be reached with muffle furnaces.

Table 2.5
Some Common Drying Agents

Agent	Capacity	Deliquescent[a]	Trade Name
$CaCl_2$ (anhydrous)	High	Yes	
$CaSO_4$	Moderate	No	Drierite (W. A. Hammond Drierite Co.)
CaO	Moderate	No	
$MgClO_4$ (anhydrous)	High	Yes	Anhydrone (J. T. Baker Chemical Co.); Dehydrite (Arthur H. Thomas Co.)
Silica gel	Low	No	
Al_2O_3	Low	No	
P_2O_5	Low	Yes	

[a]Becomes liquid by absorbing moisture. Take care of liquids generated. For example, P_2O_5 generates H_3PO_4.

A **drying oven** is used to dry samples prior to weighing. A typical drying oven is shown in Figure 2.14. These ovens are well ventilated for uniform heating. The usual drying temperature is about 110°C, but many laboratory ovens can be heated up to temperatures of 200 to 300°C.

Fig. 2.14. Drying oven. (Courtesy of Arthur H. Thomas Company.)

HOODS

A **fume hood** is used when chemicals or solutions are to be evaporated. When perchloric acid or acid solutions of perchlorates are to be evaporated, the fumes should be collected, or the evaporation should be carried out in fume hoods specially designed for perchloric acid work (i.e., constructed from components resistant to attack by perchloric acid).

When performing trace analysis, as in trace metal analysis, care must be taken to prevent contamination. The conventional fume hood is one of the "dirtiest" areas of the laboratory since laboratory air is drawn into the hood and over the sample. **Laminar-flow hoods** or workstations are available for providing very clean work areas. Rather than drawing unfiltered laboratory air into the work area, the air is prefiltered and then flows over the work area and out into the room to create a positive pressure and prevent unfiltered air from flowing in. A typical laminar-flow workstation is shown in Figure 2.15. The high-efficiency particulate air (HEPA) filter removes all particles larger than 0.3 µm from the air. Vertical laminar-flow stations are preferred when fumes are generated that should not be blown over the operator. Facilities are available to exhaust noxious fumes. **Biohazard hoods** can also be found in many modern analytical and clinical laboratories. They are different from exhaust hoods. Their main purpose is to provide a safe place to work with potentially infectious material and particulates. They are often outfitted with high-intensity UV lamps that can be turned on prior to or after working (never during) in order to disinfect the workspace. All analysts should receive proper training prior to handling biohazard materials.

Laminar-flow hoods provide clean work areas.

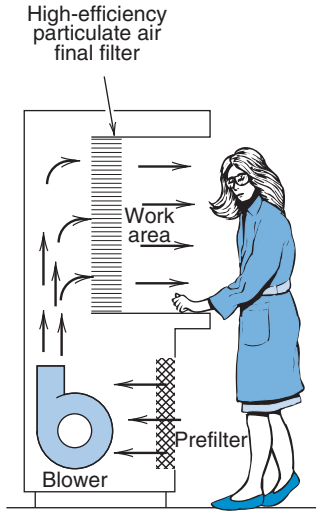


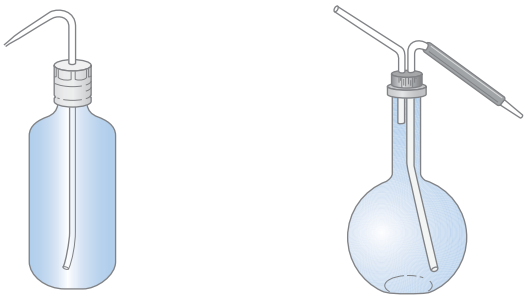
Fig. 2.15. Laminar-flow workstation. (Courtesy of Dexion, Inc., 344 Beltine Boulevard, Minneapolis, MN.)

WASH BOTTLES

A **wash bottle** of some sort should be handy in any analytical laboratory, to be used for quantitative transfer of precipitates and solutions and to wash precipitates. These are commercially available in a variety of shapes and sizes, as seen in Figure 2.16. Alternatively they may be constructed from a Florence flask and glass tubing, as in Figure 2.16*b*.

CENTRIFUGES AND FILTERS

A **centrifuge** has many useful applications, particularly in the clinical laboratory, where blood may have to be separated into fractions such as serum or plasma, and proteins may have to be separated by precipitation followed by centrifuging. Many



(*a*) (*b*)

Fig. 2.16. Wash bottles: (*a*) polyethylene, squeeze type; (*b*) glass, blow type.

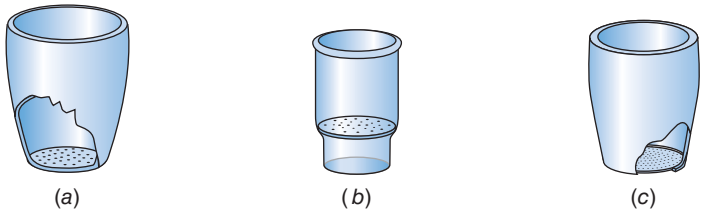


Fig. 2.17. Filtering crucibles: (*a*) Gooch crucible; (*b*) sintered-glass crucible; (*c*) porcelain filter crucible.

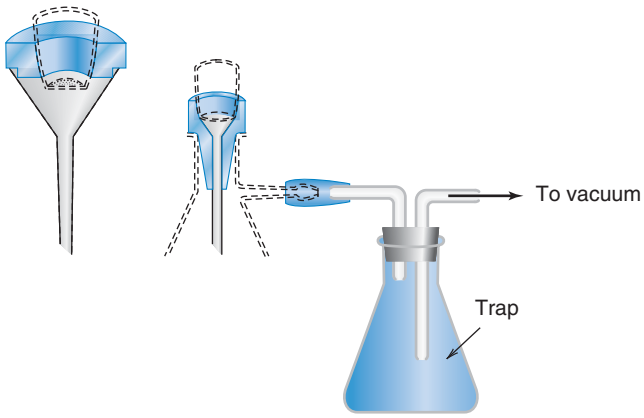


Fig. 2.18. Crucible holders.

laboratories also have an **ultracentrifuge**. Such an instrument has a larger capacity and can achieve higher speeds (gravitational force) in order to more readily separate sample components. Centrifugal filters are available with different molecular weight (MW) cutoff filter elements. They consist of disposable centrifuge tubes, separated by a horizontally placed filter element. A sample (typically biological) is put in the top compartment and the device is then subjected to centrifugation. Either the low MW material (often a clear filtrate) or the higher MW material retained by the filter can be of interest.

Filters for filtering precipitates (e.g., in gravimetric analysis) are of various types. The Gooch crucible, sintered-glass crucible, and porcelain filter crucible are illustrated in Figure 2.17. The **Gooch crucible** is porcelain and has holes in the bottom; a glass fiber filter disk is supported on top of it. The glass fiber filter disk will handle fine precipitates. The **sintered-glass crucible** contains a sintered-glass bottom, which is available in fine (F), medium (M), or coarse (C) porosity. The **porcelain filter crucible** contains a porous unglazed bottom. Glass filters are not recommended for concentrated alkali solutions because of the possibility of attack by these solutions. See Table 2.1 for maximum working temperatures for different types of crucible materials.

Gelatinous precipitates such as hydrous iron oxide should not be filtered in filter crucibles because they clog the pores. Even with filter paper, the filtration of the precipitates can be slow.

Filter crucibles are used with a **crucible holder** mounted on a filtering flask (Figure 2.18). A safety bottle is connected between the flask and the aspirator.

Ashless filter paper is generally used for quantitative work in which the paper is ignited away and leaves a precipitate suitable for weighing (see Chapter 10). There are various grades of filter papers for different types of precipitates. These are listed in Table 2.6 for Whatman papers.

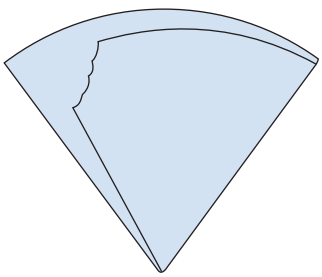


Fig. 2.19. Properly folded filter paper.

TECHNIQUES OF FILTRATION

By proper fitting of the filter paper, the rate of filtration can be increased. A properly folded filter paper is illustrated in Figure 2.19. The filter paper is folded in the shape of a cone, with the overlapped edges of the two quarters not quite meeting (0.5 cm apart).

Table 2.6
Whatman Filter Papers

Precipitate	Whatman No.
Very fine (e.g., $BaSO_4$)	50 (2.7 μm)
Small or medium (e.g., AgCl)	52 (7 μm)
Gelatinous or large crystals (e.g., $Fe_2O_3 \cdot xH_2O$)	54 (22 μm)

See http://www.whatman.com/QuantitativeFilterPapersHardenedLowAshGrades.aspx

About 1 cm is torn away from the corner of the inside edge. This will allow a good seal against the funnel to prevent air bubbles from being drawn in. After the folded paper is placed in the funnel, it is wetted with distilled water. The stem is filled with water and the top of the wet paper is pressed against the funnel to make a seal. With a proper fit, no air bubbles will be sucked into the funnel, and the suction supplied by the weight of the water in the stem will increase the rate of filtration. The filtration should be started immediately. The precipitate should occupy not more than one-third to one-half of the filter paper in the funnel because many precipitates tend to "creep." Do not allow the water level to go over the top of the paper.

The precipitate should be allowed to settle in the beaker before filtration is begun. The bulk of the clear liquid can then be decanted and filtered at a rapid rate before the precipitate fills the pores of the filter paper.

Let the precipitate settle before filtering.

Care must be taken in the decanting and the transferring of the precipitate to avoid losses. This is properly done by use of a stirring rod and a wash bottle, as illustrated in Figure 2.20. Note: the wash liquid is not distilled water—see Chapter 10. The solution is decanted by pouring it down the glass rod, which guides it into the filter without splashing. The precipitate is most readily washed while still in the beaker. After the mother liquor has been decanted off, wash the sides of the beaker down with several milliliters of the wash liquid, and then allow the precipitate to settle as before. Decant the wash liquid into the filter and repeat the washing operation two or three times. Then transfer the precipitate to the filter by holding the glass rod and beaker in one hand, as illustrated, and wash it out of the beaker with wash liquid from the wash bottle.

Wash the precipitate while it is in the beaker.

If the precipitate must be collected quantitatively, as in gravimetric analysis, the last portions of precipitate are removed by scrubbing the walls with a moistened **rubber policeman**, which contains a flexible rubber scraper attached to a glass rod (Figure 2.21). [For a description of the origin of its name, see J. W. Jensen, *J. Chem. Ed.*, **85** (6) (2008) 776.] Wash the remainder of loosened precipitate from the beaker and from the policeman. If the precipitate is being collected in a filter paper, then instead of a rubber policeman, a small piece of the ashless filter paper can be rubbed on the beaker walls to remove the last bits of precipitate and added to the filter. This should be held with a pair of forceps.

After the precipitate is transferred to the filter, it is washed with five or six small portions of wash liquid. This is more effective than adding one large volume. Divert the liquid around the top edge of the filter to wash the precipitate down into the cone. Each portion should be allowed to drain before adding the next one. Check for completeness of washing by testing for the precipitating agent in the last few drops of the washings. Note: there will always be some precipitate in the wash due to finite solubility, i.e., finite K_{sp}, but it will be undetectable after sufficient washing.

Test for completeness of washing.

Fig. 2.21. Rubber policeman.

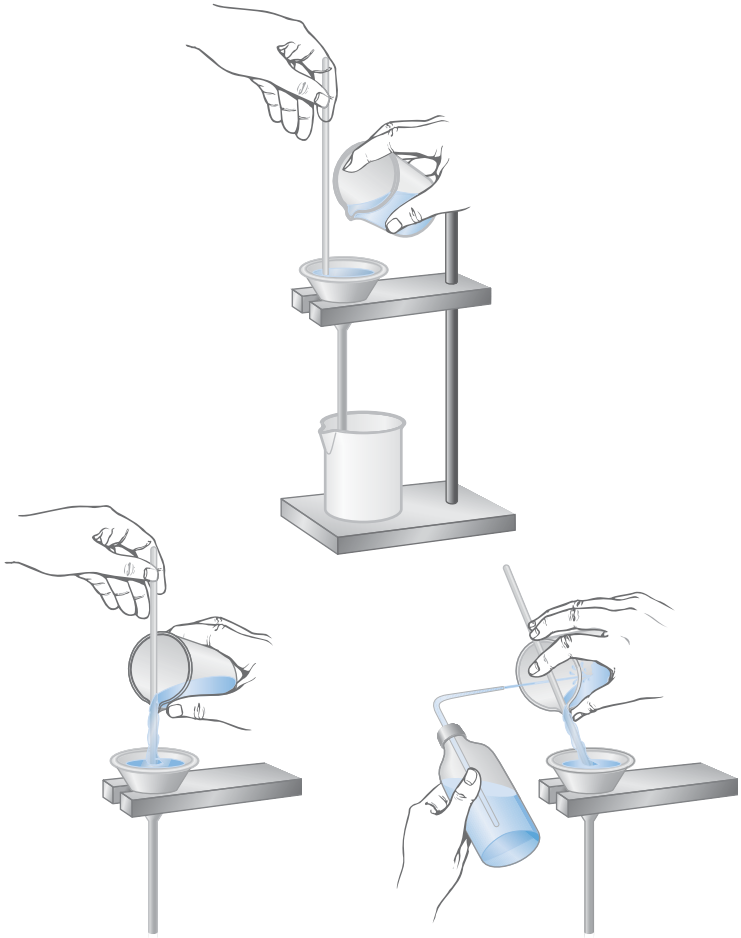


Fig. 2.20. Proper technique for transfer of a precipitate.

2.8 Igniting Precipitates—Gravimetric Analysis

If a precipitate is to be ignited in a porcelain filter crucible, the moisture should be driven off first at a low heat. The ignition may be done in a muffle furnace or by heating with a burner. If a burner is to be used, the filter crucible should be placed in a porcelain or platinum crucible to prevent reducing gases of the flame diffusing through the pores of the filter.

When precipitates are collected on filter paper, the cone-shaped filter containing the precipitate is removed from the funnel, the upper edge is flattened, and the corners are folded in. Then, the top is folded over and the paper and contents are placed in a crucible with the bulk of the precipitate on the bottom. The paper must now be dried and charred off. The crucible is placed at an angle on a triangle support with the crucible cover slightly ajar, as illustrated in Figure 2.22. The moisture is removed by low heat from the burner, with care taken to avoid splattering. The heating is gradually increased as moisture is evolved and the paper begins to char. Care should be taken to avoid directing the reducing portion of the flame into the crucible. A sudden increase in the volume of smoke evolved indicates that the paper is about to burst into flame, and the burner should be removed. If it does burst into flame, it should be smothered

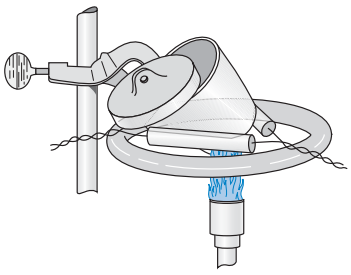


Fig. 2.22. Crucible and cover supported on a wire triangle for charring off paper.

quickly by replacing the crucible cover. Carbon particles will undoubtedly appear on the cover, and these will ultimately have to be ignited. Finally, when no more smoke is detected, the charred paper is burned off by gradually increasing the flame temperature. The carbon residue should glow but should not flame. Continue heating until all the carbon and tars on the crucible and its cover are burned off. The crucible and precipitate are now ready for igniting. The ignition can be continued with the burner used at highest temperature or with the muffle furnace.

Do the initial ignition slowly.

Before a precipitate is collected in a filter crucible or transferred to a crucible, the crucible should be dried to constant weight (e.g., 1 h of heating, followed by cooling and weighing and repeating the cycle) if the precipitate is to be dried, or it should be ignited to constant weight if the precipitate is to be ignited. Constant weight is considered to have been achieved with an analytical balance when successive weighings agree within about 0.3 or 0.4 mg. The crucible plus the precipitate are heated to constant weight in a similar manner. After the first heating, the time of heating can be reduced by half. The crucible should be allowed to cool in a desiccator for at least $\frac{1}{2}$ h before weighing. Red-hot crucibles should be allowed to cool below redness before placing them in the desiccator (use crucible tongs—usually nickel plated or stainless steel to minimize contamination from rust). Before weighing a covered crucible, check for any radiating heat by placing your hand near it (don't touch).

Dry and weigh the crucible before adding the precipitate!

2.9 Obtaining the Sample—Is It Solid, Liquid, or Gas?

Collecting a representative sample is an aspect of analytical chemistry that the beginning analytical student is often not concerned with because the samples handed to him or her are assumed to be homogeneous and representative. Yet this process can be the most critical aspect of an analysis. The significance and accuracy of measurements can be limited by the sampling process. Unless sampling is done properly, it becomes the weak link in the chain of the analysis. A life could sometimes depend on the proper handling of a blood sample during and after sampling. If the analyst is given a sample and does not actively participate in the sampling process, then the results obtained can only be attributed to the sample "as it was received." And the chain of custody as mentioned earlier must be documented.

See Chapter 3 for important statistical considerations in sampling.

Many professional societies have specified definite instructions for sampling given materials [e.g., the American Society for Testing and Materials (ASTM: www.astm.org), the Association of Official Analytical Chemists International (AOAC International: www.aoac.org), and the American Public Health Association (APHA: www.apha.org)]. By appropriate application of experience and statistics, these materials can be sampled as accurately as the analysis can be performed. Often, however, the matter is left up to the analyst. The ease or complexity of sampling will, of course, depend on the nature of the sample.

The problem involves obtaining a sample that is representative of the whole. This sample is called the **gross sample**. Its size may vary from a few grams or less to several pounds, depending on the type of bulk material. Once a representative gross sample is obtained, it may have to be reduced to a sufficiently small size to be handled. This is called the **sample**. Once the sample is obtained, an aliquot, or portion, of it will be analyzed. This aliquot is called the **analysis sample**. Several replicate analyses on the same sample may be performed by taking separate aliquots.

Replication in sampling and analysis are key considerations.

In the clinical laboratory, the gross sample is usually satisfactory for use as the sample because it is not large and it is homogeneous (e.g., blood and urine samples). The analysis sample will usually be from a few milliliters to a fraction of a drop (a few microliters) in quantity.

Some of the problems associated with obtaining gross samples of solids, liquids, and gases are considered below.

Sampling (From the journals collection of the Chemical Heritage Foundations' Othmer Library.)

1. Solids. Inhomogeneity of the material, variation in particle size, and variation within the particle make sampling of solids more difficult than other materials. The easiest but usually most unreliable way to sample a material is the **grab sample**, which is one sample taken at random and assumed to be representative. The grab sample will be satisfactory only if the material from which it is taken is homogeneous. For most reliable results, it is best to take 1/50 to 1/100 of the total bulk for the gross sample, unless the sample is fairly homogeneous. The larger the particle size, the larger the gross sample should be.

The easiest and most reliable time to sample large bodies of solid materials is while they are being moved. In this way any portion of the bulk material can usually be exposed for sampling. Thus, a systematic sampling can be performed to obtain aliquots representing all portions of the bulk. Some samples follow.

In the loading or unloading of bags of cement, a representative sample can be obtained by taking every fiftieth or so bag or by taking a sample from each bag. In the moving of grain by wheelbarrow, representative wheelbarrow loads or a shovelful from each wheelbarrow can be taken. All of these aliquots are combined to form the gross sample.

2. Liquids. Liquid samples tend to be homogeneous and representative samples are much easier to get. Liquids mix by diffusion only very slowly and must be shaken to obtain a homogeneous mixture. If the material is indeed homogeneous, a simple grab (single random) sample will suffice. For all practical purposes, this method is satisfactory for taking blood samples. The composition of some samples vary on when it is taken. This is the case for urine samples, Therefore 24-h urine sample collections are generally more representative than a single "spot sample".

The timing of sampling of biological fluids is, however, very important. The composition of blood varies considerably before and after meals, and for many analyses a sample is collected after the patient has fasted for a number of hours. Preservatives such as sodium fluoride for glucose preservation and anticoagulants may be added to blood samples when they are collected.

See Chapter 25 on the text's website for more on sampling biological fluids.

Blood samples may be analyzed as *whole blood*, or they may be separated to yield *plasma* or *serum* according to the requirements of the particular analysis. Most commonly, the concentration of the substance external to the red cells (the extracellular concentration) will be a significant indication of physiological condition, and so serum or plasma is taken for analysis.

If liquid samples are not homogeneous, and if they are small enough, they can be shaken and sampled immediately. For example, there may be particles in the liquid that have tended to settle. Large bodies of liquids are best sampled after a transfer or, if in a pipe, after passing through a pump when they have undergone thorough mixing. Large stationary liquids can be sampled with a "*thief*" *sampler*, which is a device for obtaining aliquots at different levels. It is best to take the sample at different depths at a diagonal, rather than straight down. The separate aliquots of liquids can be analyzed individually and the results combined, or the aliquots can be combined into one gross sample and replicate analyses performed. This latter procedure is probably preferred because the analyst will then have some idea of the precision of the analysis.

See Chapter 26 on the text's website for more on sampling environmental samples.

3. Gases The usual method of sampling gases involves sampling into an evacuated container, often a specially treated stainless steel canister or an inert polyvinyl fluoride (Tedlar) bag is commonly used. The sample may be collected rapidly (a grab sample)

or over a long period of time, using a small orifice to slowly fill the bag. A grab sample is satisfactory in many cases. To collect a breath sample, for example, the subject could blow into an evacuated bag or blow up a mylar balloon. Auto exhaust could be collected in a large evacuated plastic bag. The sample may be supersaturated with moisture relative to ambient temperature at which the sample container is. Moisture will condense in the sampling container after sample collection and the analyte of interest (e.g., ammonia in breath or nitrous acid in car exhaust) will be removed by the condensed moisture. The sample container must be heated and the sample transferred through a heated transfer line if the analyte is to be recovered.

The volume of gross gas sample collected may or may not need to be known. Often, the *concentration* of a certain analyte in the gas sample is measured, rather than the *amount*. The temperature and pressure of the sample will, of course, be important in determining the volume and hence the concentration.

Gas sampling techniques mentioned here does not concern gases dissolved in liquids, such CO_2 or O_2 in blood. These are treated as liquid samples and are then handled accordingly to measure the gas in the liquid or to release it from the liquid prior to measurement.

2.10 Operations of Drying and Preparing a Solution of the Analyte

After a sample has been collected, a solution of the analyte must usually be prepared before the analysis can be continued. Drying of the sample may be required, and it must be weighed or the volume measured. If the sample is already a solution (e.g., serum, urine, or water), then extraction, precipitation, or concentration of the analyte may be in order, and this may also be true with other samples.

In this section we describe common means for preparing solutions of inorganic and organic materials. Included are the dissolution of metals and inorganic compounds in various acids or in basic fluxes (fusion), the destruction of organic and biological materials for determination of inorganic constituents (using wet digestion or dry ashing), and the removal of proteins from biological materials so they do not interfere in the analysis of organic or inorganic constituents.

DRYING THE SAMPLE

Solid samples will usually contain variable amounts of adsorbed water. With inorganic materials, the sample will generally be dried before weighing. This is accomplished by placing it in a drying oven at 105 to 110°C for 1 or 2 h. Other nonessential water, such as that entrapped within the crystals, may require higher temperatures for removal.

Decomposition or side reactions of the sample must be considered during drying. Thermally unstable samples can be dried in a desiccator; using a vacuum desiccator will hasten the drying process. A lyophilizer (freeze dryer) can also be used to remove a fairly large amount of water from a sample that contains thermally labile material; the sample must be frozen prior to placing it in a vessel within, or attached to, the apparatus. If the need to sample is weighed without drying, the results will be reported on an "as is" basis.

Plant and tissue samples can usually be dried by heating. See Chapter 1 for a discussion of the various weight bases (wet, dry, ash) used in connection with reporting analytical results for these samples.

SAMPLE DISSOLUTION

Before the analyte can be measured, some sort of sample manipulation is generally necessary to get the analyte into solution or, for biological samples, to rid it of interfering substances, such as proteins. Complex samples can be subjected to centrifugal filtration prior to analysis (e.g., perchlorate and iodide in milk have been chromatographically determined after centrifugal filtration). There are two types of sample preparation: those that totally destroy the sample matrix and those that are nondestructive or only partially destructive. The former type can generally be used only when the analyte is inorganic or can be converted to an inorganic derivative for measurement (e.g., Kjeldahl analysis, in which organic nitrogen is converted to ammonium ion—see below). Iodine in food is similarly determined after total oxidative digestion to HIO_3. Destructive digestion typically must be used if trace element analysis must be conducted in a largely organic matrix.

DISSOLVING INORGANIC SOLIDS

Strong mineral acids are good solvents for many inorganics. *Hydrochloric acid* is a good general solvent for dissolving metals that are above hydrogen in the electromotive series. *Nitric acid* is a strong oxidizing acid and will dissolve most of the common metals, nonferrous alloys, and the "acid-insoluble" sulfides.

Perchloric acid, when heated to drive off water, becomes a very strong and efficient oxidizing acid in the dehydrated state. It dissolves most common metals and destroys traces of organic matter. It must be used with extreme caution because it will react explosively with many easily oxidizable substances, especially organic matter.

Fusion is used when acids do not dissolve the sample.

Some instruments today are extraordinarily sensitive. An inductively coupled plasma mass spectrometer (ICP-MS) is essential for measuring trace impurities in semiconductor grade silicon, for example. The silicon sample is dissolved in a mixture of nitric and hydrofluoric acids before analysis. To carry out such ultra trace analysis the acids must also be ultra-pure. Such ultra-pure "semiconductor grade" acids are also very expensive.

Fusion is used when acids do not dissolve the sample.

Some inorganic materials will not dissolve in acids, and **fusion** with an acidic or basic **flux** in the molten state must be used to solubilize them. The sample is mixed with the flux in a sample-to-flux ratio of about 1 to 10 or 20, and the combination is heated in an appropriate crucible until the flux becomes molten. When the melt becomes clear, usually in about 30 min, the reaction is complete. The cooled solid is then dissolved in dilute acid or in water. During the fusion process, insoluble materials in the sample react with the flux to form a soluble product. Sodium carbonate is one of the most useful basic fluxes, and acid-soluble carbonates are produced.

DESTRUCTION OF ORGANIC MATERIALS FOR INORGANIC ANALYSIS—BURNING OR ACID OXIDATION

Animal and plant tissue, biological fluids, and organic compounds are usually decomposed by **wet digestion** with a boiling oxidizing acid or mixture of acids, or by **dry ashing** at a high temperature (400 to 700°C) in a muffle furnace. In wet digestion, the acids oxidize organic matter to carbon dioxide, water, and other volatile products, which are driven off, leaving behind salts or acids of the inorganic constituents. In dry ashing, atmospheric oxygen serves as the oxidant; that is, the organic matter is burned off, leaving an inorganic residue. Auxiliary oxidants (e.g., $NaNO_3$) can be used as a flux during dry ashing.

In dry ashing, the organic matter is burned off.

1. Dry Ashing. Although various types of dry ashing and wet digestion combinations are used with about equal frequency by analysts for organic and biological materials,

simple dry ashing with no chemical aids is probably the most commonly employed technique. Lead, zinc, cobalt, antimony, chromium, molybdenum, strontium, and iron traces can be recovered with little loss by retention or volatilization. Usually a porcelain crucible can be used. Lead is volatilized at temperatures in excess of about 500°C, especially if chloride is present, as in blood or urine. Platinum crucibles are preferred for lead for minimal retention losses.

If an oxidizing material is added to the sample, the ashing efficiency is enhanced. Magnesium nitrate is one of the most useful aids, and with this it is possible to recover arsenic, copper, and silver, in addition to the above-listed elements.

Liquids and wet tissues are dried on a steam bath or by gentle heat before they are placed in a muffle furnace. The heat from the furnace should be applied gradually up to full temperature to prevent rapid combustion and foaming.

After dry ashing is complete, the residue is usually leached from the vessel with 1 or 2 mL hot concentrated or 6 *M* hydrochloric acid and transferred to a flask or beaker for further treatment.

Another dry technique is that of **low-temperature ashing**. A radio-frequency discharge is used to produce activated oxygen radicals, which are very reactive and will attack organic matter at low temperatures. Temperatures of less than 100°C can be maintained, and volatility losses are minimized. Introduction of elements from the container and the atmosphere is reduced, and so are retention losses. Radiotracer studies have demonstrated that 17 representative elements are quantitatively recovered after complete oxidation of organic substrate.

Elemental analysis in the case of organic compounds (e.g., for carbon or hydrogen) is usually performed by **oxygen combustion** in a tube, followed by an absorption train. Oxygen is passed over the sample in a platinum boat, which is heated and quantitatively converts carbon to CO_2 and hydrogen to H_2O. These combustion gases pass into the absorption train, where they are absorbed in preweighed tubes containing a suitable absorbent. For example, **Ascarite** II is used to absorb the CO_2, and **Dehydrite** (magnesium perchlorate) is used to absorb the H_2O. The gain in weight of the absorption tubes is a measure of the CO_2 and H_2O liberated from the sample. Details of this technique are important, and, should you have occasion to use it, you are referred to more comprehensive texts on elemental analysis. Modern elemental analyzers are more automated and may be based on chromatographic separation of the combustion gases followed by detection with a thermal conductivity detector—Chapter 20 (see, e.g., http://www-odp.tamu.edu/publications/tnotes/tn30/tn30_10.htm).

2. Wet Digestion. Next to dry ashing, wet digestion with a mixture of nitric and sulfuric acids is the second most frequently used oxidation procedure. Usually a small amount (e.g., 5 mL) of sulfuric acid is used with larger volumes of nitric acid (20 to 30 mL). Wet digestions are usually performed in a Kjeldahl flask (Figure 2.24). The nitric acid destroys the bulk of the organic matter, but it does not get hot enough to destroy the last traces. It is boiled off during the digestion process until only sulfuric acid remains and dense, white SO_3 fumes are evolved and begin to reflux in the flask. At this point, the solution gets very hot, and the sulfuric acid acts on the remaining organic material. Charring may occur at this point if there is considerable or very resistant organic matter left. If the organic matter persists, more nitric acid may be added. Digestion is continued until the solution clears. All digestion procedures must be performed in a fume hood.

In wet ashing, the organic matter is oxidized with an oxidizing acid.

A much more efficient digestion mixture uses a mixture of nitric, perchloric, and sulfuric acids in a volume ratio of about 3:1:1. Ten milliliters of this mixture will usually suffice for 10 g fresh tissue or blood. The perchloric acid is an extremely efficient oxidizing agent when it is dehydrated and hot and will destroy the last traces of organic matter with relative ease. Samples are heated until nitric acid is boiled off and perchloric acid fumes appear; these, are less dense than SO_3 but fill the flask

more readily. The hot perchloric acid is boiled, usually until fumes of SO_3 appear, signaling the evaporation of all the perchloric acid. Sufficient nitric acid must be added at the beginning to dissolve and destroy the bulk of organic matter, and there must be sulfuric acid present to prevent the sample from going to dryness, or else there is danger of explosion from the perchloric acid. A hood specially designed for perchloric acid work must be used for all digestions incorporating perchloric acid. Typically, a nitric-sulfuric acid digestion is first carried out to remove the more easily oxidizable material before digestion with the perchloric acid cocktail is carried out.

Perchloric acid digestion is even more efficient if a small amount of molybdenum(VI) catalyst is added. As soon as water and nitric acid are evaporated, oxidation proceeds vigorously with foaming, and the digestion is complete in a few seconds. The digestion time is reduced considerably.

Perchloric acid must be used with caution!

A mixture of nitric and perchloric acids is also commonly used. The nitric acid boils off first, and care must be taken to prevent evaporation of the perchloric acid to near dryness, or a violent explosion may result; this procedure *is not recommended* unless you have considerable experience in digestion procedures. **Perchloric acid should never be added directly to organic or biological material**. Always add an excess of nitric acid first. Explosions with perchloric acid are generally associated with formation of peroxides, and the acid turns dark in color (e.g., yellowish brown) prior to explosion. Certain organic compounds such as ethanol, cellulose, and polyhydric alcohols can cause hot concentrated perchloric acid to explode violently; this is presumably due to formation of ethyl perchlorate.

A mixture of nitric, perchloric, and sulfuric acids allows zinc, selenium, arsenic, copper, cobalt, silver, cadmium, antimony, chromium, molybdenum, strontium, and iron to be quantitatively recovered. Lead is often lost if sulfuric acid is used. The mixture of nitric and perchloric acids can be used for lead and all the above elements. Perchloric acid must be present to prevent losses of selenium. It maintains strong oxidizing conditions and prevents charring that would result in formation of volatile compounds of lower oxidation states of selenium. Samples containing mercury cannot be dry ashed. Wet digestion that involves the simultaneous application of heat must be done using a reflux apparatus because of the volatile nature of mercury and its compounds. Cold or room temperature procedures are often preferred to obtain partial destruction of organic matter. For example, in urine samples, which contain a relatively small amount of organic matter compared with blood, mercury can be reduced to the element with copper(I) and hydroxylamine hydrochloride and the organic matter destroyed by potassium permanganate at room temperature. The mercury can then be dissolved and the analysis continued. Urinary mercury can be mineralized using Fenton's reagent (Fe(II) and H_2O_2) and determined as the elemental vapor after addition of sodium borohydride, a powerful reducing agent.

In Kjeldahl digestions, nitrogen is converted to ammonium ion, which is then distilled as ammonia and titrated.

Many nitrogen-containing compounds can be determined by **Kjeldahl digestion** to convert the nitrogen to ammonium sulfate. The digestion mixture consists of sulfuric acid plus potassium sulfate to increase the boiling point of the acid and thus increase its efficiency. A catalyst is also added (such as copper or selenium). After destruction of the organic matter, sodium hydroxide is added to make the solution alkaline, and the ammonia is distilled into an excess of standard hydrochloric acid. The excess acid is back-titrated with standard alkali to determine the amount of ammonia collected. With a knowledge of the percent nitrogen composition in the compound of interest, the amount of the compound can be calculated from the amount of ammonia determined. This is the most accurate method for determining protein content. Protein contains a definite percentage of nitrogen, which is converted to ammonium sulfate during the digestion. See Chapter 8 for further details. Note: of course, if other nitrogen-containing species are present, the nitrogen determination will not accurately reflect the protein content. This was amply demonstrated in China when melamine, an inexpensive

organic amine base containing six nitrogen atoms, was added to milk formula to boost the apparent "protein" content. This caused the death of many infants in China.

Dry and wet ashing each has advantages and limitations.

The relative merits of various oxidation methods have been studied extensively. However, there may be no universal and generally applicable dry ashing method. Dry ashing is recommended for its simplicity and relative freedom from positive errors (contamination) since few or no reagents are added. The potential errors of dry oxidation are volatilization of elements and losses by retention on the walls of the vessel. Adsorbed metals on the vessel may in turn contaminate future samples. Wet digestion is considered superior in terms of rapidity (although it does require more operator attention), low level of temperature maintained, and freedom from loss by retention. The chief error attributed to wet digestion is the introduction of impurities from the reagents necessary for the reaction. This problem has been minimized as commercial reagent-grade acids have become available in greater purity and specially prepared high-purity acids can now be obtained commercially, albeit not inexpensively. The time required for ashing or digestion will vary with the sample and the technique employed. Two to four hours are common for dry ashing and half to one hour is common for wet digestion.

MICROWAVE PREPARATION OF SAMPLES

Microwave ovens are now widely used for rapid and efficient drying and acid decomposition of samples. Laboratory microwave ovens are specially designed to overcome limitations of household ovens, and these are discussed below. Advantages of microwave digestions include reduction of dissolution times from hours to minutes and low blank levels due to reduced amounts of reagents required.

1. How Do Microwaves Heat? The microwave region is between infrared radiation and radio waves in the electromagnetic spectrum, in the frequency range of 300 to 300,000 MHz (3×10^8 to 3×10^{11} Hz, or beginning at about 1000 μm wavelength—see Figure 16.2). Microwaves consist of an electric field and a magnetic field perpendicular to the electric field. The electric field is responsible for energy transfer between the microwave source and the irradiated sample. Microwave energy affects molecules in two ways: dipole rotation and ionic conduction. The first is the more generally important. When the microwave energy passes through the sample, molecules with non-zero dipole moments will try to align with the electric field, and the more polar ones will have the stronger interaction with the field. This molecular motion (rotation) results in heating. The energy transfer, a function of the dipole moment and the dielectric constant, is most efficient when the molecules are able to relax quickly, that is, when the relaxation time matches the microwave frequency. Large molecules such as polymers relax slowly, but once the temperature increases and they relax more rapidly, they can absorb the energy more efficiently. Small molecules such as water, though, relax more quickly than the resonating microwave energy, and they move farther away from the resonance frequency and absorb less energy as they heat up.

The ionic conduction effect arises because ionic species in the presence of an electric field will migrate in one direction or the other. Energy is transferred from the electric field, causing ionic interactions that speed up the heating of a solution. Ionic absorbers become stronger absorbers of microwave energy as they are heated since ionic conductance increases with temperature. Deionized water heats slowly, but if salt is added, it heats rapidly. Acids, of course, are good conductors and heat rapidly.

Microwaves heat by causing molecules to rotate and ions to migrate.

So microwave energy heats by causing movement of molecules due to dipole rotation and movement of ions due to ionic conductance. The microwave energy interacts with different materials in different ways. Reflective materials such as metals are good heat conductors: They do not heat and instead will reflect the microwave energy. (It is not good practice to put metals in microwave ovens due to electrical discharge occurring between one very highly charged metal segment to another.) Transparent materials are insulators because they transmit the microwave energy and

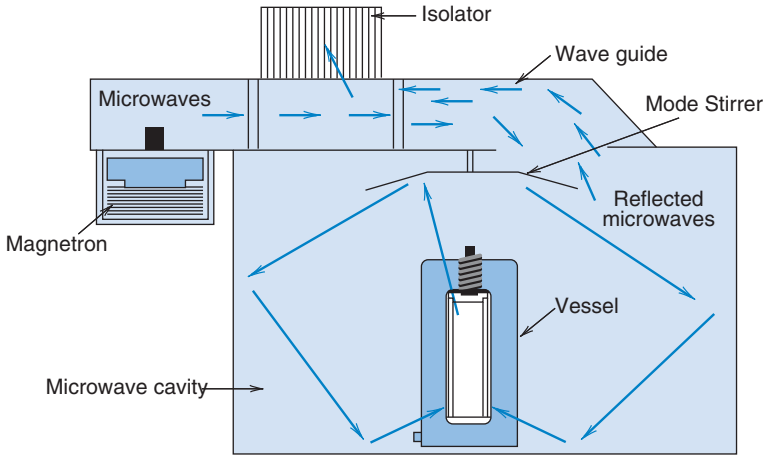


Fig. 2.23. Schematic of a microwave system. [From G. Le Blanc, *LC/GC Suppl.*, **17**(6S) (1999) S30.] (Courtesy of *LC/GC Magazine*).

also do not heat. The absorptive materials, the molecules and ions discussed above, are the ones that receive microwaves and are heated. Microwave energy is too low to break chemical bonds (a feature that has generated interest in using microwave energy to speed up chemical reactions in syntheses). The properties of reflective and insulator materials are utilized in designing microwave digestion systems.

Household microwave ovens don't work for small sample heating.

2. Design of Laboratory Microwave Ovens. Home microwave ovens were initially used for laboratory purposes, but it soon became apparent that modifications were needed. Laboratory samples are usually much smaller than food samples that are cooked and absorb only a small fraction of the energy produced by the magnetron of the oven. The energy not absorbed by the sample is bounced back to the magnetron, causing it to overheat and burn out. Also, arcing could occur. So laboratory ovens are designed to protect the magnetron from stray energy. The main components of these ovens (Figure 2.23) include the magnetron, an isolator, a waveguide, the cavity, and a mode stirrer. Microwave energy generated by the magnetron is propagated down the waveguide into the cavity. The stirrer distributes the energy in different directions. The isolator, made of a ferromagnetic material and placed between the magnetron and the waveguide, deflects the microwave energy returning from the cavity into a fan-cooled ceramic load, keeping it away from the magnetron.

The frequency used for cooking turns out to be good for chemistry as well, and the standard is 2450 MHz. Powers of 1200 W are typically used.

3. Acid Digestions. Digestions are normally done in closed plastic containers, either Teflon PFA (perfluoroalkoxy ethylene) or polycarbonate (insulators). This is to avoid acid fumes in the oven. It provides additional advantages. Pressure is increased and the boiling point of the acid is raised (the acid is superheated). So digestions occur more rapidly. Also, volatile metals are not lost. Modern ovens provide for control of pressure and temperature. Fiber-optic temperature probes are used that are transparent to microwave energy. Temperature control has enabled the use of the oven for microwave-assisted molecular extractions, by maintaining the temperature low enough to avoid molecular decomposition.

PARTIAL DESTRUCTION OR NONDESTRUCTION OF SAMPLE MATRIX

Obviously, when the substance to be determined is organic in nature, nondestructive means of preparing the sample must be used. For the determination of metallic elements, it is also sometimes unnecessary to destroy the molecular structure of the

sample, particularly with biological fluids. For example, several metals in serum or urine can be determined by atomic absorption spectroscopy by direct aspiration of the sample or a diluted sample into a flame. Constituents of solid materials such as soils can sometimes be extracted by an appropriate reagent. Thorough grinding, mixing, and refluxing are necessary to extract the analyte. Many trace metals can be extracted from soils with 1 *M* ammonium chloride or acetic acid solution. Some, such as selenium, can be distilled as the volatile chloride or bromide.

PROTEIN-FREE FILTRATES

Proteins in biological fluids interfere with many analyses and must be removed nondestructively. Several reagents will precipitate (coagulate) proteins. Trichloroacetic acid (TCA), tungstic acid (sodium tungstate plus sulfuric acid), and barium hydroxide plus zinc sulfate (a neutral mixture) are some of the common ones. A measured volume of sample (e.g., serum) is usually treated with a measured volume of reagent. Following precipitation of the protein (approximately 10 min), the sample is filtered through dry filter paper without washing, or else it is centrifuged. An aliquot of the **protein-free filtrate** (PFF) is then taken for analysis. Molecular weight selective centrifugal filtration can sometimes be used. Details for preparing specific types of protein-free filtrates are given in the text's website in Chapter 25 (under Collection and Preservation of Samples) as well as in experiments requiring them.

See Chapter 25 on the text's website for the preparation of protein-free filtrates.

LABORATORY TECHNIQUES FOR DRYING AND DISSOLVING

When a solid sample is to be dried in a weighing bottle, the cap is removed from the bottle and, to avoid spilling, both are placed in a beaker and covered with a ribbed watch glass. Some form of identification should be placed on the beaker.

The weighed sample may be dissolved in a beaker or Erlenmeyer flask. If there is any fizzing action, cover the vessel with a watch glass. After dissolution is complete, wash the walls of the vessel down with distilled water. Also wash the watch glass so the washings fall into the vessel. You may have to evaporate the solution to decrease the volume. This is best done by covering the beaker with a ribbed watch glass to allow space for evaporation. Low heat should be applied to prevent bumping; a steam bath or variable-temperature hot plate is satisfactory.

Use of a **Kjeldahl flask** for dissolution will avoid some of the difficulties of splattering or bumping. Kjeldahl flasks are also useful for performing digestions. They derive their name from their original use in digesting samples for Kjeldahl nitrogen analysis. They are well suited to all types of wet digestions of organic samples and acid dissolution of metals. Kjeldahl flasks come in assorted sizes from 10 to 800 mL. Some of these are shown in Figure 2.24. The sample and appropriate acids are placed in the round bottom of the flask and the flask is tilted while it is heated. In this way the acid can be boiled or refluxed with little danger of loss by "bumping." The flask may be heated with a flame or in special electrically heated Kjeldahl digestion racks, which heat several samples simultaneously.

Take care in drying or dissolving samples.

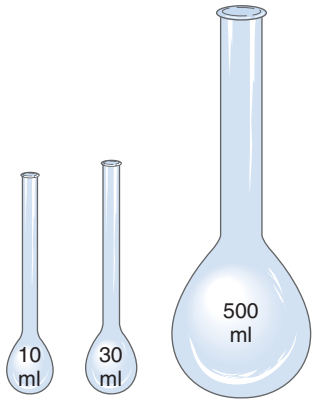


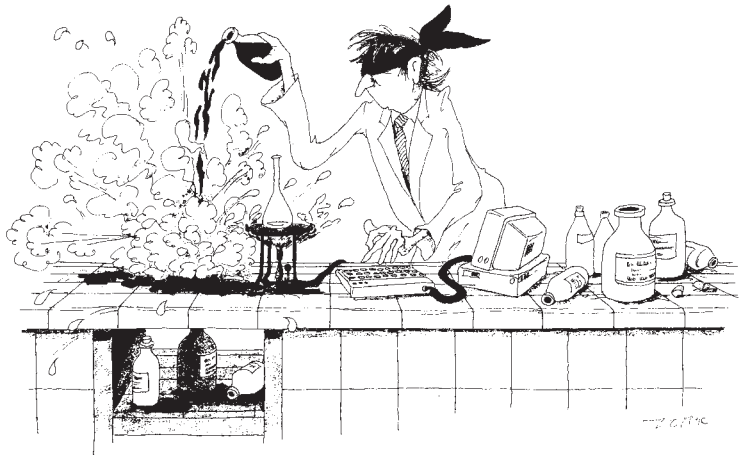
Fig. 2.24. Kjeldahl flasks.

2.11 Laboratory Safety

Before beginning any of the experiments, you must familiarize yourself with laboratory safety procedures. Appendix D on the text website discusses general safety rules. You should read this material before beginning experiments. Your instructor will provide you with specific guidelines and rules for operation in the laboratory and the disposal of

You ***must*** familiarize yourself with laboratory safety rules and procedures before conducting experiments! Read Appendix D and the material provided by your instructor. Get a free copy of Reference 31.

chemicals. For a more complete discussion of safety in the laboratory, you are referred to *Safety in Academic Chemistry Laboratories*, published by The American Chemical Society (Reference 31). This guide discusses personal protection and laboratory protocol, recommended laboratory techniques, chemical hazards, instructions on reading and understanding material safety data sheets (MSDSs), and safety equipment and emergency procedures. Rules are given for waste disposal, waste classification terminology, Occupational Safety and Health Administration (OSHA) laboratory standards for exposures to hazardous chemicals, and EPA requirements. The handling and treatment of inorganic and organic peroxides are discussed in detail, and an extensive list of incompatible chemicals is given, and maximum allowable container capacities for flammable and combustible liquids are listed. This resourceful booklet is recommended reading for students and instructors. It is available for free (one copy) from The American Chemical Society, Washington, DC (1-800-227-5558).



(Courtesy of Merck KGaA. Reproduced by permission.)

The Waste Management Manual for Laboratory Personnel, also published by The American Chemical Society, provides an overview of government regulations (Reference 32).

Professor's Favorite Example

Contributed by Professor Akos Vertes, George Washington University

The Shroud of Turin Dating — A Sampling Problem

Various means have been enlisted to ascertain the validity and age of the Shroud of Turin (http://en.wikipedia.org/wiki/Shroud_of_Turin). One such study was radiocarbon dating done in 1988. Samples were obtained to be given to three separate laboratories for independent analyses. Details are given in: http://www.shroud.com/nature.htm. The paper describes in detail how these important samples were obtained and different sample preparation procedures used by the different laboratories. Three control samples of other known ancient textiles were treated and analyzed in the same way. Check the paper to see the results!

Is the controversy concluded?

Questions

1. Describe the basic pieces of apparatus used for volumetric measurements. List whether each is designed to contain or to deliver the specified volume.
2. Describe the principle and operation of the analytical balance.
3. Why is a microbalance more sensitive than an analytical balance?
4. What does TD on glassware mean? TC?
5. Explain weighing by difference.
6. List the general rules for the use of the balance.
7. Describe the preparation of a standard HCl solution and a standard NaOH solution.
8. Describe the principles of dry ashing and wet digestion of organic and biological materials. List the advantages of each.
9. What are the two principal means of dissolving inorganic materials?
10. What is a PFF? How would you prepare it?
11. What set of conditions must be carefully avoided to use perchloric acid safely for digesting organic materials?
12. What is a gross sample? Sample? Analysis sample? Grab sample?
13. What happens when microwave energy heats samples?

Problems

GLASSWARE CALIBRATION/TEMPERATURE CORRECTIONS

14. You calibrate a 25-mL volumetric flask by filling to the mark with distilled water, equilibrated at 22°C. The dry stoppered flask weighs 27.278 g and the filled flask and stopper is 52.127 g. The balance uses stainless steel weights. What is the volume of the flask? What is it at the standard 20°C. Also insert the weight in air at 22°C into Table 2.4 (available on the textbook website), and compare the values obtained.
15. You calibrate a 25-mL pipet at 25°C using steel weights. The weight of the delivered volume of water is 24.971 g. What is the volume of the pipet at 25 and 20°C?
16. You calibrate a 50-mL buret in the winter time at 20°C, with the following corrections:

Buret Reading (mL)	Correction (mL)
10	+0.02
20	+0.03
30	0.00
40	−0.04
50	−0.02

You use the buret on a hot summer day at 30°C. What are the corrections then?

17. You prepare a standard solution at 21°C, and use it at 29°C. If the standardized concentration is 0.05129 *M*, what is it when you use the solution?

PROFESSOR'S FAVORITE PROBLEMS

Contributed by Professor Bin Wang, Marshall University

18. For an electronic analytical balance with 0.1 mg readability, what is the maximum mass that can be weighed (capacity)?
    (a) 500–1000 g; (b) 100–300 g; (c) 10–20 g; (d) several g or less
19. The densities of air, calibration weights, and salt are 0.0012 g/mL, 7.8 g/cm^3, and 2.16 g/mL, respectively. If the apparent mass of salt (i.e., NaCl) weighed in air is 15.914 g, what is its true mass?

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Chapter Five
STOICHIOMETRIC CALCULATIONS: THE WORKHORSE OF THE ANALYST

Learning Objectives

WHAT ARE SOME OF THE KEY THINGS WE WILL LEARN FROM THIS CHAPTER?

- How to calculate molarities and moles (key equations: 5.4, 5.5), p. 152
- How to express analytical results, p. 159
- How to calculate weight and percent analyted from molarities, volumes, and reaction ratios (key equations: 5.5, 5.17–5.20, 5.25), pp. 152, 169, 171
- Weight relationships for gravimetric analysis (key equation: 5.28), p. 181

Analytical chemistry deals with measurements of analytes in solids and concentrations in solution, from which we calculate masses. Thus, we prepare solutions of known concentrations that can be used to calibrate instruments or to titrate sample solutions. We calculate the mass of an analyte in a solution from its concentration and the volume. We calculate the mass of product expected from the mass of reactants. All of these calculations require a knowledge of **stoichiometry**, that is, the ratios in which chemicals react, from which we apply appropriate conversion factors to arrive at the desired calculated results.

Stoichiometry deals with the ratios in which chemicals react.

In this chapter we review the fundamental concepts of mass, moles, and equivalents; the ways in which analytical results may be expressed for solids and liquids; and the principles of volumetric analysis and how stoichiometric relationships are used in titrations to calculate the mass of analyte.

5.1 Review of the Fundamentals

Quantitative analysis is based on a few fundamental atomic and molecular concepts, which we review below. You have undoubtedly been introduced to these in your general chemistry course, but we briefly review them here since they are so fundamental to quantitative calculations.

THE BASICS: ATOMIC, MOLECULAR, AND FORMULA WEIGHTS

The atomic weight for any element is the weight of a specified number of atoms of that element, and that number is the same from one element to another. A gram-atomic weight of any element contains exactly the same number of atoms of that element

as there are carbon atoms in exactly 12 g of carbon 12. This number is Avogadro's number, 6.022×10^{23}, the number of atoms present in 1 g-at wt of any element.[1]

Since naturally occurring elements consist of mixtures of isotopes, the chemical atomic weights will be an average of the isotope weights of each element, taking into account their relative naturally occurring abundances. For example, bromine has two isotopes: ^{79}Br with atomic weight 78.981338 at a 50.69% relative abundance, and ^{81}Br with atomic weight 80.9162921 with a 49.31% relative abundance. These average to 79.904, the natural atomic weight we use in chemical calculations. Another measurement used by chemists is **molecular weight** (mw), defined as the sum of the atomic weights of the atoms that make up a compound. The term **formula weight** (fw) is a more accurate description for substances that don't exist as molecules but exist as ionic compounds (strong electrolytes—acids, bases, salts). The term **molar mass** is sometimes used in place of formula weight.

We will use formula weight (fw) to express grams per mole.

Theodore W. Richards, the first American Nobel Laureate in Chemistry, won his accolades to a large extent for his exact measurements. In particular, he is credited with the measurement of the exact atomic weight of chlorine, which he measured through the formation of AgCl.

WHAT IS A DALTON?

Biologists and biochemists sometimes use the unit **dalton** (Da) to report masses of large biomolecules and small biological entities such as chromosomes, ribosomes, viruses, and mitochondria, where the term *molecular weight* would be inappropriate. The mass of a single carbon-12 atom is equivalent to 12 daltons, and 1 dalton is therefore 1.661×10^{-24} g, the reciprocal of Avogadro's number. The number of daltons in a single molecule is numerically equivalent to the molecular weight (g/mol). Strictly speaking, it is not correct to use the dalton as a unit of molecular weight, and it should be reserved for the types of substances mentioned above. For example, the mass of an *Escherichia coli* bacterium cell is about 1×10^{-12} g, or 6×10^{11} daltons.

MOLES: THE BASIC UNIT FOR EQUATING THINGS

The chemist knows that atoms and molecules react in definite proportions. Unfortunately, he or she cannot conveniently count the number of atoms or molecules that participate in a reaction. But since the chemist has determined their relative masses, he or she can describe their reactions on the basis of the relative masses of atoms and molecules reacting, instead of the number of atoms and molecules reacting. For example, in the reaction

$$Ag^+ + Cl^- \rightarrow \underline{AgCl}$$

There are 6.022×10^{23} atoms in a mole of atoms.

we know that one silver ion will combine with one chloride ion. We know further, since the atomic weight of silver is 107.870 and the atomic weight of chlorine is 35.453, that 107.870 mass units of the silver will combine with 35.453 mass units of chlorine. To simplify calculations, chemists have developed the concept of the **mole**, which is

[1] There is a proposal to change the definition of Avogadro's number in redefining the kilogram to be an invariant unit. The kilogram is the only base unit in the International System of Units (SI) that is defined by a physical artifact rather than an unvarying physical property of nature, the others being the meter (length), second (time), ampere (electric current), kelvin (temperature), mole (amount of substance), and candela (light intensity). It is currently equal to the mass of a small cylinder of platinum-iridium alloy, known as the international prototype, that was ratified as the official kilogram in 1889, and is kept in a vault at the International Bureau of Weights & Measures near Paris. But it has inexplicably lost about 50 μg over time compared with copies. There are two proposals for an invariant definition of the kilogram, one based on Plank's constant and one based on Avogadro's constant, either of which would marginally change the value or definition of Avogadro's number and hence the definition of the mole. But the change would be insignificant for the units we use. Details of the proposals may be found in "Avogadro's Number Is Up . . . ," P. J. Karol, *Chem. & Eng. News*, March 17 (2008) 48, "Redefining the Kilogram," S. K. Ritter, *Chem. & Eng. News*, May 26 (2008) 43, and "Redefining the Kilogram and Mole," P. F. Rusch, *Chem. & Eng. News*, May 30 (2011) 58: http://pubs.acs.org/isubscribe/journals/cen/89/i22/html/8922acscomment.html.

Avogadro's number (6.022×10^{23}) of atoms, molecules, ions, or other species. Numerically, it is the atomic, molecular, or formula weight of a substance expressed in **grams**.[2]

Now, since a mole of any substance contains the same number of atoms or molecules as a mole of any other substance, atoms will react in the same mole ratio as their atom ratio in the reaction. In the above example, one silver ion reacts with one chloride ion, and so each mole of silver ion will react with one mole of chloride ion. (Each 107.87 g of silver will react with 35.453 g of chlorine.)

Example 5.1

Calculate the weight of one mole of $CaSO_4 \cdot 7H_2O$.

Solution

One mole is the formula weight expressed in grams. The formula weight is

Ca	40.08
S	32.06
11 O	176.00
14 H	14.11
	262.25 g/mol

The number of moles of a substance is calculated from

$$\text{Moles} = \frac{\text{grams}}{\text{formula weight (g/mol)}} \tag{5.1}$$

where formula weight represents the atomic or molecular weight of the substance. Thus,

$$\text{Moles } Na_2SO_4 = \frac{\text{g}}{\text{fw}} = \frac{\text{g}}{142.04 \text{ g/mol}}$$

$$\text{Moles } Ag^+ = \frac{\text{g}}{\text{fw}} = \frac{\text{g}}{107.870 \text{ g/mol}}$$

Since many experiments deal with very small quantities, a more convenient form of measurement is the **millimole**. The formula for calculating millimoles is

g/mol = mg/mmol = formula weight; g/L = mg/mL; mol/L = mmol/mL = molarity.

$$\text{Millimoles} = \frac{\text{milligrams}}{\text{formula weight (mg/mmol)}} \tag{5.2}$$

Just as we can calculate the number of moles from the grams of material, we can likewise calculate the grams of material from the number of moles:

$$\text{g } Na_2SO_4 = \text{moles} \times \text{fw} = \text{moles} \times 142.04 \text{ g/mol}$$

$$\text{g Ag} = \text{moles} \times \text{fw} = \text{moles} \times 107.870 \text{ g/mol}$$

Again, we usually work with millimole quantities, so

$$\text{Milligrams} = \text{millimoles} \times \text{formula weight (mg/mmol)} \tag{5.3}$$

[2]Actually, the term *gram-atomic weight* is more correct for atoms, *gram-formula weight* for ionic substances, and *gram-molecular weight* for molecules, but we will use *moles* in a broad sense to include all substances. In place of gram-formula weight we will simply use *formula weight* (fw).

Note that g/mol is the same as mg/mmol, g/L the same as mg/mL, and mol/L the same as mmol/mL.

Example 5.2

Calculate the number of moles in 500 mg Na_2WO_4 (sodium tungstate).

Solution

$$\frac{500 \text{ mg}}{293.8 \text{ mg/mmol}} \times 0.001 \text{ mol/mmol} = 0.00170 \text{ mol}$$

Example 5.3

What is the weight, in milligrams, of 0.250 mmol Fe_2O_3 (ferric oxide)?

Solution

$$0.250 \text{ mmol} \times 159.7 \text{ mg/mmol} = 39.9 \text{ mg}$$

5.2 How Do We Express Concentrations of Solutions?

Chemists express solution concentrations in a number of ways. Some are more useful than others in quantitative calculations. We will review here the common concentration units that chemists use. Their use in quantitative volumetric calculations is treated in more detail below.

MOLARITY—THE MOST WIDELY USED

The mole concept is useful in expressing concentrations of solutions, especially in analytical chemistry, where we need to know the volume ratios in which solutions of different materials will react. A one-**molar** solution is defined as one that contains one mole of substance in each liter of a solution. It is prepared by dissolving one mole of the substance in the solvent and diluting to a final volume of one liter in a volumetric flask; or a fraction or multiple of the mole may be dissolved and diluted to the corresponding fraction or multiple of a liter (e.g., 0.01 mol in 10 mL). More generally, the **molarity** of a solution is expressed as moles per liter or as millimoles per milliliter. Molar is abbreviated as *M*, and we talk of the *molarity* of a solution when we speak of its concentration. A one-molar solution of silver nitrate and a one-molar solution of sodium chloride will react on an equal-volume basis, since they react in a 1:1 ratio: $Ag^+ + Cl^- \rightarrow \underline{AgCl}$. We can be more general and calculate the moles of substance in any volume of the solution.

$$\boxed{\begin{aligned}\text{Moles} &= (\text{moles/liter}) \times \text{liters} \\ &= \text{molarity} \times \text{liters}\end{aligned}} \qquad (5.4)$$

We often work with millimoles in analytical chemistry. Remember this formula!

The liter is an impractical unit for the relatively small quantities encountered in titrations, and we normally work with milliliters. This is what your buret reads. So,

$$\boxed{\begin{aligned}\text{Millimoles} &= \text{molarity} \times \text{milliliters} \\ (\text{or mmol} &= M \times \text{mL})\end{aligned}} \qquad (5.5)$$

Example 5.4

A solution is prepared by dissolving 1.26 g $AgNO_3$ in a 250-mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles $AgNO_3$ were dissolved?

Solution

$$M = \frac{1.26 \text{ g}/169.9 \text{ g/mol}}{0.250 \text{ L}} = 0.0297 \text{ mol/L (or } 0.0297 \text{ mmol/mL)}$$

Then,

$$\text{Millimoles} = (0.0297 \text{ mmol/mL})(250 \text{ mL}) = 7.42 \text{ mmol}$$

■

Always remember that *the units in a calculation must combine to give the proper units in the answer*. Thus, in this example, grams cancel to leave the proper unit, moles/liter, or molarity. Using units in the calculation to check if the final units are proper is called **dimensional analysis**. Accurate use of dimensional analysis is essential to properly setting up computations.

Always use dimensional analysis to set up a calculation properly. Don't just memorize a formula.

Example 5.5

How many grams per milliliter of NaCl are contained in a 0.250 *M* solution?

Solution

$$0.250 \text{ mol/L} = 0.250 \text{ mmol/mL}$$

$$0.250 \text{ mmol/mL} \times 58.4 \text{ mg/mmol} \times 0.001 \text{ g/mg} = 0.0146 \text{ g/mL}$$

■

Example 5.6

How many grams Na_2SO_4 should be weighed out to prepare 500 mL of a 0.100 *M* solution?

Solution

$$500 \text{ mL} \times 0.100 \text{ mmol/mL} = 50.0 \text{ mmol}$$

$$50.0 \text{ mmol} \times 142 \text{ mg/mmol} \times 0.001 \text{ g/mg} = 7.10 \text{ g}$$

■

Example 5.7

Calculate the concentration of potassium ion in grams per liter after mixing 100 mL of 0.250 *M* KCl and 200 mL of 0.100 *M* K_2SO_4.

Solution

$$\begin{aligned}\text{mmol } K^+ &= \text{mmol KCl} + 2 \times \text{mmol } K_2SO_4 \\ &= 100 \text{ mL} \times 0.250 \text{ mmol/mL} \\ &\quad +2 \times 200 \text{ mL} \times 0.100 \text{ mmol/mL}\end{aligned}$$

$$= 65.0 \text{ mmol in } 300 \text{ mL}$$

$$\frac{65.0 \text{ mmol} \times 39.1 \text{ mg/mmol} \times 0.001 \text{ g/mg} \times 1000 \text{ mL/L}}{300 \text{ mL}} = 8.47 \text{ g/L}$$

NORMALITY

The equivalent weight (or the number of reacting units) depends on the chemical reaction. It may vary most often in redox reactions, when different products are obtained.

Although molarity is widely used in chemistry, some chemists use a unit of concentration in quantitative analysis called **normality** (N). A one-**normal** solution contains one equivalent per liter. An **equivalent** represents the mass of material providing Avogadro's *number of reacting units*. A reacting unit is a *proton* or an *electron*. The number of equivalents is given by the number of moles multiplied by the number of reacting units per molecule or atom; the **equivalent weight** is the formula weight divided by the number of reacting units. Table 5.1 lists the reacting units used for different types of reactions. For acids and bases, the number of reacting units is based on the number of protons (i.e., hydrogen ions) an acid will furnish or a base will react with. For oxidation–reduction reactions it is based on the number of electrons an oxidizing or reducing agent will take on or supply. Thus, for example, sulfuric acid, H_2SO_4, has two reacting units of protons; that is, there are two equivalents of protons in each mole. Therefore,

$$\text{Equivalent weight} = \frac{98.08 \text{ g/mol}}{2 \text{ eq/mol}} = 49.04 \text{ g/eq}$$

Equivalent weight g/eq = mg/meq; eq/L = meq/mL = normality.

So, the normality of a sulfuric acid solution is twice its molarity, that is, $N =$ (g/eq wt)/L. The number of equivalents is given by

$$\text{Number of equivalents (eq)} = \frac{\text{wt (g)}}{\text{eq wt (g/eq)}} = \text{normality (eq/L)} \times \text{volume (L)} \tag{5.6}$$

Just as we ordinarilly use millimoles (mmol) instead of moles, we typically use milliequivalents (meq) instead of equivalents

$$\text{meq} = \frac{\text{mg}}{\text{eq wt (mg/meq)}} = \text{normality (meq/mL)} \times \text{mL} \tag{5.7}$$

In clinical chemistry, equivalents are frequently defined in terms of the number of charges on an ion rather than on the number of reacting units. Thus, for example, the equivalent weight of Ca^{2+} is one-half its atomic weight, and the number of equivalents is twice the number of moles. This use is convenient for electroneutrality calculations. We discuss equivalents in more detail in Section 5.3.

There is no ambiguity in a molar concentration. Instead of normality, eq/L is often presently used.

While normality has been used extensively in the past and is found in the scientific literature, it is not as widely used today as molarity. We discuss normality in

Table 5.1
Reacting Units in Different Reactions

Reaction Type	Reacting Unit
Acid–base	H^+
Oxidation–reduction	Electron

the book's **website** for those who do make use of it. We will use moles and molarity throughout most of this text so there will be no ambiguity about what the concentration represents. Molarity calculations require a knowledge of the stoichiometry of reactions, that is, the ratio in which substances react. The journal *Analytical Chemistry* does not allow normality in articles it publishes, but other publications do. The unit eq/L is the same as normality and is accepted by most publications.

FORMALITY—INSTEAD OF MOLARITY

Chemists sometimes use the term **formality** for solutions of ionic salts that do not exist as molecules in the solid or in solution. The concentration is given as **formal** (*F*). Operationally, formality is identical to molarity: The former is sometimes reserved for describing makeup concentrations of solutions (i.e., total analytical concentration), and the latter for equilibrium concentrations. For convenience, we shall use molarity exclusively, a common practice.

Formality is numerically the same as molarity.

MOLALITY—THE TEMPERATURE-INDEPENDENT CONCENTRATION

In addition to molarity and normality, another useful concentration unit is **molality**, *m*. A one-**molal** solution contains one mole per 1000 g of **solvent**. The molal concentration is convenient in physicochemical measurements of the colligative properties of substances, such as freezing point depression, vapor pressure lowering, and osmotic pressure because colligative properties depend solely on the number of solute particles present in solution per mole of solvent. Molal concentrations are not temperature dependent as molar and normal concentrations are (since the solution volume in molar and normal concentrations is temperature dependent).

Molality does not change with temperature.

DENSITY CALCULATIONS—HOW DO WE CONVERT TO MOLARITY?

The concentrations of many fairly concentrated commercial acids and bases are usually given in terms of percent by weight. It is frequently necessary to prepare solutions of a given approximate molarity from these substances. In order to do so, we must know the density in order to calculate the molarity. **Density** is the weight per unit volume at the specified temperature, usually g/mL or g/cm^3 at 20°C. (One milliliter is the volume occupied by 1 cm^3.)

Sometimes substances list **specific gravity** rather than density. Specific gravity is defined as the ratio of the mass of a body (e.g., a solution), usually at 20°C, to the mass of an equal volume of water at 4°C (or sometimes 20°C). That is, specific gravity is the *ratio of the densities of the two substances;* it is a dimensionless quantity. Since the density of water at 4°C is 1.00000 g/mL, density and specific gravity are equal when referred to water at 4°C. But normally specific gravity is referred to water at 20°C; density is equal to specific gravity × 0.99821 (the density of water is 0.99821 g/mL at 20°C).

$$\text{Density of solution at } 20^\circ\text{C} = \text{Specific gravity of solution} \times 0.99821 \text{ g/mL}$$

Note that the density of the solution at a temperature other than 20°C cannot be precisely computed from the specific gravity specified for 20°C without knowing the volumetric expansion behavior of the solution, which is not the same as that of water.

Example 5.8

How many milliliters of concentrated sulfuric acid, 94.0% (g/100 g solution), density 1.831 g/cm^3, are required to prepare 1 liter of a 0.100 *M* solution?

Solution

Consider 1 cm^3 = 1 mL. The concentrated acid contains 0.940 g H_2SO_4 per gram of solution, and the solution weighs 1.831 g/mL. The product of these two numbers, then, gives the gram H_2SO_4 per milliliter of solution:

$$M = \frac{(0.940 \text{ g } H_2SO_4/\text{g solution})(1.831 \text{ g/mL})}{98.1 \text{ g/mol}} \times 1000 \text{ mL/L}$$

$$= 17.5 \text{ mol } H_2SO_4/\text{L solution}$$

We must dilute this solution to prepare 1 liter of a 0.100 *M* solution. The same number of millimoles of H_2SO_4 must be taken as will be contained in the final solution. Since mmol = *M* × mL and mmol dilute acid = mmol concentrated acid,

$$0.100\ M \times 1000 \text{ mL} = 17.5\ M \times \text{mL}$$

$$x = 5.71 \text{ mL concentrated acid to be diluted to 1000 mL}$$

Mass is conserved:

$$M_1V_1 = M_2V_2$$

If a solution of molarity M_1 and volume V_1 is diluted to V_2, the molarity M_2 will obey this relationship. The general equation

$$C_1V_1 = C_2V_2$$

will hold as long as C_1 and C_2 are in the same units, regardless of the specific unit.
Memorize this equation.

See Sections 5.5 and the text website for volumetric calculations using molarity (or normality).

Molarity and normality are the most useful concentrations in quantitative analysis. Calculations using these for volumetric analysis are discussed in more detail below.

ANALYTICAL AND EQUILIBRIUM CONCENTRATIONS—THEY ARE NOT THE SAME

Analytical chemists prepare solutions of known analytical concentrations, but the dissolved substances may partially or totally dissociate to give equilibrium concentrations of different species. Acetic acid, for example, is a weak acid that dissociates a few percent depending on the concentration,

$$HOAc \rightleftharpoons H^+ + OAc^-$$

to give equilibrium amounts of the proton and the acetate ion. The more dilute the solutions, the greater the dissociation. We often use these equilibrium concentrations in calculations involving equilibrium constants (Chapter 6), usually using molarity concentrations. The **analytical molarity** is given by the notation C_X, while **equilibrium molarity** is given by [X]. A solution of 1 *M* $CaCl_2$ (analytical molarity) is completely ionized into constituent ions in solution and gives at equilibrium, 0 *M* $CaCl_2$, 1 *M* Ca^{2+}, and 2 *M* Cl^- (equilibrium molarities). Hence, we say the solution is 1 *M* in Ca^{2+} and 2 *M* in Cl^-.

The analytical concentration represents the concentration of total dissolved substance, i.e., the sum of all species of the substance in solution = C_X.

An equilibrium concentration is that of a given dissolved form of the substance = [X].

DILUTIONS—PREPARING THE RIGHT CONCENTRATION

We often must prepare dilute solutions from more concentrated stock solutions. For example, we may prepare a dilute HCl solution from concentrated HCl to be used for titrations (following standardization). Or, we may have a stock standard solution from which we wish to prepare a series of more dilute standards. The millimoles of stock solution taken for dilution will be identical to the millimoles in the final diluted solution, remember, $C_1V_1 = C_2V_2$.

The millimoles taken for dilution will be the same as the millimoles in the diluted solution, i.e., $M_{stock} \times mL_{stock} = M_{diluted} \times mL_{diluted}$

Example 5.9

You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 *M* solution of $KMnO_4$ and a series of 100-mL volumetric flasks. What volumes of the stock solution will you have to pipet into the flasks to prepare standards of 1.00, 2.00, 5.00, and 10.0×10^{-3} *M* $KMnO_4$ solutions?

Solution

x mL of the stock solution of 0.100 *M* concentration will be diluted to 100 mL of some specified concentration, say C_2. Remembering

$$C_1V_1 = C_2V_2$$

Let us do this for the first concentration, $C_2 = 1.00 \times 10^{-3}$. Here V_1 is *x*, $C_1 = 0.100\ M$ and $V_2 = 100$ mL

$$0.100\ M \times x\ \text{mL} = 1.00 \times 10^{-3}\ M \times 100\ \text{mL}$$

$$x = 1.00\ \text{mL}$$

Similarly, for the other solutions we will need 2.00, 5.00, and 10.0 mL of the stock solution, which will be diluted to 100 mL. ■

Example 5.10

You are analyzing for the manganese content in an ore sample by dissolving it and oxidizing the manganese to permanganate for spectrophotometric measurement. The ore contains about 5% Mn. A 5-g sample is dissolved and diluted to 100 mL, following the oxidation step. By how much must the solution be diluted to be in the range of the calibration curve prepared in Example 5.9, that is, about 3×10^{-3} *M* permanganate?

Solution

The solution contains 0.05×5-g sample = 0.25 g Mn. This corresponds to [0.25 g/(55 g Mn/mol)]/100 mL = 4.5×10^{-3} mol MnO_4^-/100 mL = $4.5 \times 10^{-2}\ M$. For $3 \times 10^{-3}\ M$, we must dilute it by $4.5 \times 10^{-2}/3 \times 10^{-3} = 15$-fold. If we have a 100-mL volumetric flask, using $C_1V_1 = C_2V_2$,

$$4.5 \times 10^{-2} M \times x\ \text{mL} = 3 \times 10^{-3} M \times 100\ \text{mL}$$

$$x = 6.7\ \text{mL needed for dilution to 100 mL}$$

Since we need to pipet accurately, we could probably take an accurate 10-mL aliquot, which would give about $4.5 \times 10^{-3} M$ permanganate for measurement. ■

MORE DILUTION CALCULATIONS

We can use the relationship $C_1V_1 = C_2V_2$ to calculate the dilution required to prepare a certain concentration of a solution from a more concentrated solution. For example, if we wish to prepare 500 mL of a 0.100 *M* solution by diluting a more concentrated solution, we can calculate it from this relationship.

Remember, the millimoles before and after dilution are the same. See Section 5.5 (and the text's website) for volumetric calculations using molarity (and normality).

Example 5.11

You wish to prepare 500 mL of a 0.100 *M* $K_2Cr_2O_7$ solution from a 0.250 *M* solution. What volume of the 0.250 *M* solution must be diluted to 500 mL?

Solution

$$M_{\text{final}} \times \text{mL}_{\text{final}} = M_{\text{original}} \times \text{mL}_{\text{original}}$$

$$0.100 \text{ mmol/mL} \times 500 \text{ mL} = 0.250 \text{ mmol/mL} \times \text{mL}_{\text{original}}$$

$$\text{mL}_{\text{original}} = 200 \text{ mL}$$

Example 5.12

What volume of 0.40 *M* $Ba(OH)_2$ must be added to 50 mL of 0.30 *M* NaOH to give a solution 0.50 *M* in OH^-?

Solution

Volumes of dilute aqueous solutions can be assumed to be additive, i.e., if x mL of $Ba(OH)_2$ is added to 50 mL NaOH, the total volume is going to be $50 + x$ mL. Wex can use a modified form of $C_1V_1 = C_2V_2$ where all the initial solution components are added in this manner and these sum up to the final solution components:

$$\Sigma C_{\text{in}} V_{\text{in}} = C_{\text{fin}} V_{\text{fin}}$$

In the present case, $M_{\text{NaOH}} V_{\text{NaOH}} + 2 \times M_{\text{Ba(OH)}_2} V_{\text{Ba(OH)}_2} = M_{\text{OH}^-} \times V_{\text{fin}}$, note that 1 *M* $Ba(OH)_2$ is 2 *M* in OH^-. Thus $0.30\,M \times 50 \text{ mL} + 2 \times 0.40\,M \times x\text{mL} = 0.50\,M \times (50 + x)$ mL.

Solving, $x = 33$ mL.

Alternatively,

Let x = mL $Ba(OH)_2$. The final volume is $(50 + x)$ mL.

$$\text{mmol } OH^- = \text{mmol NaOH} + 2 \times \text{mmol } Ba(OH)_2$$

$$0.50\,M \times (50 + x)\text{mL} = 0.30\,M \text{ NaOH} \times 50 \text{ mL} + 2 \times 0.40\,M \text{ } Ba(OH)_2 \times x \text{ mL}$$

$$x = 33 \text{ mL } Ba(OH)_2$$

Often, the analyst is confronted with serial dilutions of a sample or standard solution. Again, obtaining the final concentration simply requires keeping track of the number of millimoles and the volumes.

Example 5.13

You are to determine the concentration of iron in a sample by spectrophotometry by reacting Fe^{2+} with 1,10-phenanthroline to form an orange-colored complex. This requires preparation of a series of standards against which to compare absorbances or color intensities (i.e., to prepare a calibration curve). A stock standard solution of $1.000 \times 10^{-3} M$ iron is prepared from ferrous ammonium sulfate. Working standards A and B are prepared by adding with pipets 2.000 and 1.000 mL, respectively, of this solution to 100-mL volumetric flasks and diluting to volume. Working standards C, D, and E are prepared by adding 20.00, 10.00, and 5.000 mL of working standard A to 100-mL volumetric flasks and diluting to volume. What are the concentrations of the prepared working solutions?

Solution

Solution A: $M_{stock} \times mL_{stock} = M_A \times mL_A$

$(1.000 \times 10^{-3}M)(2.000\ mL) = M_A \times 100.0\ mL$

$M_A = 2.000 \times 10^{-5}M$

Solution B: $(1.000 \times 10^{-3}M)(1.000\ mL) = M_B \times 100.0\ mL$

$M_B = 1.000 \times 10^{-5}M$

Solution C: $M_A \times mL_A = M_C \times mL_C$

$(2.000 \times 10^{-5}M)(20.00\ mL) = M_C \times 100.0\ mL$

$M_C = 4.000 \times 10^{-6}M$

Solution D: $(2.000 \times 10^{-5}M)(10.00\ mL) = M_D \times 100.0\ mL$

$M_D = 2.000 \times 10^{-6}M$

Solution E: $(2.000 \times 10^{-5}M)(5.000\ mL) = M_E \times 100.0\ mL$

$M_E = 1.000 \times 10^{-6}M$ ■

The solute + solvent method of dilution should not be used for quantitative dilutions.

The above calculations apply to all types of reactions, including acid–base, redox, precipitation, and complexometric reactions. The primary requirement before making calculations is to know the ratio in which the substances react, that is, start with a balanced reaction.

Solution preparation procedures in the chemical literature often call for the dilution of concentrated stock solutions, and authors may use different terms. For example, a procedure may call for 1 + 9 dilution (solute + solvent) of sulfuric acid. In some cases, a 1:10 dilution (original volume:final volume) may be indicated. The first procedure calls for diluting a concentrated solution to 1/10th of its original concentration by adding 1 part to 9 parts of solvent; the second procedure by diluting to 10 times the original volume. The first procedure does not give an exact 10-fold dilution because volumes are not completely additive, except when all components are dilute aqueous solutions, whereas the second procedure does (e.g., adding 10 mL with a pipet to a 100-mL volumetric flask and diluting to volume—fill the flask partially with water before adding sulfuric acid!). The solute + solvent approach is fine for reagents whose concentrations need not be known accurately.

Added volumes are not completely additive, especially mixed solvents. Water and ethanol always have negative excess volumes when mixed, indicating the partial molar volume of each component is less when mixed than its molar volume when pure. That is, volume of pure alcohol plus volume of water does not equal the volume of vodka!

5.3 Expressions of Analytical Results—So Many Ways

We can report the results of analysis in many ways, and the beginning analytical chemist should be familiar with some of the common expressions and units of measure employed. Results will nearly always be reported as *concentration*, on either a weight or a volume basis: the quantity of analyte per unit weight or per volume of sample. The units used for the analyte will vary.

We shall first review the common units of weight and volume in the metric system and then describe methods of expressing results. The gram (g) is the basic unit of mass and is the unit employed most often in macro analyses. For small samples or trace constituents, chemists use smaller units. The milligram (mg) is 10^{-3} g, the microgram (μg) is 10^{-6} g, and the nanogram (ng) is 10^{-9} g. The basic unit of volume is the liter (L). The milliliter (mL) is 10^{-3} L and is used commonly in volumetric analysis. The microliter (μL) is 10^{-6} L (10^{-3} mL), and the nanoliter (nL) is 10^{-9} L (10^{-6} mL). (Prefixes for even smaller quantities include pico for 10^{-12} and femto for 10^{-15}.)

Y = yotta = 10^{24}
Z = zetta = 10^{21}
E = exa = 10^{18}
P = peta = 10^{15}
T = tera = 10^{12}
G = giga = 10^{9}
M = mega = 10^{6}
k = kilo = 10^{3}
d = deci = 10^{-1}
c = centi = 10^{-2}
m = milli = 10^{-3}
μ = micro = 10^{-6}
n = nano = 10^{-9}
p = pico = 10^{-12}
f = femto = 10^{-15}
a = atto = 10^{-18}
z = zepto = 10^{-21}
y = yocto = 10^{-24}

SOLID SAMPLES

Mass and weight are really different. See Chapter 2. We deal with masses but will use mass and weight interchangeably.

Calculations for solid samples are based on weight.[3] The most common way of expressing the results of macro determinations is to give the weight of analyte as a **percent** of the weight of sample (weight/weight basis). The weight units of analyte and sample are the same. For example, a limestone sample weighing 1.267 g and containing 0.3684 g iron would contain

$$\frac{0.3684\ \text{g}}{1.267\ \text{g}} \times 100\% = 29.08\%\ \text{Fe}$$

The general formula for calculating percent on a weight/weight basis, which is the same as parts per hundred, then is

$$\%(\text{wt/wt}) = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^2\ (\%/\text{g solute/g sample}) \tag{5.8}$$

It is important to note that in such calculations, grams of solute do *not* cancel with grams of sample solution; the fraction represents grams of solute per gram of sample. Multiplication of the above by 10^2 converts to grams of solute per 100 g of sample. Since the conversion factors for converting weight of solute and weight of sample (weights expressed in any units) to grams of solute and grams of sample are always the same, the conversion factors will always cancel. Thus, we can use any weight in the definition.

1 ppt (thousand) = 1000 ppm = 1,000,000 ppb; 1 ppm = 1000 ppb = 1,000,000 ppt (trillion). Usually ppt refers to parts per trillion, but in some cases it could be used as parts per thousand. Take note of the units when you see this!

Trace concentrations are usually given in smaller units, such as **parts per thousand** (ppt, ‰), **parts per million** (ppm), or **parts per billion** (ppb). These are calculated in a manner similar to parts per hundred (%):

$$\text{ppt (wt/wt)} = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^3\ (\text{ppt/g solute/g sample}) \tag{5.9}$$

$$\text{ppm (wt/wt)} = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^6\ (\text{ppm/g solute/g sample}) \tag{5.10}$$

$$\text{ppb (wt/wt)} = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^9\ (\text{ppb/g solute/g sample}) \tag{5.11}$$

ppt = mg/g = g/kg

ppm = μg/g = mg/kg

ppb = ng/g = μg/kg

You can use any weight units in your calculations so long as both analyte and sample weights are in the same units. **Parts per trillion** (parts per 10^{12} parts) is also abbreviated ppt, so be careful to define which one you mean. Some authors like to use ppth to denote parts per thousand and pptr to denote parts per trillion. In the above example, we have 29.08 parts per hundred of iron in the sample, or 290.8 parts per thousand and 290,800 parts per million (290,800 g of iron per 1 million grams of sample, 290,800 lb of iron per 1 million pounds of sample, etc.). Working backward, 1 ppm corresponds to 0.0001 part per hundred, or 10^{-4}%. Table 5.2 summarizes the concentration relationships for ppm and ppb. Note that ppm is simply mg/kg or μg/g and that ppb is μg/kg, or ng/g.

Trace gas concentrations are also expressed in ppb, ppm, and so forth. In this case the ratio refers not to mass ratios, but to volume ratios (which for gases is the same as mole ratios). Thus, present atmospheric CO_2 concentration of 390 ppm means that each liter of air (this is a million microliters) contains 390 microliters of CO_2.

[3] They are really based on mass, but the term *weight* is commonly used. See Chapter 2 for a description and determination of mass and weight.

Table 5.2

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	μL/L
(1 ppm = 10^{-4}%)		μg/g	μg/mL	nL/mL
Parts per billion	ppb	μg/kg	μg/L	nL/L
(1 ppb = 10^{-7}% = 10^{-3} ppm)		ng/g	ng/mL	pL/mL[a]
Milligram percent	mg%	mg/100 g	mg/100 mL	

[a]pL = picoliter = 10^{-12} L.

Sometimes for this reason, these concentrations are written as ppmv or ppbv, and so on, indicating "by volume".

Example 5.14

A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 μg zinc. What is the concentration of zinc in the plant in ppm? In ppb?

Solution

$$\frac{3.6\ \mu g}{2.6\ g} = 1.4\ \mu g/g \equiv 1.4\ ppm$$

$$\frac{3.6 \times 10^3\ ng}{2.6\ g} = 1.4 \times 10^3\ ng/g \equiv 1400\ ppb$$

One ppm is equal to 1000 ppb. One ppb is equal to 10^{-7}%. ■

Clinical chemists sometimes prefer to use the unit **milligram percent** (mg%) rather than ppm for small concentrations. This is defined as milligrams of analyte per 100 g of sample. The sample in Example 5.14 would then contain (3.6×10^{-3} mg/2.6 g) × 100 mg% = 0.14 mg% zinc.

Example 5.15 Concentrations of Gases and Particles in Air

The current National Ambient Air Quality Standards for the seven criteria pollutants listed by the U.S. Environmental Protection Agency is listed below from http://www.epa.gov/air/criteria.html. Other than lead and particulate matter, all others are gases. For particulate matter, wt/vol (μg/m^3) units are used; m^3 (equal to 1000 L) rather than μg/L. The gas concentrations are expressed by ppm(v) or ppb(v). Concentrations of CO are also given in mg/m^3 as CO largely comes from automotive exhaust and mass of CO emitted per vehicle-mile driven is often of interest.

(a) Show how 35 ppm CO is 40 mg/m^3.

(b) What is 75 ppb SO_2 at 25°C in μg/m^3?

National Ambient Air Quality Standards

Pollutant	Primary Standards		Secondary Standards	
	Level	Averaging Time	Level	Averaging Time
Carbon Monoxide	9 ppm (10 mg/m^3)	8-hour (1)	None	
	35 ppm (40 mg/m^3)	1-hour (1)	None	
Lead	0.15 μg/m^3 (2)	Rolling 3-Month Average	Same as Primary	
	1.5 μg/m^3	Quarterly Average	Same as Primary	
Nitrogen Dioxide	53 ppb (3)	Annual (Arithmetic Average)	Same as Primary	
	100 ppb	1-hour (4)	None	
Particulate Matter (PM_{10})	150 μg/m^3	24-hour (5)	Same as Primary	
Particulate Matter ($PM_{2.5}$)	15.0 μg/m^3	Annual (6) (Arithmetic Average)	Same as Primary	
	35 μg/m^3	24-hour (7)	Same as Primary	
Ozone	0.075 ppm (2008 std)	8-hour (8)	Same as Primary	
	0.08 ppm (1997 std)	8-hour (9)	Same as Primary	
	0.12 ppm	1-hour (10)	Same as Primary	
Sulfur Dioxide	0.03 ppm	Annual (Arithmetic Average)	0.5 ppm	3-hour (1)
	0.14 ppm	24-hour (1)	None	
	75 ppb (11)	1-hour	None	

Solution

Because gas volumes change as a function of temperature and pressure, we must refer to some temperature and pressure. When this is not specified, we assume a temperature of 25°C and a pressure of 1 atm. The ideal gas laws ($PV = RT$, where R is the universal gas constant, 0.0821 L-atm/(mole K)) dictate that the volume of 1 mole of any gas at 1 atm pressure and 25°C (298.15 K) is 24.5 L (at 0 °C, this is 22.4 L).

(a) 35 ppm is 35 μmol CO per 1 mole air. Since FW of CO is 28, we can write this as 35 μmole × 28 μg/μmole = 980 μg CO in 24.5 L air.

$$\frac{980\ \mu g}{24.5\ L} \times \frac{1\ mg}{1000\ \mu g} \times \frac{1000\ L}{1\ m^3} = 40\ mg/m^3$$

(b) 75 ppb SO_2 is 75 nmol SO_2 in 24.5 L air. The FW of SO_2 is 64, so

$$\frac{75\ nmol}{24.5\ L} \times \frac{1\ \mu mol}{1000\ nmol} \times \frac{64\ \mu g}{\mu mol} \times \frac{1000\ L}{1\ m^3} = 19_6\ \mu g/m^3;\ \text{round to } 0.20\ mg/m^3.$$

■

LIQUID SAMPLES

A deciliter is 0.1 L or 100 mL.

You can report results for liquid samples on a weight/weight basis, as above, or they may be reported on a **weight/volume basis**. The latter is more common, at least in the clinical laboratory. The calculations are similar to those above. Percent on a weight/volume basis is equal to grams of analyte per 100 mL of sample, while mg% is equal to milligrams of analyte per 100 mL of sample. This latter unit is often used by clinical chemists for biological fluids, and their accepted terminology is *milligrams per deciliter (mg/dL)* to distinguish from mg% on a weight/weight basis. Whenever a concentration is expressed as a percentage, it should be clearly specified whether this is wt/vol or wt/wt. In all but dilute aqueous solutions, this distinction is important. In dilute aqueous solutions, wt/vol and wt/wt ratios are numerically the same because the density of water is unity (1 mL = 1 g) for all practical purposes. Parts per million, parts per billion, and parts per trillion can also be expressed on a weight/volume basis; ppm is calculated from mg/L or μg/mL; ppb is calculated from μg/L or ng/mL;

and ppt is calculated from pg/mL or ng/L. Alternatively, the following fundamental calculations may be used:

$$\%(\text{wt/vol}) = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^2 \ (\%/\text{g solute/mL sample}) \quad (5.12)$$

$$\text{ppm (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^6 \ (\text{ppm/g solute/mL sample}) \quad (5.13)$$

$$\text{ppb (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^9 \ (\text{ppb/g solute/mL sample}) \quad (5.14)$$

$$\text{ppt (wt/vol)} = \left[\frac{\text{wt solute (g)}}{\text{vol sample (mL)}}\right] \times 10^{12} \ (\text{ppt/g solute/mL sample}) \quad (5.15)$$

In dilute aqueous solution

ppm = μg/mL = mg/L

ppb = ng/mL = μg/L

ppt = pg/mL = ng/L

Note that % (wt/vol) is not pounds/100 gal of solution; the units must be expressed in grams of solute and milliliters of solution. To avoid ambiguities, increasingly it is recommended that ppm, ppb, and ppt units are not used to describe solution phase concentrations; most journals require that μg/mL or ng/mL units should be used instead.

Example 5.16

A 25.0-μL serum sample was analyzed for glucose content and found to contain 26.7 μg. Calculate the concentration of glucose in μg/mL and in mg/dL.

Solution

$$25.0\ \cancel{\mu\text{L}} \times \frac{1\ \text{mL}}{1000\ \cancel{\mu\text{L}}} = 2.50 \times 10^{-2}\ \text{mL}$$

$$26.7\ \cancel{\mu\text{g}} \times \frac{1\ \text{g}}{10^5\ \cancel{\mu\text{g}}} = 2.67 \times 10^{-5}\ \text{g}$$

$$\text{Glucose Concentration} = \frac{2.67 \times 10^{-5}\ \text{g glucose}}{2.50 \times 10^{-2}\ \text{mL serum}} \times 10^6\ \mu\text{g/g} = 1.07 \times 10^3\ \mu\text{g/mL}$$

This is numerically the same in ppm units. Also,

$$\text{Glucose Concentration} = 1.07 \times 10^3\ \frac{\mu\text{g}}{\text{mL}} \times \frac{0.001\ \text{mg}}{1\ \mu\text{g}} \times \frac{100\ \text{mL}}{1\ \text{dL}}$$

$$= 107\ \text{mg/dL}$$

[Note the relationship: 10 ppm (wt/vol) = 1 mg/dL]

What does 1 μg/mL, often called 1 ppm, represent in terms of moles per liter? It depends on the formula weight.

The relationship between μg/mL and molarity (*M*) units depends on the formula weight.

Let's do some actual conversions using real formula weights. We begin with a solution that contains 2.5 μg/mL benzene. The formula weight (C_6H_6) is 78.1. The concentration in moles per liter is $(2.5 \times 10^{-3}\ \text{g/L})/(78\ \text{g/mol}) = 3.8 \times 10^{-5}\ M$ Another solution contains $5.8 \times 10^{-8} M$ lead. The concentration in parts per billion is $(5.8 \times 10^{-8}\ \text{mol/L})(207\ \text{g/mol}) = 1.2_0 \times 10^{-5}$ g/L. For parts per billion (μg/L), then $(1.2_0 \times 10^{-5}\ \text{g/L}) \times (10^6\ \mu\text{g/g}) = 1.2_0 \times 10^1\ \mu\text{g/L}$ or 12 ppb. A drinking water sample that contains 350 pg/L of carbon tetrachloride has a concentration in ng/L

of $(350 \times 10^{-12}$ g/L)/$(10^9$ ng/g) $= 350 \times 10^{-3}$ ng/L $= 0.35$ ng/L or 0.35 ppt. The molar concentration is $(350 \times 10^{-12}$g/L)/(154 g/mol) $= 2.3 \times 10^{-12}$ *M*. (Chlorine-treated water may contain traces of chlorinated hydrocarbons—this is very low.)

A key point to remember is that solutions that have the same numerical concentrations on a weight/weight or weight/volume basis do not have the same number of molecules[4], but solutions of the same molarity do.

Example 5.17

(a) Calculate the molar concentrations of 1 mg/L (1.00 ppm) solutions each of Li^+ and Pb^{2+}. (b) What weight of $Pb(NO_3)_2$ will have to be dissolved in 1 liter of water to prepare a 100 mg/L (100 ppm) Pb^{2+} solution?

Solution

(a) Li concentration = 1.00 mg/L Pb concentration = 1.00 mg/L

$$M_{Li} = \frac{1.00 \text{ mg Li/L} \times 10^{-3}\text{g/mg}}{6.94 \text{ g Li/mol}} = 1.44 \times 10^{-4} \text{ mol/L Li}$$

$$M_{Pb} = \frac{1.00 \text{ mg Pb/L} \times 10^{-3}\text{g/mg}}{207 \text{ g Pb/mol}} = 4.83 \times 10^{-6} \text{ mol/L Pb}$$

Because lead is much heavier than lithium, a given weight contains a smaller number of moles and its molar concentration is less.

(b) If 1 ppm Pb $= 4.83 \times 10^{-6}$mol/L Pb
100 ppm Pb $= 4.83 \times 10^{-4}$mol/L Pb
Therefore, we need 4.83×10^{-4} mol $Pb(NO_3)_2$.

$$4.83 \times 10^{-4} \text{ mol} \times 283.2 \text{ g } Pb(NO_3)_2\text{/mol} = 0.137 \text{ g } Pb(NO_3)_2$$

For dilute aqueous solutions, wt/wt ≈ wt/vol because the density of water is near 1.000 mg/ml.

The concentration units wt/wt and wt/vol are related through the density. They are numerically the same for dilute aqueous solutions as the density is 1 g/mL.

If the analyte is a liquid dissolved in another liquid, the results may be expressed on a **volume:volume** basis, but you will likely encounter this only in rare situations. One exception is specification of eluents in liquid chromatography, 40:60 methanol:water connotes that 40 volumes of methanol added to 60 volumes of water; the final volume is generally not available in such specifications. On the other hand, in a vol/vol designation, the first volume refers to that of the solute and the second to that of the solution; this unit is commonly used in the alcoholic beverage industry to specify ethanol content. You would handle the calculations in the same manner as those above, using the same volume units for solute and solution. As illustrated in Example 5.15, gas concentrations may be reported on a weight/volume, volume/volume, and rarely, on a weight/weight basis.

Alcohol in wine and liquor is expressed as vol/vol (200 proof = 100%vol/vol). Since the specific gravity of alcohol is 0.8, wt/vol concentration = 0.8 × (vol/vol) = 0.4 × proof

It is always best to specify clearly what is meant. In the absence of clear labels, it is best to assume that solids are being reported wt/wt, gases vol/vol, and liquids may be reported wt/wt (concentrated acid and base reagents), wt/vol (most dilute aqueous solutions), or vol/vol (the U.S. alcoholic beverage industry).

Clinical chemists frequently prefer to use a unit other than weight for expressing the amount of major electrolytes in biological fluids ($Na^+, K^+, Ca^{2+}, Mg^{2+}$,

[4]Unless they have the same formula weight.

Table 5.3

Major Electrolyte Composition of Normal Human Plasma[a]

Cations	meq/L	Anions	meq/L
Na^+	143	Cl^-	104
K^+	4.5	HCO_3^-	29
Ca^{2+}	5	Protein	16
Mg^{2+}	2.5	HPO_4^-	2
		SO_4^{2-}	1
		Organic acids	3
Total	155	Total	155

[a]Reproduced from Joseph S. Annino, *Clinical Chemistry*, 3rd ed., by Boston: Little, Brown, 1964.

At blood pH of 7.4, the phosphate actually exists primarily as a mixture of mono- and dihydrogen phosphate.

Cl^-, $H_2PO_4^-$, etc.). This is the unit **milliequivalent** (meq). In this context, milliequivalent is defined as the number of millimoles of analyte multiplied by the charge on the analyte ion. Results are generally reported as meq/L. This concept gives an overall view of the electrolyte balance. The physician can tell at a glance if total electrolyte concentration has increased or decreased markedly. Obviously, the milliequivalents of cations will be equal to the milliequivalents of anions. One mole of a monovalent (+1) cation (1 eq) and half a mole of a divalent (−2) anion (1 eq) have the same number of positive and negative charges (one mole each). As an example of electrolyte or charge balance, Table 5.3 summarizes the averages of major electrolyte compositions normally present in human blood plasma and urine. Chapter 25 discusses the ranges and physiological significant of some chemical constituents of the human body.

The equivalents of cations and anions in any solution must be equal.

We can calculate the milliequivalents of a substance from its weight in milligrams simply as follows (similar to how we calculate millimoles):

$$\text{meq} = \frac{\text{mg}}{\text{eq wt (mg/meq)}} = \frac{\text{mg}}{\text{fw (mg/mmol)}/n\ \text{(meq/mmol)}} \qquad (5.16)$$

n = charge on ion

The equivalent weight of Na^+ is 23.0 (mg/mmol)/1 (meq/mmol) = 23.0 mg/meq.
The equivalent weight of Ca^{2+} is 40.1 (mg/mmol)/2 (meq/mmol) = 20.0 mg/meq.

Example 5.18

The concentration of zinc ion in blood serum is about 1 mg/L. Express this as meq/L.

Solution

The equivalent weight of Zn^{2+} is 65.4 (mg/mmol)/2 (meq/mmol) = 32.7 mg/meq. Therefore,

$$\frac{1\ \text{mg Zn/L}}{32.7\ \text{mg/meq}} = 3.06 \times 10^{-2}\ \text{meq/L Zn}$$

This unit is more often used for the major electrolyte constituents as in Table 5.3 rather than the trace constituents, as in the example here. ■

REPORTING CONCENTRATIONS AS DIFFERENT CHEMICAL SPECIES

We may express results in any form of the analyte. This is often done to facilitate the interpretation by other professionals.

Thus far, we have implied that the analyte is determined in the form it exists or for which we want to report the results. However, this is often not true. In the determination of the iron content of an ore, for example, we may measure the iron in the form of Fe_2O_3 and then report it as % Fe. Or we may determine the iron in the form of Fe^{2+} (e.g., by titration) and report it as % Fe_2O_3. This is perfectly proper so long as we know the relationship between what is really being measured and the form it is to be reported in. We may actually determine the calcium content of water, for example, but we may wish to report it as parts per million (mg/L) of $CaCO_3$ (this is the typical way of expressing *water hardness*). We know that each gram of Ca^{2+} is equivalent to (or could be converted to) grams of $CaCO_3$ by multiplying grams Ca by fw $CaCO_3$/fw Ca^{2+}. That is, multiplying the milligrams of Ca^{2+} determined by 100.09/40.08 will give us the equivalent number of milligrams of $CaCO_3$. The calcium does not have to exist in this form (we may not even know in what form it actually exists); we simply have calculated the weight that could exist and will report the result as if it did. Specific operations necessary for calculating the weight of the desired constituent will be described below.

Water hardness due to calcium ion is expressed as ppm $CaCO_3$. Conveniently, the fw of $CaCO_3$ is 100. Converting from ppm $CaCO_3$ to molar units is very simple!

At this point we should mention some of the different weight criteria used for expressing results with biological tissues and solids. The sample may be weighed in one of three physical forms; wet, dry, or ashed. This can apply also to fluids, although fluid volume taken is usually used for the analysis. The wet weight is taken on the fresh, untreated sample. The dry weight is taken after the sample has been dried by heating, desiccation, or freeze-drying. If the test substance is unstable to heat, the sample should not be dried by heating. The weight of the ash residue after the organic matter has been burned off is sometimes used as the weight. This can obviously be used only for mineral (inorganic) analysis.

5.4 Volumetric Analysis: How Do We Make Stoichiometric Calculations?

Volumetric or titrimetric analyses are among the most useful and accurate analytical techniques, especially for millimole amounts of analyte. They are rapid and can be automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, for example, pH measurement. Other than pedagogic purposes, manual titrations nowadays are generally used only in situations that require high accuracy for relatively small numbers of samples. They are used, for example, to calibrate or validate more routine instrumental methods. Automated titrations are useful when large numbers of samples must be processed. (A titration may be automated, for instance, by means of a color change or a pH change that activates a motor-driven buret to stop delivery. The volume delivered may be electronically registered. (Automatic titrators are discussed in Chapter 14.) Below, we describe the types of titrations that can be performed and the applicable principles, including the requirements of a titration and of standard solutions. The volumetric relationship described earlier in this chapter may be used for calculating quantitative information about the titrated analyte. Volumetric calculations are given in Section 5.5.

TITRATION—WHAT ARE THE REQUIREMENTS?

We calculate the moles of analyte titrated from the moles of titrant added and the ratio in which they react.

In a **titration**, the test substance (analyte) reacts with an added reagent of known concentration, generally instantaneously. The reagent of known concentration is referred to as a **standard solution**. It is typically delivered from a buret; the solution

delivered by the buret is called the **titrant**. (In some instances, the reverse may also be carried out where a known volume of the standard solution is taken and it is titrated with the analyte of unknown concentration as the titrant.) The volume of titrant required to just completely react with the analyte is measured. Since we know the reagent concentration as well as the reaction stoichiometry between the analyte and the reagent, we can calculate the amount of analyte. The requirements of a titration are as follows:

1. The reaction must be **stoichiometric**. That is, there must be a well-defined and known reaction between the analyte and the titrant. In the titration of acetic acid in vinegar with sodium hydroxide, for example, a well-defined reaction takes place:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

2. The reaction should be *rapid*. Most ionic reactions, as above, are very rapid.
3. There should be *no side reactions*; the reaction should be specific. If there are interfering substances, these must be removed or independently determined and their influence subtracted from the overall signal ($C_{analyte} = C_{total} - C_{interference}$). In the above example, there should be no other acids present.
4. There should be a *marked change in some property of the solution when the reaction is complete*. This may be a change in color of the solution or in some electrical or other physical property of the solution. In the titration of acetic acid with sodium hydroxide, there is a marked increase in the pH of the solution when the reaction is complete. A color change is usually brought about by addition of an **indicator**, whose color is dependent on the properties of the solution, for example, the pH.
5. The point at which an equivalent or stoichiometric amount of titrant is added is called the **equivalence point**. The point at which the reaction is *observed* to be complete is called the **end point**, that is, when a change in some property of the solution is detected. The end point should coincide with the equivalence point or be at a reproducible interval from it.
6. The reaction should be **quantitative**. That is, the equilibrium of the reaction should be far to the right so that a sufficiently *sharp* change will occur at the end point to obtain the desired accuracy. If the equilibrium does not lie far to the right, then there will be gradual change in the property marking the end point (e.g., pH) and this will be difficult to detect precisely.

The *equivalence point* is the theoretical end of the titration where the number equivalents of the analyte exactly equals the number of equivalents of the titrant added. The *end point* is the observed end of the titration. The difference is the titration error.

STANDARD SOLUTIONS—THERE ARE DIFFERENT KINDS

A standard solution is prepared by dissolving an accurately weighed quantity of a highly pure material called a **primary standard** and diluting to an accurately known volume in a volumetric flask. Alternatively, if the material is not sufficiently pure, a solution is prepared to give approximately the desired concentration, and this is **standardized** by titrating a weighed quantity of a primary standard. For example, sodium hydroxide is not sufficiently pure to prepare a standard solution directly. It is therefore standardized by titrating a primary standard acid, such as potassium acid phthalate (KHP). Potassium acid phthalate is a solid that can be weighed accurately. Standardization calculations are treated below.

A solution standardized by titrating a primary standard is itself a secondary standard. It will be less accurate than a primary standard solution due to the errors of titrations.

A **primary standard** should fulfill these requirements:

1. It should be *100.00% pure*, although 0.01 to 0.02% impurity is tolerable if it is accurately known.
2. It should be *stable to drying* temperatures, and it should be stable indefinitely at room temperature. The primary standard is always dried before weighing.[5]
3. It should be *readily* and relatively inexpensively *available*.
4. Although not essential, it should have a *high formula weight*. This is so that a relatively large amount of it will have to be weighed. The relative error in weighing a greater amount of material will be smaller than that for a small amount.
5. If it is to be used in titration, it should possess the *properties required for a titration* listed above. In particular, the equilibrium of the reaction should be far to the right so that a sharp end point will be obtained.

A high formula weight means a larger weight must be taken for a given molar concentration of titrant to be made. This reduces the relative error in weighing.

CLASSIFICATION OF TITRATION METHODS—WHAT KINDS ARE THERE?

There are four general classes of volumetric or titrimetric methods.

1. *Acid–Base.* Many compounds, both inorganic and organic, are either acids or bases and can be titrated, respectively, with a standard solution of a strong base or a strong acid. The end points of these titrations are easy to detect, either by means of an indicator or by following the change in pH with a pH meter. The acidity and basicity of many organic acids and bases can be enhanced by titrating in a *nonaqueous solvent*. The result is a sharper end point, and weaker acids and bases can be titrated in this manner.
2. *Precipitation.* In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate. Again, indicators can be used to detect the end point, or the potential of the solution can be monitored electrically.
3. *Complexometric.* In complexometric titrations, the titrant is a reagent that forms a water-soluble complex with the analyte, a metal ion. The titrant is often a **chelating agent**.[6] Ethylenediaminetetraacetic acid (EDTA) is one of the most useful chelating agents used for titration. It will react with a large number of metal ions, and the reactions can be controlled by adjustment of pH. Indicators can be used to form a highly colored complex with the metal ion.
4. *Reduction–Oxidation.* These "redox" titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa. An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them. There must be a sufficiently large difference between the oxidizing and reducing capabilities of these agents for the reaction to go to completion and give a sharp end point; that is, one should be a fairly strong oxidizing agent (strong tendency to gain electrons) and the other a fairly strong reducing agent (strong tendency to lose electrons). Appropriate indicators for these titrations are available; various electrometric means to detect the end point may also be used.

[5] There are a few exceptions when the primary standard is a hydrate.

[6] A chelating agent (the term is derived from the Greek word for *clawlike*) is a type of complexing agent that contains two or more groups capable of complexing with a metal ion. EDTA has six such groups.

These different types of titrations and the means of detecting their end points will be treated separately in succeeding chapters.

5.5 Volumetric Calculations—Let's Use Molarity

We shall use molarity throughout the majority of the text for volumetric calculations. Some instructors prefer to introduce the concept of normality, and students are likely to encounter it in reference books. A section on normality-based calculations can be found in the text **website**.

In Equations 5.1–5.5, we previously discussed the ways of expressing in molar and millimolar units.

By rearranging these equations, we obtain the expressions for calculating other quantities.

$$M\ (\text{mol/L}) \times \text{L} = \text{mol} \qquad M\ (\text{mmol/mL}) \times \text{mL} = \text{mmol} \tag{5.17}$$

$$\text{g} = \text{mol} \times \text{fw}\ (\text{g/mol}) \qquad \text{mg} = \text{mmol} \times \text{fw}\ (\text{mg/mmol}) \tag{5.18}$$

$$\text{g} = M\ (\text{mol/L}) \times \text{L} \times \text{fw}\ (\text{g/mol}) \tag{5.19}$$

$$\text{mg} = M\ (\text{mmol/mL}) \times \text{mL} \times \text{fw}\ (\text{mg/mmol})$$

Learn these relationships well. They are the basis of all volumetric calculations, solution preparation, and dilutions. Think units!

We usually work with millimole (mmol) and milliliter (mL) quantities in titrations; therefore, the right-hand equations are more useful. Note that the expression for formula weight contains the same numerical value whether it be in g/mol or mg/mmol. Note also that care must be taken in utilizing "milli" quantities (millimoles, milligrams, milliliters). Incorrect use could result in calculations errors of 1000-fold.

Assume 25.0 mL of 0.100 *M* $AgNO_3$ is required to titrate a sample containing sodium chloride. The reaction is

$$Cl^-(aq) + Ag^+(aq) \rightarrow \underline{AgCl}(s)$$

Since Ag^+ and Cl^- react on a 1:1 molar basis, the number of millimoles of Cl^- is equal to the number of millimoles of Ag^+ needed for titration. We can calculate the milligrams of NaCl as follows:

For 1:1 reactions, $\text{mmol}_{\text{analyte}} = \text{mmol}_{\text{titrant}}$.

$$\begin{aligned}\text{mmol}_{\text{NaCl}} &= \text{mL}_{\text{AgNO}_3} \times M_{\text{AgNO}_3} \\ &= 25.0\ \text{mL} \times 0.100\ (\text{mmol/mL}) = 2.50\ \text{mmol} \\ \text{mg}_{\text{NaCl}} &= \text{mmol} \times \text{fw}_{\text{NaCl}} \\ &= 2.50\ \text{mmol} \times 58.44\ \text{mg/mmol} = 146\ \text{mg}\end{aligned}$$

We can calculate the percentage of analyte A that reacts on a *1:1 mole basis* with the titrant using the following general formula:

$$\begin{aligned}\%\text{Analyte} &= \text{fraction}_{\text{analyte}} \times 100\% = \frac{\text{mg}_{\text{analyte}}}{\text{mg}_{\text{sample}}} \times 100\% \\ &= \frac{\text{mmol analyte} \times \text{fw}_{\text{analyte}}(\text{mg/mol})}{\text{mg}_{\text{sample}}} \times 100\% \\ &= \frac{M_{\text{titrant}}(\text{mmol/mL}) \times \text{mL}_{\text{titrant}} \times \text{fw}_{\text{analyte}}(\text{mg/mmol})}{\text{mg}_{\text{sample}}} \times 100\%\end{aligned} \tag{5.20}$$

Note that this computation is a summary of the individual calculation steps taken to arrive at the fraction of analyte in the sample using proper dimensional analysis. You should use it in that sense rather than simply memorizing a formula.

Example 5.19

A 0.4671-g sample containing sodium bicarbonate was dissolved and titrated with standard 0.1067 *M* hydrochloric acid solution, requiring 40.72 mL. The reaction is

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

Calculate the percent sodium bicarbonate in the sample.

Solution

The millimoles of sodium bicarbonate are equal to the millimoles of acid used to titrate it, since they react in a 1:1 ratio.

$$\text{mmol}_{HCl} = 0.1067 \text{ mmol/mL} \times 40.72 \text{ mL} = 4.344_8 \text{ mmol}_{HCl} \equiv \text{mmol } NaHCO_3$$

(Extra figures are carried so an identical answer is obtained when all steps are done together below.)

$$\text{mg}_{NaHCO_3} = 4.3448 \text{ mmol} \times 84.01 \text{ mg/mmol} = 365.0_1 \text{ mg } NaHCO_3$$

$$\%NaHCO_3 = \frac{365.0_1 \text{ mg } NaHCO_3}{467.1 \text{ mg}_{\text{sample}}} \times 100\% = 78.14\% \text{ } NaHCO_3$$

Or, combining all the steps,

$$\begin{aligned} \%\ NaHCO_3 &= \frac{M_{HCl} \times \text{mL}_{HCl} \times \text{fw}_{NaHCO_3}}{\text{mg}_{\text{sample}}} \times 100\% \\ &= \frac{0.1067 \text{ mmol HCl/mL} \times 40.72 \text{ mL HCl} \times 84.01 \text{ mg } NaHCO_3\text{/mmol}}{467.1 \text{ mg}} \times 100\% \\ &= 78.14\% \text{ } NaHCO_3 \end{aligned}$$

SOME USEFUL THINGS TO KNOW FOR MOLARITY CALCULATIONS

When the reaction is not 1:1, a stoichiometric factor must be used to equate the moles of analyte and titrant.

Many substances do not react on a 1:1 mole basis, and so the simple calculation in the above example cannot be applied to all reactions. It is possible, however, to write a generalized formula for calculations applicable to *all* reactions based on the **balanced equation** for reactions.

Consider the general reaction

$$aA + tT \rightarrow P \tag{5.21}$$

where A is the analyte, T is the titrant, and they react in the ratio a/t to give products P. Then, noting the units and using dimensional analysis,

Still think units! We have added $\text{mmol}_{\text{analyte}}/\text{mmol}_{\text{titrant}}$.

$$\text{mmol}_A = \text{mmol}_T \times \frac{a}{t} \text{ (mmol A/mmol T)} \tag{5.22}$$

$$\text{mmol}_A = M_T \text{ (mmol/mL)} \times \text{mL}_T \times \frac{a}{t} \text{ (mmol A/mmol T)} \tag{5.23}$$

$$\text{mg}_A = \text{mmol}_A \times \text{fw}_A \text{ (mg/mmol)} \tag{5.24}$$

$$\text{mg}_A = M_T \text{ (mmol/mL)} \times \text{mL}_T \times \frac{a}{t}\text{(mmol A/mmol T)} \times \text{fw}_A \text{ (mg/mmol)} \tag{5.25}$$

Note that the a/t factor serves to equate the analyte and titrant. To avoid a mistake in setting up the factor, it is helpful to remember that when you calculate the amount of analyte, you must multiply the amount of titrant by the a/t ratio (a comes first). Conversely, if you are calculating the amount of titrant (e.g., molarity) from a known amount of analyte titrated, you must multiply the amount of analyte by the t/a ratio (t comes first). The best way, of course, to ascertain the correct ratio is to always do a dimensional analysis to obtain the correct units.

In a manner similar to that used to derive Equation 5.22, we can list the steps in arriving at a general expression for calculating the percent analyte A in a sample determined by titrating a known weight of sample with a standard solution of titrant T:

$$\begin{aligned}\%\text{Analyte} &= \text{fraction}_{\text{analyte}} \times 100\% = \frac{\text{mg}_{\text{analyte}}}{\text{mg}_{\text{sample}}} \times 100\% \\ &= \frac{\text{mmol}_{\text{titrant}} \times (a/t)(\text{mmol}_{\text{analyte}}/\text{mmol}_{\text{titrant}}) \times \text{fw}_{\text{analyte}} \text{ (mg/mmol)}}{\text{mg}_{\text{sample}}} \times 100\% \\ &= \frac{M_{\text{titrant}}(\text{mmol/mL}) \times \text{mL}_{\text{titrant}} \times (a/t)(\text{mmol}_{\text{analyte}}/\text{mmol}_{\text{titrant}}) \times \text{fw}_{\text{analyte}} \text{ (mg/mmol)}}{\text{mg}_{\text{sample}}} \\ &\quad \times 100\%\end{aligned} \tag{5.26}$$

Again, note that we simply use dimensional analysis, that is, we perform stepwise calculations in which units cancel to give the desired units. In this general procedure, the dimensional analysis includes the stoichiometric factor a/t that converts millimoles of titrant to an equivalent number of millimoles of titrated analyte.

Example 5.20

A 0.2638-g soda ash sample is analyzed by titrating the sodium carbonate with the standard 0.1288 M hydrochloride solution, requiring 38.27 mL. The reaction is

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

Calculate the percent sodium carbonate in the sample.

Solution

The millimoles of sodium carbonate is equal to one-half the millimoles of acid used to titrate it, since they react in a 1:2 ratio $\left(a/t = \frac{1}{2}\right)$.

$$\text{mmol}_{HCl} = 0.1288 \text{ mmol/mL} \times 38.27 \text{ mL} = 4.929 \text{ mmol HCl}$$

$$\text{mmol}_{NaCO_3} = 4.929 \text{ mmol HCl} \times \frac{1}{2}(\text{mmol } Na_2CO_3/\text{mmol HCl}) = 2.464_5 \text{ mmol } Na_2CO_3$$

$$\text{mg}_{Na_2CO_3} = 2.464_5 \text{ mmol} \times 105.99 \text{ mg } Na_2CO_3/\text{mmol} = 261.2_1 \text{ mg } Na_2CO_3$$

$$\%Na_2CO_3 = \frac{261.2_1 \text{ mg } Na_2CO_3}{263.8 \text{ mg}_{\text{sample}}} \times 100\% = 99.02\% \text{ } Na_2CO_3$$

Or, combining all the steps at once,

$$\%Na_2CO_3 = \frac{M_{HCl} \times mL_{HCl} \times \frac{1}{2}(\text{mmol } Na_2CO_3/\text{mmol HCl}) \times fw_{Na_2CO_3}}{mg_{sample}} \times 100\%$$

$$= \frac{0.1288 \text{ mmol HCl} \times 38.27 \text{ mL HCl} \times \frac{1}{2} (\text{mmol } Na_2CO_3/\text{mmol HCl}) \times 105.99 (\text{mg } Na_2CO_3/\text{mmol})}{263.8 \text{ mg}_{sample}} \times 100\%$$

$$= 99.02\% \text{ } Na_2CO_3$$

Example 5.21

How many milliliters of 0.25 *M* solution of H_2SO_4 will react with 10 mL of a 0.25 *M* solution of NaOH?

Solution

The reaction is

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

One-half as many millimoles of H_2SO_4 as of NaOH will react, or

$$M_{H_2SO_4} \times mL_{H_2SO_4} = M_{NaOH} \times mL_{NaOH} \times \frac{1}{2} (\text{mmol } H_2SO_4/\text{mmol NaOH})$$

Therefore,

$$mL_{H_2SO_4} = \frac{0.25 \text{ mmol NaOH/mL} \times 10 \text{ mL NaOH} \times \frac{1}{2}(\text{mmol } H_2SO_4/\text{mmol NaOH})}{0.25 \text{ mmol } H_2SO_4/\text{mL}}$$

$$= 5.0 \text{ mL } H_2SO_4$$

Note that, in this case, we multiplied the amount of titrant by the a/t ratio (mmol analyte/mmol titrant).

Example 5.22

A sample of impure salicylic acid, $C_6H_4(OH)COOH$ (one titratable proton), is analyzed by titration. What size sample should be taken so that the percent purity is equal to five times the milliliters of 0.0500 *M* NaOH used to titrate it?

Solution

Let x = mL NaOH; % salicylic acid (HA) = $5x$:

$$\%\text{ HA} = \frac{M_{NaOH} \times mL_{NaOH} \times 1 (\text{mmol HA/mmol NaOH}) \times fw_{HA} (\text{mg/mmol})}{mg_{sample}} \times 100\%$$

$$5x\% = \frac{0.0500\ M \times x \text{ mL NaOH} \times 1 \times 138 \text{ mg HA/mmol}}{mg_{sample}} \times 100\%$$

$$mg_{sample} = 138 \text{ mg}$$

You can apply the above examples of acid–base calculations to the titrations described in Chapter 8.

STANDARDIZATION AND TITRATION CALCULATIONS—THEY ARE THE REVERSE OF ONE ANOTHER

When a titrant material of high or known purity is not available, the concentration of the approximately prepared titrant solution must be accurately determined by **standardization**; that is, by titrating an accurately weighed quantity (a known number of millimoles) of a primary standard. From the volume of titrant used to titrate the primary standard, we can calculate the molar concentration of the titrant.

In standardization, generally it is the concentration of the titrant that is unknown and the moles of analyte (primary standard) are known.

Taking the analyte A in Equation 5.21 to be the primary standard,

$$\text{mmol}_{\text{standard}} = \frac{\text{mg}_{\text{standard}}}{\text{fw}_{\text{standard}}\ (\text{mg/mmol})}$$

$$\text{mmol}_{\text{titrant}} = M_{\text{titrant}}\ (\text{mmol/mL}) \times \text{mL}_{\text{titrant}}$$

$$= \text{mmol}_{\text{standard}} \times t/a\ (\text{mmol}_{\text{titrant}}/\text{mmol}_{\text{standard}})$$

$$M_{\text{titrant}}\ (\text{mmol/mL}) = \frac{\text{mmol}_{\text{standard}} \times t/a\ (\text{mmol}_{\text{titrant}}/\text{mmol}_{\text{standard}})}{\text{mL}_{\text{titrant}}}$$

Or, combining all steps at once,

$$M_{\text{titrant}}\ (\text{mmol/mL}) = \frac{\text{mg}_{\text{standard}}/\text{fw}_{\text{standard}}\ (\text{mg/mmol}) \times t/a\ (\text{mmol}_{\text{titrant}}/\text{mmol}_{\text{standard}})}{\text{mL}_{\text{titrant}}} \quad (5.27)$$

Units!

Note once again that dimensional analysis (cancellation of units) results in the desired units of mmol/mL.

Example 5.23

An approximate 0.1 *M* hydrochloric acid solution is prepared by 120-fold dilution of concentrated hydrochloric acid. It is standardized by titrating 0.1876 g of dried primary standard sodium carbonate:

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

The titration required 35.86 mL acid. Calculate the molar concentration of the hydrochloric acid.

Solution

The millimoles of hydrochloric acid are equal to twice the millimoles of sodium carbonate titrated.

$$\text{mmol}_{Na_2CO_3} = 187.6\ \text{mg}\ Na_2CO_3/105.99\ (\text{mg}\ Na_2CO_3/\text{mmol}) = 1.770_0\ \text{mmol}\ Na_2CO_3$$

$$\text{mmol}_{\text{HCl}} = M_{\text{HCl}}\ (\text{mmol/mL}) \times 35.86\ \text{mL HCl} = 1.770_0\ \text{mmol}\ Na_2CO_3$$

$$\times 2\ (\text{mmol HCl/mmol}\ Na_2CO_3)$$

$$M_{\text{HCl}} = \frac{1.770_0\ \text{mmol}\ Na_2CO_3 \times 2\ (\text{mmol HCl/mmol}\ Na_2CO_3)}{35.86\ \text{mL HCl}} = 0.09872\ \text{M}$$

Or, combining all steps at once,

$$M_{HCl} = \frac{(mg_{Na_2CO_3}/fw_{Na_2CO_3}) \times (2/1)(\text{mmol HCl/mmol } Na_2CO_3)}{mL_{HCl}}$$

$$= \frac{[187.6 \text{ mg}/105.99 \text{ (mg/mmol)}] \times 2 \text{ (mmol HCl/mmol } Na_2CO_3)}{35.86 \text{ mL}}$$

$$= 0.09872 \text{ mmol/mL}$$

Note that we multiplied the amount of analyte, Na_2CO_3, by the t/a ratio (mmol titrant/mmol analyte). Note also that although all measurements were to four significant figures, we computed the formula weight of Na_2CO_3 to five figures. This is because with four figures, it would have had an uncertainty of about one part per thousand compared to 187.6 with an uncertainty of about half that. It is not bad practice, as a matter of routine, to carry the formula weight to one additional figure. ■

The following examples illustrate titration calculations for different types of reactions and stoichiometry.

Example 5.24

This is a "redox" titration (see Chapter 14).

The iron(II) in an acidified solution is titrated with a 0.0206 M solution of potassium permanganate:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

If the titration required 40.2 mL, how many milligrams iron are in the solution?

Solution

There are five times as many millimoles of iron as there are of permanganate that react with it, so

$$\text{mmol}_{Fe} = \frac{mg_{Fe}}{fw_{Fe}} = M_{KMnO_4} \times mL_{KMnO_4} \times \frac{5}{1} \text{ (mmol Fe/mmol } KMnO_4)$$

$$mg_{Fe} = 0.0206 \text{ mmol } KMnO_4/\text{mL} \times 40.2 \text{ mL } KMnO_4 \times 5 \text{ (mmol Fe/mmol } MnO_4^-)$$

$$\times 55.8 \text{ mg Fe/mmol}$$

$$= 231 \text{ mg Fe}$$

■

Calculations of this type are used for the redox titrations described in Chapter 14.

Following is a list of typical precipitation and complexometric titration reactions and the factors for calculating the milligrams of analyte from millimoles of titrant.[7]

$Cl^- + Ag^+ \rightarrow \underline{AgCl}$	$mg_{Cl^-} = M_{Ag^+} \times mL_{Ag^+} \times 1 \text{ (mmol } Cl^-/\text{mmol } Ag^+) \times fw_{Cl^-}$
$2Cl^- + Pb^{2+} \rightarrow \underline{PbCl_2}$	$mg_{Cl^-} = M_{Pb^{2+}} \times mL_{Pb^{2+}} \times 2 \text{ (mmol } Cl^-/\text{mmol } Pb^{2+}) \times fw_{Cl^-}$
$PO_4^{3-} + 3Ag^+ \rightarrow \underline{Ag_3PO_4}$	$mg_{PO_4^{3-}} = M_{Ag^+} \times mL_{Ag^+} \times \frac{1}{3} \text{ (mmol } PO_4^{3-}/\text{mmol } Ag^+) \times fw_{PO_4^{3-}}$
$2CN^- + Ag^+ \rightarrow Ag(CN)_2^-$	$mg_{CN^-} = M_{Ag^+} \times mL_{Ag^+} \times 2 \text{ (mmol } CN^-/\text{mmol } Ag^+) \times fw_{CN^-}$
$2CN^- + 2Ag^+ \rightarrow \underline{Ag[Ag(CN)_2]}$	$mg_{CN^-} = M_{Ag^+} \times mL_{Ag^+} \times 1 \text{ (mmol } CN^-/\text{mmol } Ag^+) \times fw_{CN^-}$
$Ba^{2+} + SO_4^{2-} \rightarrow \underline{BaSO_4}$	$mg_{Ba^{2+}} = M_{SO_4^{2-}} \times 1 \text{ (mmol } Ba^{2+}/\text{mmol } SO_4^{2-}) \times fw_{Ba^{2+}}$
$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+$	$mg_{Ca^{2+}} = M_{EDTA} \times 1 \text{ (mmol } Ca^{2+}/\text{mmol EDTA}) \times fw_{Ca^{2+}}$

[7] H_4Y = EDTA in the last equation.

These formulas are useful calculations involving the precipitation and complexometric titrations described in Chapters 8 and 11.

Example 5.25

Aluminum is determined by titrating with EDTA:

$$Al^{3+} + H_2Y^{2-} \rightarrow AlY^- + 2H^+$$

This is a "complexometric" titration (see Chapter 9). EDTA has four protons, and in this titration, two are dissociated at the pH of the titration.

A 1.00-g sample requires 20.5 mL EDTA for titration. The EDTA was standardized by titrating 25.0 mL of a 0.100 *M* $CaCl_2$ solution, requiring 30.0 mL EDTA. Calculate the percent Al_2O_3 in the sample.

Solution

Since Ca^{2+} and EDTA react on a 1:1 mole ratio,

$$M_{EDTA} = \frac{0.100 \text{ mmol } CaCl_2/\text{mL} \times 25.0 \text{ mL } CaCl_2}{30.0 \text{ mL EDTA}} = 0.0833 \text{ mmol/mL}$$

The millimoles Al^{3+} are equal to the millimoles EDTA used in the sample titration, but there are one-half this number of millimoles of Al_2O_3 (since $1Al^{3+} \rightarrow \frac{1}{2}Al_2O_3$). Therefore,

$$\%\ Al_2O_3 = \frac{M_{EDTA} \times mL_{EDTA} \times \frac{1}{2} (\text{mmol } Al_2O_3/\text{mmol EDTA}) \times fw_{Al_2O_3}}{mg_{sample}} \times 100\%$$

$$\%\ Al_2O_3 = \frac{0.0833 \text{ mmol EDTA/mL} \times 20.5 \text{ mL EDTA} \times \frac{1}{2} \times 101.96 \text{ mg } Al_2O_3/\text{mmol}}{1000\text{-mg sample}}$$

$$\times 100\% = 8.71\%\ Al_2O_3$$

■

WHAT IF THE ANALYTE AND TITRANT CAN REACT IN DIFFERENT RATIOS?

As you might be aware from your introductory chemistry course, some substances can undergo reaction to different products. The factor used in calculating millimoles of such a substance from the millimoles of titrant reacted with it will depend on the specific reaction. Sodium carbonate, for example, can react as a diprotic or a monoprotic base:

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

or

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

In the first case, mmol Na_2CO_3 = mmol acid $\times \frac{1}{2}$ (mmol CO_3^{2-}/mmol H^+). In the second case, mmol Na_2CO_3 = mmol acid. Similarly, phosphoric acid can be titrated as a monoprotic or a diprotic acid:

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$

or

$$H_3PO_4 + 2OH^- \rightarrow HPO_4^{2-} + 2H_2O$$

Example 5.26

In acid solution, potassium permanganate reacts with H_2O_2 to form Mn^{2+}:

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

In neutral solution, it reacts with $MnSO_4$ to form MnO_2:

$$3Mn^{2+} + 2MnO_4^- + 4OH^- \rightarrow \underline{5MnO_2} + 2H_2O$$

Calculate the number of milliliters of 0.100 *M* $KMnO_4$ that will react with 50.0 mL of 0.200 *M* H_2O_2 and with 50.0 mL of 0.200 *M* $MnSO_4$.

Solution

Keep track of millimoles!

The number of millimoles of MnO_4^- will be equal to two-fifths of the number of millimoles of H_2O_2 reacted:

$$M_{MnO_4^-} \times mL_{MnO_4^-} = M_{H_2O_2} \times mL_{H_2O_2} \times \frac{2}{5} \text{ (mmol } MnO_4^-/\text{mmol } H_2O_2)$$

$$mL_{MnO_4^-} = \frac{0.200 \text{ mmol } H_2O_2/\text{mL} \times 50.0 \text{ mL } H_2O_2 \times \frac{2}{5}}{0.100 \text{ mmol } MnO_4^-/\text{mL}} = 40.0 \text{ mL } KMnO_4$$

The number of millimoles of MnO_4^- reacting with Mn^{2+} will be equal to two-thirds of the number of millimoles of Mn^{2+}:

$$M_{MnO_4^-} \times mL_{MnO_4^-} = M_{Mn^{2+}} \times \frac{2}{3} \text{ (mmol } MnO_4^-/\text{mmol } Mn^{2+})$$

$$mL_{MnO_4^-} = \frac{0.200 \text{ mmol } Mn^{2+}/\text{mL} \times 50.0 \text{ mL } Mn^{2+} \times \frac{2}{3}}{0.100 \text{ mmol } MnO_4^-/\text{mL}} = 66.7 \text{ mL } KMnO_4$$

Example 5.27

Oxalic acid, $H_2C_2O_4$, is a reducing agent that reacts with $KMnO_4$ as follows:

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Its two protons are also titratable with a base. How many milliliters of 0.100 *M* NaOH and 0.100 *M* $KMnO_4$ will react with 500 mg $H_2C_2O_4$?

Solution

$$\text{mmol NaOH} = 2 \times \text{mmol } H_2C_2O_4$$

$$0.100 \text{ mmol/mL} \times x \text{ mL NaOH} = \frac{500 \text{ mg} H_2C_2O_4}{90.0 \text{ mg/mmol}} \times 2 \text{ (mmol } OH^-/\text{mmol } H_2C_2O_4)$$

$$x = 111 \text{ mL NaOH}$$

$$\text{mmol } KMnO_4 = \frac{2}{5} \times \text{mmol } H_2C_2O_4$$

$$0.100 \text{ mmol/mL} \times x \text{ mL } KMnO_4 = \frac{500 \text{ mg } H_2C_2O_4}{90.0 \text{ mg/mmol}} \times \frac{2}{5} \text{ (mmol } KMnO_4/\text{mmol } H_2C_2O_4)$$

$$x = 22.2 \text{ mL } KMnO_4$$

Example 5.28

Pure $Na_2C_2O_4$ plus $KHC_2O_4 \cdot H_2C_2O_4$ (three replaceable protons, KH_3A_2) are mixed in such a proportion that each gram of the mixture will react with equal volumes of 0.100 *M* $KMnO_4$ and 0.100 *M* NaOH. What is the proportion?

Solution

Assume 10.0-mL titrant, so it will react with 1.00 mmol NaOH or $KMnO_4$. The acidity is due to $KHC_2O_4 \cdot H_2C_2O_4$ denoted in the following as KH_3A_2:

$$\text{mmol } KH_3A_2 = \text{mmol NaOH} \times \frac{1}{3}(\text{mmol } KH_3A_2/\text{mmol } OH^-)$$

$$1.00 \text{ mmol NaOH} \times \frac{1}{3} = 0.333 \text{ mmol } KH_3A_2$$

From Example 5.27, each mmol $Na_2C_2O_4$ (Na_2A) reacts with $\frac{2}{5}$ mmol $KMnO_4$.

$$\text{mmol } KMnO_4 = \text{mmol } Na_2A \times \frac{2}{5}\ (\text{mmol } MnO_4^-/\text{mmol } Na_2A) + \text{mmol } KH_3A_2 \times \frac{4}{5}\ (\text{mmol } MnO_4^-/\text{mmol } KH_3A_2)$$

$$1.00 \text{ mmol } KMnO_4 = \text{mmol } Na_2A \times \frac{2}{5} + 0.333 \text{ mmol } KH_3A_2 \times \frac{4}{5}$$

$$\text{mmol } Na_2A = 1.8_3 \text{ mmol}$$

The ratio is 1.8_3 mmol Na_2A/0.333 mmol $KH_3A_2 = 5.5_0$ mmol Na_2A/mmol KH_3A_2. The weight ratio is

$$\frac{5.5_0 \text{ mmol } Na_2A \times 134 \text{ mg/mmol}}{218 \text{ mg } KH_3A_2/\text{mmol}} = 3.38 \text{ g } Na_2A/\text{g } KH_3A_2$$

IF THE REACTION IS SLOW, DO A BACK-TITRATION

In back-titrations, a known number of millimoles of reactant is taken, in excess of the analyte. The unreacted portion is titrated.

Sometimes a reaction is slow to go to completion, and a sharp end point cannot be obtained. One example is the titration of antacid tablets with a strong acid such as HCl. In these cases, a **back-titration** will often yield useful results. In this technique, a measured amount of the reagent, which would normally be the titrant, is added to the sample so that there is a slight excess. After the reaction with the analyte is allowed to go to completion, the amount of excess (unreacted) reagent is determined by titration with another standard solution; the kinetics of the analyte reaction may be increased in the presence of excess reagent. So by knowing the number of millimoles of reagent taken and by measuring the number of millimoles remaining unreacted, we can calculate the number of millimoles of sample that reacted with the reagent:

$$\text{mmol reagent reacted} = \text{mmol taken} - \text{mmol back-titrated}$$

$$\text{mg analyte} = \text{mmol reagent reacted} \times \text{factor (mmol analyte/mmol reagent)} \times \text{fw analyte (mg/mmol)}$$

Example 5.29

Chromium(III) is slow to react with EDTA (H_4Y) and is therefore determined by back-titration. Chromium(III) picolinate, $Cr(C_6H_4NO_2)_3$, is sold as a nutritional supplement for athletes with the claim that it aids muscle building. A nutraceutical preparation containing chromium(III) is analyzed by treating a 2.63-g sample with 5.00 mL of 0.0103 *M* EDTA. Following reaction, the unreacted EDTA is back-titrated with 1.32 mL of 0.0122 *M* zinc solution. What is the percent chromium picolinate in the pharmaceutical preparation?

Solution

Both Cr^{3+} and Zn^{2+} react in a 1:1 ratio with EDTA:

$$Cr^{3+} + H_4Y \rightarrow CrY^- + 4H^+$$

$$Zn^{2+} + H_4Y \rightarrow ZnY^2 + 4H^+$$

The millimoles of EDTA taken is

$$0.0103 \text{ mmol EDTA/mL} \times 5.00 \text{ mL EDTA} = 0.0515 \text{ mmol EDTA}$$

The millimoles of unreacted EDTA is

$$0.0112 \text{ mmol } Zn^{2+}\text{/mL} \times 1.32 \text{ mL } Zn^{2+} = 0.0148 \text{ mmol unreacted EDTA}$$

The millimoles of reacted EDTA is

$$0.0515 \text{ mmol taken} - 0.0148 \text{ mmol left} = 0.0367 \text{ mmol EDTA} \equiv \text{mmol } Cr^{3+}$$

The milligrams of $Cr(C_6H_4NO_2)_3$ titrated is

$$0.0367 \text{ mmol } Cr(C_6H_4NO_2)_3 \times 418.3 \text{ mg/mmol} = 15.35 \text{ mg } Cr(C_6H_4NO_2)_3$$

$$\%Cr(C_6H_4NO_2)_3 = \frac{15.35 \text{ mg } Cr(C_6H_4NO_2)_3}{2630 \text{ mg sample}} \times 100\% = 0.584\% \text{ } Cr(C_6H_4NO_2)_3$$

Or, combining all steps,

$$\%Cr(C_6H_4NO_2)_3$$

$$= \frac{(M_{EDTA} \times mL_{EDTA} - M_{Zn} \times mL_{Zn^{2+}}) \times 1(\text{mmol } Cr(C_6H_4NO_2)_3\text{/mmol EDTA}) \times fw_{Cr(C_6H_4NO_2)_3}}{mg_{sample}} \times 100\%$$

$$= \frac{(0.0103 \text{ mmol EDTA/mL} \times 5.00 \text{ mL EDTA} - 0.0112 \text{ mmol } Zn^{2+}\text{/mL} \times 1.32 \text{ mL } Zn^{2+}) \times 1 \times 418.3 \text{ mg } Cr(C_6H_4NO_2)_3\text{/mmol}}{2630 \text{ mg sample}} \times 100\%$$

$$= 0.584\% \text{ } Cr(C_6H_4NO_2)_3$$

Example 5.30

A 0.200-g sample of pyrolusite is analyzed for manganese content as follows. Add 50.0 mL of a 0.100 *M* solution of ferrous ammonium sulfate to reduce the MnO_2 to Mn^{2+}. After reduction is complete, the excess ferrous ion is titrated in acid solution with 0.0200 *M* $KMnO_4$, requiring 15.0 mL. Calculate the percentage of manganese in the sample as Mn_3O_4 (the manganese may or may not exist in this form, but we can make the calculations on the assumption that it does).

Solution

The reaction between Fe^{2+} and MnO_4^- is

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

and so there are five times as many millimoles of excess Fe^{2+} as of MnO_4^- that reacted with it.

The reactant may react in different ratios with the analyte and titrant.

The reaction between Fe^{2+} and MnO_2 is

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$$

and there are one-half as many millimoles of MnO_2 as millimoles of Fe^{2+} that react with it. There are one-third as many millimoles of Mn_3O_4 as of MnO_2 ($1MnO_2 \rightarrow \frac{1}{3}Mn_3O_4$). Therefore,

$$\begin{aligned}
\text{mmol } Fe^{2+} \text{ reacted} &= 0.100 \text{ mmol } Fe^{2+}/\text{mL} \times 50.0 \text{ mL } Fe^{2+} - 0.0200 \text{ mmol } MnO_4^-/\text{mL} \\
&\quad \times 15.0 \text{ mL } MnO_4^- \times 5 \text{ mmol } Fe^{2+}/\text{mmol } MnO_4^- \\
&= 3.5 \text{ mmol } Fe^{2+} \text{ reacted} \\
\text{mmol } MnO_2 &= 3.5 \text{ mmol } Fe^{2+} \times \frac{1}{2} \text{ (mmol } MnO_2/\text{mmol } Fe^{2+}) = 1.75 \text{ mmol } MnO_2 \\
\text{mmol } Mn_3O_4 &= 1.7_5 \text{ mmol } MnO_2 \times \frac{1}{3} \text{ (mmol } Mn_3O_4)/\text{mmol } MnO_2) \\
&= 0.58_3 \text{ mmol } Mn_3O_4 \\
\%\ Mn_3O_4 &= \frac{0.58_3 \text{ mmol } Mn_3O_4 \times 228.8 \text{ (mg } Mn_3O_4/\text{mmol)}}{200 \text{ mg sample}} \times 100\% \\
&= 66.7\%\ Mn_3O_4
\end{aligned}$$

Or, combining all steps at once,

$$\begin{aligned}
\%\ Mn_3O_4 &= \{[M_{Fe^{2+}} \times \text{mL}_{Fe^{2-}} - M_{MnO_4^-} \times \text{mL}_{MnO_4^-} \times 5(\text{mmol } Fe^{2+}/\text{mmol } MnO_4^-) \\
&\quad \times \frac{1}{2} \text{ (mmol } MnO_2/\text{mmol } Fe^{2+}) \times \frac{1}{3} \text{ (mmol } Mn_3O_4/\text{mmol } MnO_2) \\
&\quad \times \text{fw}_{Mn_3O_4}]/\text{mg}_{\text{sample}}\} \times 100\% \\
&= \frac{(0.100 \times 50.0 - 0.0200 \times 15.0 \times 5) \times \frac{1}{2} \times \frac{1}{3} \times 228.8 \text{ mg/mmol}}{200 \text{ mg sample}} \times 100\% \\
&= 66.7\%\ Mn_3O_4
\end{aligned}$$

■

5.6 Titer—How to Make Rapid Routine Calculations

For routine titrations, it is often convenient to calculate the **titer** of the titrant. The titer is the weight of analyte that is chemically equivalent to 1 mL of the titrant, usually expressed in milligrams. For example, if a potassium dichromate solution has a titer of 1.267 mg Fe, each milliliter potassium dichromate will react with 1.267 mg iron, and the weight of iron titrated is obtained by simply multiplying the volume of titrant used by the titer. The titer can be expressed in terms of any form of the analyte desired, for example, milligrams FeO or Fe_2O_3.

Titer = milligrams analyte that react with 1 mL of titrant.

Example 5.31

A standard solution of potassium dichromate contains 5.442 g/L. What is its titer in terms of milligrams Fe_3O_4?

Solution

The iron is titrated as Fe^{2+} and each $Cr_2O_7^{2-}$ will react with $6Fe^{2+}$ (or the iron from $2Fe_3O_4$):

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

The molarity of the $K_2Cr_2O_7$, solution is

$$M_{Cr_2O_7^{2-}} = \frac{\text{g/L}}{\text{fw}_{K_2Cr_2O_7}} = \frac{5.442 \text{ g/L}}{294.19 \text{ g/mol}} = 0.01850 \text{ mol/L}$$

Therefore the titer is

$$0.01850 \left(\frac{\text{mmol } K_2Cr_2O_7}{\text{mL}}\right) \times \frac{2}{1} \left(\frac{\text{mmol } Fe_3O_4}{\text{mmol } K_2Cr_2O_7}\right) \times 231.54 \left(\frac{\text{mg } Fe_3O_4}{\text{mmol } Fe_3O_4}\right)$$
$$= 8.567 \text{ mg } Fe_3O_4/\text{mL } K_2Cr_2O_7$$

5.7 Weight Relationships—You Need These for Gravimetric Calculations

In the technique of gravimetric analysis (Chapter 10), the analyte is converted to an insoluble form, which is weighed. From the weight of the precipitate formed and the weight relationship between the analyte and the precipitate, we can calculate the weight of analyte. We review here some of the calculation concepts.

The analyte is almost always weighed in a form different from what we wish to report. We must, therefore, calculate the weight of the desired substance from the weight of the gravimetric precipitate. We can do this by using a direct proportion. For example, if we are analyzing for the percentage of chloride in a sample by weighing it as AgCl, we can write

$$Cl^- \xrightarrow{\text{precipitating reagent}} AgCl(s)$$

We derive one mole AgCl from one mole Cl^-, so

$$\frac{\text{g } Cl^-}{\text{g AgCl}} = \frac{\text{at wt Cl}}{\text{fw AgCl}}$$

or

$$\text{g } Cl^- = \text{g AgCl} \times \frac{\text{at wt Cl}}{\text{fw AgCl}}$$

In gravimetric analysis, the moles of analyte is a multiple of the moles of precipitate formed (the moles of analyte contained in each mole of precipitate).

Note that when we specify at wt or fw of a substance x, it implicitly has the units g x/mol x. In other words, the weight of Cl contained in or used to create AgCl is equal to the weight of AgCl times the **fraction** of Cl in it.

Calculation of the corresponding weight of Cl_2 that would be contained in the sample would proceed thus:

$$Cl_2 \xrightarrow{\text{precipitating reagent}} 2AgCl(s)$$

We derive two moles of AgCl from each mole of Cl_2, so

$$\frac{\text{g } Cl_2}{\text{g AgCl}} = \frac{\text{fw } Cl_2}{2 \times \text{fw AgCl}}$$

and

$$\text{g } Cl_2 = \text{g AgCl} \times \frac{\text{fw } Cl_2}{2\ (\text{fw AgCl})}$$

or

$$\text{g } Cl_2 = \text{g AgCl} \times \frac{70.906}{2 \times 143.32}$$

We may also write

Remember to keep track of the units!

$$\text{g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol } Cl_2}{2 \text{ mol AgCl}} \times \frac{70.906 \text{ g } Cl_2}{1 \text{ mol } Cl_2} = \text{g } Cl_2$$

The **gravimetric factor** (GF) is the appropriate ratio of the formula weight of the substance *sought* to that of the substance *weighed*:

The gravimetric factor is the weight of analyte per unit weight of precipitate.

$$\text{GF} = \text{gravimetric factor} = \frac{\text{fw of substance sought}}{\text{fw of substance weighed}} \times \frac{a}{b}\ (\text{mol sought/mol weighed}) \tag{5.28}$$

where a and b are integers that make the formula weights in the numerator and denominator chemically equivalent. In the above examples, the gravimetric factors were (fw Cl/fw AgCl) × 1/1, and (fw Cl_2/fw AgCl) × $\frac{1}{2}$. Note that one or both of the formula weights may be multiplied by an integer in order to keep the same number of atoms of the key element in the numerator and denominator.

The weight of the substance sought is obtained by multiplying the weight of the precipitate by the gravimetric factor:

$$\text{weight (g)} \times \frac{\text{fw of substance sought}}{\text{fw of substance weighed}} \times \frac{a}{b} = \text{sought (g)} \tag{5.29}$$

Note that the *species* and the *units* of the equation can be checked by dimensional analysis (canceling of like species and units).

Note also that we have calculated the amount of Cl_2 gas *derivable* from the sample instead of the amount of Cl^- ion, the form in which it probably exists in the sample and the form in which it is weighed. If we precipitate the chloride as $PbCl_2$,

$$2Cl^- \xrightarrow{\text{precipitating agent}} PbCl_2$$

and

$$Cl_2 \rightarrow PbCl_2$$

then,

$$\text{g } Cl^- = \text{g } PbCl_2 \times \frac{2(\text{fw Cl})}{\text{fw } PbCl_2} = \text{g } PbCl_2 \times \text{GF}$$

or

$$\text{g } Cl_2 = \text{g } PbCl_2 \times \frac{\text{fw } Cl_2}{\text{fw } PbCl_2} = \text{g } PbCl_2 \times \text{GF}$$

Conversion from weight of one substance to the derived there from weight of another is done using dimensional analysis of the units to arrive at the desired weight. The gravimetric factor is one step of that calculation and is useful for routine calculations. That is, if we know the gravimetric factor, we simply multiply the weight of the precipitate by the gravimetric factor to arrive at the weight of the analyte.

The grams of analyte = grams precipitate × GF.

Example 5.32

Calculate the weight of barium and the weight of Cl present in 25.0 g $BaCl_2$.

Solution

$$25.0 \text{ g } BaCl_2 \times \frac{\text{fw Ba}}{\text{fw } BaCl_2} =$$

$$25.0 \text{ g} \times \frac{137.3}{208.2} = 16.5 \text{ g Ba}$$

$$25.0 \text{ g } BaCl_2 \times \frac{2 \times \text{fw Cl}}{\text{fw } BaCl_2} =$$

$$25.0 \text{ g} \times \frac{2 \times 35.45}{208.2} = 8.51 \text{ g Cl}$$

Example 5.33

Aluminum in an ore sample is determined by dissolving it and then precipitating with base as $Al(OH)_3$ and igniting to Al_2O_3, which is weighed. What weight of aluminum was in the sample if the ignited precipitate weighed 0.2385 g?

Solution

$$\text{g Al} = \text{g } Al_2O_3 \times \frac{2 \times \text{fw Al}}{\text{fw } Al_2O_3}$$

$$= 0.2385 \text{ g} \times \frac{2 \times 26.982}{101.96} = 0.1262_3 \text{ g Al}$$

The gravimetric factor is

$$\frac{2 \times \text{fw Al}}{\text{fw } Al_2O_3} = \frac{2 \times 26.982}{101.96} = 0.52927 \text{ (g Al/g } Al_2O_3)$$

or $0.2385 \text{ g } Al_2O_3 \times 0.52927 \text{ (g Al/g } Al_2O_3) = 0.1262_3 \text{ g Al}$

Following are some other examples of gravimetric factors:

Sought	Weighed	Gravimetric Factor
SO_3	$BaSO_4$	$\frac{\text{fw } SO_3}{\text{fw } BaSO_4}$
Fe_3O_4	Fe_2O_3	$\frac{2 \times \text{fw } Fe_3O_4}{3 \times \text{fw } Fe_2O_3}$
Fe	Fe_2O_3	$\frac{2 \times \text{fw Fe}}{\text{fw } Fe_2O_3}$
MgO	$Mg_2P_2O_7$	$\frac{2 \times \text{fw MgO}}{\text{fw } Mg_2P_2O_7}$
P_2O_5	$Mg_2P_2O_7$	$\frac{\text{fw } P_2O_5}{\text{fw } Mg_2P_2O_7}$

The operations of gravimetric analyses are described in detail in Chapter 10.

More examples of gravimetric calculations are given in Chapter 10.

Questions

1. Distinguish between the expression of concentration on weight/weight, weight/volume, and volume/volume bases.
2. Express ppm and ppb on weight/weight, weight/volume, and volume/volume bases.
3. Define the term "equivalent weight," used for electrolytes in clinical chemistry. Why is this used?
4. List the requirements for a titration. What are the four classes of titrations?
5. What is the equivalence point of a titration? The end point?
6. What is a standard solution? How is it prepared?
7. What are the requirements of a primary standard?
8. Why should a primary standard have a high formula weight?

Problems

WEIGHT/MOLE CALCULATIONS

9. Calculate the grams of substance required to prepare the following solutions: (a) 250 mL of 5.00% (wt/vol) $NaNO_3$; (b) 500 mL of 1.00% (wt/vol) NH_4NO_3, (c) 1000 mL of 10.0% (wt/vol) $AgNO_3$.
10. What is the wt/vol % of the solute in each of the following solutions? (a) 52.3 g Na_2SO_4/L, (b) 275 g KBr in 500 mL, (c) 3.65 g SO_2 in 200 mL.
11. Calculate the formula weights of the following substances: (a) $BaCl_2 \cdot 2H_2O$, (b) $KHC_2O_4 \cdot H_2C_2O_4$, (c) $Ag_2Cr_2O_7$, (d) $Ca_3(PO_4)_2$.
12. Calculate the number of millimoles contained in 500 mg of each of the following substances: (a) $BaCrO_4$, (b) $CHCl_3$, (c) $KIO_3 \cdot HIO_3$, (d) $MgNH_4PO_4$, (e) $Mg_2P_2O_7$, (f) $FeSO_4 \cdot C_2H_4(NH_3)_2SO_4 \cdot 4H_2O$.
13. Calculate the number of grams of each of the substances in Problem 12 that would have to be dissolved and diluted to 100 mL to prepare a 0.200 *M* solution.
14. Calculate the number of milligrams of each of the following substances you would have to weigh out in order to prepare the listed solutions: (a) 1.00 L of 1.00 *M* NaCl, (b) 0.500 L of 0.200 *M* sucrose ($C_{12}H_{22}O_{11}$), (c) 10.0 mL of 0.500 *M* sucrose, (d) 0.0100 L of 0.200 *M* Na_2SO_4, (e) 250 mL of 0.500 *M* KOH, (f) 250 mL of 0.900% NaCl (g/100 mL solution).
15. The chemical stockroom is supplied with the following stock solutions: 0.100 *M* HCl, 0.0200 *M* NaOH, 0.0500 *M* KOH, 10.0% HBr (wt/vol), and 5.00% Na_2CO_3 (wt/vol). What volume of stock solution would be needed to obtain the following amounts of solutes? (a) 0.0500 mol HCl, (b) 0.0100 mol NaOH, (c) 0.100 mol KOH, (d) 5.00 g HBr, (e) 4.00 g Na_2CO_3, (f) 1.00 mol HBr, (g) 0.500 mol Na_2CO_3.

MOLARITY CALCULATIONS

16. Calculate the molar concentrations of all the cations and anions in a solution prepared by mixing 10.0 mL each of the following solutions: 0.100 *M* $Mn(NO_3)_2$, 0.100 *M* KNO_3, and 0.100 *M* K_2SO_4.
17. A solution containing 10.0 mmol $CaCl_2$ is diluted to 1 L. Calculate the number of grams of $CaCl_2 \cdot 2H_2O$ per milliliter of the final solution.
18. Calculate the molarity of each of the following solutions: (a) 10.0 g H_2SO_4 in 250 mL of solution, (b) 6.00 g NaOH in 500 mL of solution, (c) 25.0 g $AgNO_3$ in 1.00 L of solution.
19. Calculate the number of grams in 500 mL of each of the following solutions: (a) 0.100 *M* Na_2SO_4, (b) 0.250 *M* $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, (c) 0.667 *M* $Ca(C_9H_6ON)_2$.
20. Calculate the grams of each substance required to prepare the following solutions: (a) 250 mL of 0.100 *M* KOH, (b) 1.00 L of 0.0275 *M* $K_2Cr_2O_7$, (c) 500 mL of 0.0500 *M* $CuSO_4$.
21. How many milliliters of concentrated hydrochloric acid, 38.0% (wt/wt), specific gravity 1.19, are required to prepare 1 L of a 0.100 *M* solution? (Assume density and specific gravity are equal within three significant figures.)

22. Calculate the molarity of each of the following commercial acid or base solutions: (a) 70.0% $HClO_4$, specific gravity 1.668, (b) 69.0% HNO_3, specific gravity 1.409, (c) 85.0% H_3PO_4, specific gravity 1.689, (d) 99.5% CH_3COOH (acetic acid), specific gravity 1.051, (e) 28.0% NH_3, specific gravity 0.898. (Assume density and specific gravity are equal within three significant figures.)

mg/L (PPM) CALCULATIONS

23. A solution contains 6.0 μmol Na_2SO_4 in 250 mL. How many mg/L sodium does it contain? Of sulfate?

24. A solution (100 mL) containing 325 mg/L K^+ is analyzed by precipitating it as the tetraphenyl borate, $K(C_6H_5)_4B$, dissolving the precipitate in acetone solution, and measuring the concentration of tetraphenyl borate ion, $(C_6H_5)_4B^-$, in the solution. If the acetone solution volume is 250 mL, what is the concentration of the tetraphenyl borate in mg/L?

25. Calculate the molar concentrations of 1.00-mg/L solutions of each of the following. (a) $AgNO_3$, (b) $Al_2(SO_4)_3$, (c) CO_2, (d) $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$, (e) HCl, (f) $HClO_4$.

26. Calculate the mg/L concentrations of 2.50×10^{-4} *M* solutions of each of the following. (a) Ca^{2+}, (b) $CaCl_2$, (c) HNO_3, (d) KCN, (e) Mn^{2+}, (f) MnO_4^-.

27. You want to prepare 1 L of a solution containing 1.00 mg/L Fe^{2+}. How many grams ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, must be dissolved and diluted in 1 L? What would be the molarity of this solution?

28. A 0.456-g sample of an ore is analyzed for chromium and found to contain 0.560 mg Cr_2O_3. Express the concentration of Cr_2O_3 in the sample as (a) percent, (b) parts per thousand, and (c) parts per million.

29. How many grams NaCl should be weighed out to prepare 1 L of a 100-mg/L solution of (a) Na^+ and (b) Cl^-?

30. You have a 250-mg/L solution of K^+ as KCl. You wish to prepare from this a 0.00100 *M* solution of Cl^-. How many milliliters must be diluted to 1 L?

31. One liter of a 500-mg/L solution of $KClO_3$ contains how many grams K^+?

DILUTION CALCULATIONS

32. A 12.5-mL portion of a solution is diluted to 500 mL, and its molarity is determined to be 0.125. What is the molarity of the original solution?

33. What volume of 0.50 *M* H_2SO_4 must be added to 65 mL of 0.20 *M* H_2SO_4 to give a final solution of 0.35 *M*? Assume volumes are additive.

34. How many milliliters of 0.10 *M* H_2SO_4 must be added to 50 mL of 0.10 M NaOH to give a solution that is 0.050 *M* in H_2SO_4? Assume volumes are additive.

35. You are required to prepare working standard solutions of 1.00×10^{-5}, 2.00×10^{-5}, 5.00×10^{-5}, and 1.00×10^{-4} *M* glucose from a 0.100 *M* stock solution. You have available 100-mL volumetric flasks and pipets of 1.00-, 2.00-, 5.00-, and 10.00-mL volume. Outline a procedure for preparing the working standards.

36. A 0.500-g sample is analyzed spectrophotometrically for manganese by dissolving it in acid and transferring to a 250-mL flask and diluting to volume. Three aliquots are analyzed by transferring 50-mL portions with a pipet to 500-mL Erlenmeyer flasks and reacting with an oxidizing agent, potassium peroxydisulfate, to convert the manganese to permanganate. After reaction, these are quantitatively transferred to 250-mL volumetric flasks, diluted to volume, and measured spectrophotometrically. By comparison with standards, the average concentration in the final solution is determined to be 1.25×10^{-5} *M*. What is the percent manganese in the sample?

37. A stock solution of analyte is made by dissolving 34.83 mg of copper (II) acetate hexahydrate (fw = 289.73 g/mol) in 25.00 mL of water. A second stock solution of internal standard is made by dissolving 28.43 mg of germanium (I) acetate (fw = 190.74 g/mol) into 25.00 mL of water. These solutions are used to make a series of standards for flame atomic absorption analysis calibration. The standard solutions (each 10.00 mL total volume) should have the following concentrations of copper: 10.00; 25.00; 50.00; 100.0; and 200.0 μM. Each calibration solution should also contain 50.00 μM of germanium.

What is the analyte stock solution concentration? What is the internal standard stock solution concentration?

Complete this table.

Concentration Cu (μM)	Volume of analyte stock (mL)	Volume of internal standard stock (mL)	Volume of diluent (mL)	Total Volume (mL)
10.00				10.00
25.00				10.00
50.00				10.00
100.0				10.00
200.0				10.00

PROFESSOR's FAVORITE PROBLEM

Contributed by Professor Wen-Yee Lee, The University of Texas at El Paso

38. Tom, an analytical chemist, bought a bag of decaffeinated coffee from a grocery store. However, Tom suspected that he might have received regular coffee and therefore decided to analyze his coffee for caffeine. In the lab, he took 0.5 mL of the brewed coffee and diluted it in water to make a 100.0 mL solution. He performed four analyses and found the concentrations to be 4.69, 3.99, 4.12, and 4.50 mg/L, respectively. (Assume the density of all solutions is 1.000 g/mL, 1 oz = 28.35 mL).

(a) Report the concentration (in mg/L) of caffeine in the brewed coffee using the format as average ± standard deviation. (Note this is not the concentration in the diluted solution.)

(b) Look up the caffeine content of regular vs. decaffeinated coffee. Do you think that Tom was given the wrong type of coffee?

(c) Caffeine intake of 300 mg per day reportedly has no adverse effects in the vast majority of the adult population. If Tom drinks 3 cups (8 oz/cup) of this coffee daily, is his intake within this known safe zone?

STANDARDIZATION CALCULATIONS

39. A preparation of soda ash is known to contain 98.6% Na_2CO_3. If a 0.678-g sample requires 36.8 mL of a sulfuric acid solution for complete neutralization, what is the molarity of the sulfuric acid solution?

40. A 0.1 *M* sodium hydroxide solution is to be standardized by titrating primary standard sulfamic acid (NH_2SO_3H). What weight of sulfamic acid should be taken so that the volume of NaOH delivered from the buret is about 40 mL?

ANALYSIS CALCULATIONS

41. A sample of USP-grade citric acid ($H_3C_6H_5O_7$, three titratable protons) is analyzed by titrating with 0.1087 *M* NaOH. If a 0.2678-g sample requires 38.31 mL for titration, what is the purity of the preparation? USP specification requires 99.5%.

42. Calcium in a 200-µL serum sample is titrated with 1.87×10^{-4} *M* EDTA solution, requiring 2.47 mL. What is the calcium concentration in the blood in mg/dL?

43. A 0.372-g sample of impure $BaCl_2 \cdot 2H_2O$ is titrated with 0.100 *M* $AgNO_3$, requiring 27.2 mL. Calculate (a) the percent Cl in the sample and (b) the percent purity of the compound.

44. An iron ore is analyzed for iron content by dissolving in acid, converting the iron to Fe^{2+}, and then titrating with standard 0.0150 *M* $K_2Cr_2O_7$ solution. If 35.6 mL is required to titrate the iron in a 1.68-g ore sample, how much iron is in the sample, expressed as percent Fe_2O_3? (See Example 5.31 for the titration reaction.)

45. Calcium in a 2.00-g sample is determined by precipitating CaC_2O_4, dissolving this in acid, and titrating the oxalate with 0.0200 *M* $KMnO_4$. What percent of CaO is in the sample if 35.6 mL $KMnO_4$ is required for titration? (The reaction is $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$.)

46. A potassium permanganate solution is prepared by dissolving 4.68 g $KMnO_4$ in water and diluting to 500 mL. How many milliliters of this will react with the iron in 0.500 g of an ore containing 35.6% Fe_2O_3? (See Example 5.30 for the titration reaction.)

47. A sample contains $BaCl_2$ plus inert matter. What weight must be taken so that when the solution is titrated with 0.100 $AgNO_3$, the milliliters of titrant will be equal to the percent $BaCl_2$ in the sample?

48. A 0.250-g sample of impure $AlCl_3$ is titrated with 0.100 *M* $AgNO_3$, requiring 48.6 mL. What volume of 0.100 *M* EDTA would react with a 0.350-g sample? (EDTA reacts with Al^{3+} in a 1:1 ratio.)

49. A 425.2-mg sample of a purified monoprotic organic acid is titrated with 0.1027 *M* NaOH, requiring 28.78 mL. What is the formula weight of the acid?

50. The purity of a 0.287-g sample of $Zn(OH)_2$ is determined by titrating with a standard HCl solution, requiring 37.8 mL. The HCl solution was standardized by precipitating AgCl in a 25.0-mL aliquot and weighing (0.462 g AgCl obtained). What is the purity of the $Zn(OH)_2$?

51. A sample of pure $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ (three replaceable hydrogens) requires 46.2 mL of 0.100 *M* NaOH for titration. How many milliliters of 0.100 *M* $KMnO_4$ will the same-size sample react with? (See Problem 45 for reaction with $KMnO_4$.)

BACK-TITRATIONS

52. A 0.500-g sample containing Na_2CO_3 plus inert matter is analyzed by adding 50.0 mL of 0.100 *M* HCl, a slight excess, boiling to remove CO_2, and then back-titrating the excess acid with 0.100 *M* NaOH. If 5.6 mL NaOH is required for the back-titration, what is the percent Na_2CO_3 in the sample?

53. A hydrogen peroxide solution is analyzed by adding a slight excess of standard $KMnO_4$ solution and back-titrating the unreacted $KMnO_4$ with standard Fe^{2+} solution. A 0.587-g sample of the H_2O_2 solution is taken, 25.0 mL of 0.0215 M $KMnO_4$ is added, and the back-titration requires 5.10 mL of 0.112 *M* Fe^{2+} solution. What is the percent H_2O_2 in the sample? (See Examples 5.26 and 5.30 for the reactions.)

54. The sulfur content of an iron pyrite ore sample is determined by converting it to H_2S gas, absorbing the H_2S in 10.0 mL of 0.00500 *M* I_2, and then back-titrating the excess I_2 with 0.00200 *M* $Na_2S_2O_3$. If 2.6 mL $Na_2S_2O_3$ is required for the titration, how many milligrams of sulfur are contained in the sample? Reactions:

$$H_2S + I_2 \rightarrow S + 2I^- + 2H^+$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

TITER

55. Express the titer of a 0.100 *M* EDTA solution in mg BaO/mL.

56. Express the titer of a 0.0500 *M* $KMnO_4$ solution in mg Fe_2O_3/mL.

57. The titer of a silver nitrate solution is 22.7 mg Cl/mL. What is its titer in mg Br/mL?

EQUIVALENT WEIGHT CALCULATIONS

58. Calculate the equivalent weights of the following substances as acids or bases: (a) HCl, (b) $Ba(OH)_2$, (c) $KH(IO_3)_2$, (d) H_2SO_3, (e) CH_3COOH.

59. Calculate the molarity of a 0.250 eq/L solution of each of the acids or bases in Problem 58.

EQUIVALENT WEIGHT

60. Calculate the equivalent weight of KHC_2O_4 (a) as an acid and (b) as a reducing agent in reaction with MnO_4^- ($5HC_2O_4^- + 2MnO_4^- + 11H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$).

61. Mercuric oxide, HgO, can be analyzed by reaction with iodide and then titration with an acid: $HgO + 4I^- \rightarrow HgI_4^{2-} + 2OH^-$. What is its equivalent weight?

62. Calculate the grams of one equivalent each of the following for the indicated reaction: (a) $FeSO_4$ ($Fe^{2+} \rightarrow Fe^{3+}$), (b) H_2S ($\rightarrow S^0$), (c) H_2O_2 ($\rightarrow O_2$), (d) H_2O_2 ($\rightarrow H_2O$).

63. $BaCl_2 \cdot 2H_2O$ is to be used to titrate Ag^+ to yield AgCl. How many milliequivalents are contained in 0.5000 g $BaCl_2 \cdot 2H_2O$?

EQUIVALENTS/L (eq/L)

64. A solution is prepared by dissolving 7.82 g NaOH and 9.26 g $Ba(OH)_2$ in water and diluting to 500 mL. What is the concentration of the solution as a base in eq/L?

65. What weight of arsenic trioxide, As_2O_3, is required to prepare 1 L of 0.1000 eq/L arsenic(III) solution (arsenic As^{3+} is oxidized to As^{5+} in redox reactions)?

66. If 2.73 g $KHC_2O_4 \cdot H_2C_2O_4$ (three ionizable protons) having 2.0% inert impurities and 1.68 g $KHC_8H_4O_4$ (one ionizable proton) are dissolved in water and diluted to 250 mL, what is the concentration of the solution as an acid in eq/L, assuming complete ionization?

67. A solution of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ (three replaceable hydrogens) is 0.200 eq/L as an acid. What is its concentration in eq/L as reducing agent? (See Problem 45 for its reaction as a reducing agent.)

68. $Na_2C_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ are mixed in such a proportion by weight that the concentration of the resulting solution as a reducing agent in eq/L is 3.62 times the concentration as an acid in eq/L. What is the proportion? (See Problem 45 for its reaction as a reducing agent.)

69. What weight of $K_2Cr_2O_7$ is required to prepare 1.000 L of 0.1000 eq/L solution? (It reacts as: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^3 + 7H_2O$.)

CHARGE EQUIVALENT CALCULATIONS

70. A chloride concentration is reported as 300 mg/dL. What is the concentration in meq/L?

71. A calcium concentration is reported as 5.00 meq/L. What is the concentration in mg/dL?

72. A urine specimen has a chloride concentration of 150 meq/L. If we assume that the chloride is present in urine as sodium chloride, what is the concentration of NaCl in g/L?

GRAVIMETRIC CALCULATIONS

73. What weight of manganese is present in 2.58 g of Mn_3O_4?

74. Zinc is determined by precipitating and weighing as $Zn_2Fe(CN)_6$.
(a) What weight of zinc is contained in a sample that gives 0.348 g precipitate?
(b) What weight of precipitate would be formed from 0.500 g of zinc?

75. Calculate the gravimetric factors for:

Substance Sought	Substance Weighed
Mn	Mn_3O_4
Mn_2O_3	Mn_3O_4
Ag_2S	$BaSO_4$
$CuCl_2$	AgCl
MgI_2	PbI_2

PROFESSOR's FAVORITE PROBLEM

Contributed by Professor Thomas L. Isenhour, Old Dominion University

76. A 10.00 g sample contains only NaCl and KCl. The sample is dissolved and $AgNO_3$ is added to precipitate AgCl. After the precipitate is washed and dried, it weighs 21.62 g. What is the weight percent of NaCl in the original sample?

Recommended References

1. T. P. Hadjiioannou, G. D. Christian, C. E. Efstathiou, and D. Nikolelis, *Problem Solving in Analytical Chemistry*. Oxford: Pergamon, 1988.
2. Q. Fernando and M. D. Ryan, *Calculations in Analytical Chemistry*. New York: Harcourt Brace Jovanovich, 1982.

Chapter Six
GENERAL CONCEPTS OF CHEMICAL EQUILIBRIUM

"The worst form of inequality is to try to make unequal things equal."
—Aristotle

Learning Objectives

WHAT ARE SOME OF THE KEY THINGS WE WILL LEARN FROM THIS CHAPTER?

- The equilibrium constant (key equations: 6.12, 6.15), pp. 194
- Calculation of equilibrium concentrations, p. 195
- Using Excel Goal Seek to solve one-variable equations, p. 197
- The systematic approach to equilibrium calculations: mass balance and charge balance equations, p. 204
- Activity and activity coefficients (key equation: 6.19), p. 211
- Thermodynamic equilibrium constants (key equation: 6.23), p. 217

Even though in a chemical reaction the reactants may almost quantitatively react to form the products, reactions *never* go in only one direction. In fact, reactions reach an equilibrium in which the rates of reactions in both directions are equal. In this chapter we review the equilibrium concept and the equilibrium constant and describe general approaches for calculations using equilibrium constants. We discuss the activity of ionic species along with the calculation of activity coefficients. These values are required for calculations using thermodynamic equilibrium constants, that is, for the diverse ion effect, described at the end of the chapter. They are also used in potentiometric calculations (Chapter 13).

6.1 Chemical Reactions: The Rate Concept

In 1863 Guldberg and Waage described what we now call the law of mass action, which states that the rate of a chemical reaction is proportional to the "active masses" of the reacting substances present at any time. The active masses may be concentrations or pressures. Guldberg and Waage derived an equilibrium constant by defining equilibrium as the condition when the rates of the forward and reverse reactions are equal. Consider the chemical reaction

$$aA + bB \rightleftharpoons cC + dD \tag{6.1}$$

According to Guldberg and Waage, the rate of the forward reaction is equal to a constant times the concentration of each species raised to the power of the number of molecules participating in the reaction: that is,[1]

$$\text{Rate}_{fwd} = k_{fwd}[A]^a[B]^b \tag{6.2}$$

where rate_{fwd} is the rate of the forward reaction and k_{fwd} is the **rate constant**, which is dependent on such factors as the temperature and the presence of catalysts. [A] and

[1] [ ] represents moles/liter and here represents the effective concentration. The effective concentration will be discussed under the diverse ion effect, when we talk about activities.

[B] represent the molar concentrations of A and B. Similarly, for the reverse reaction, Guldberg and Waage wrote

$$\text{Rate}_{rev} = k_{rev}[\text{C}]^c[\text{D}]^d \tag{6.3}$$

and for a system at equilibrium, the forward and reverse rates are equal:

At equilibrium, the rate of the reverse reaction equals the rate of the forward reaction.

$$k_{fwd}[\text{A}]^a[\text{B}]^b = k_{rev}[\text{C}]^c[\text{D}]^d \tag{6.4}$$

Rearranging these equations gives the **molar equilibrium constant** (which holds for dilute solutions) for the reaction, K:

$$\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} = \frac{k_{fwd}}{k_{rev}} = K \tag{6.5}$$

The expression obtained here is the correct expression for the equilibrium constant, *but the method of derivation has no general validity*. This is because reaction rates actually depend on the *mechanism* of the reaction, determined by the number of colliding species, whereas the equilibrium constant expression depends only on the *stoichiometry* of the chemical reaction. The sum of the exponents in the rate constant gives the *order* of the reaction, and this may be entirely different from the stoichiometry of the reaction (see Chapter 22). An example is the rate of reduction of $S_2O_8^{2-}$ with I^-:

$$S_2O_8^{2-} + 3I^- \rightarrow 2SO_4^{2-} + I_3^-$$

The rate is actually given by $k_{fwd}[S_2O_8^{2-}][I^-]$ (a second-order reaction) and not $k_{fwd}[S_2O_8^{2-}][I^-]^3$, as might be expected from the balanced chemical reaction (a fourth-order reaction would be predicted). The only sound theoretical basis for the equilibrium constant comes from thermodynamic arguments. See Gibbs free energy in Section 6.3 for the thermodynamic computation of equilibrium constant values.

The value of K can be calculated empirically by measuring the concentrations of A, B, C, and D at equilibrium. Note that the more favorable the rate constant of the forward reaction relative to the backward reaction, the larger will be the equilibrium constant and the farther to the right the reaction will be at equilibrium.

The larger the equilibrium constant, the farther to the right is the reaction at equilibrium.

When the reaction between A and B is initiated, the rate of the forward reaction is large because the concentrations of A and B are large, whereas the backward reaction is slow because the concentrations of C and D are small (that rate is initially zero). As the reaction progresses, concentrations of A and B decrease and concentrations of C and D increase, so that the rate of the forward reaction diminishes while that for the backward reaction increases (Figure 6.1). Eventually, the two rates become equal, and the system is in a state of equilibrium. At this point, the individual concentrations of A, B, C, and D remain constant (the relative values will depend on the reaction stoichiometry, the initial concentrations, and how far the equilibrium lies to the right). However, the system remains in dynamic equilibrium, with the forward and backward reactions continuing at equal rates.

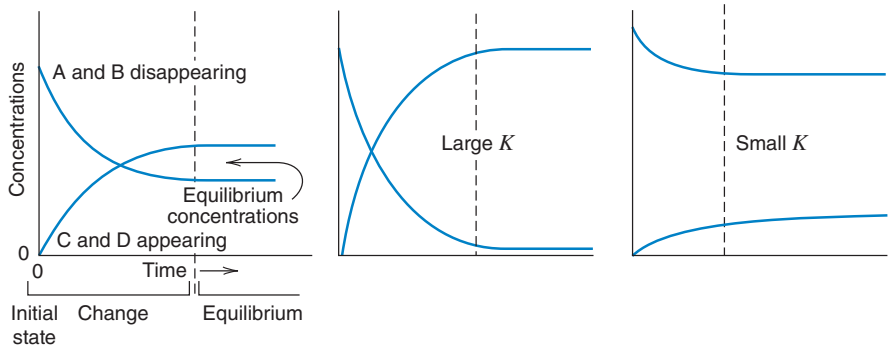


Fig. 6.1. Progress of a chemical reaction.

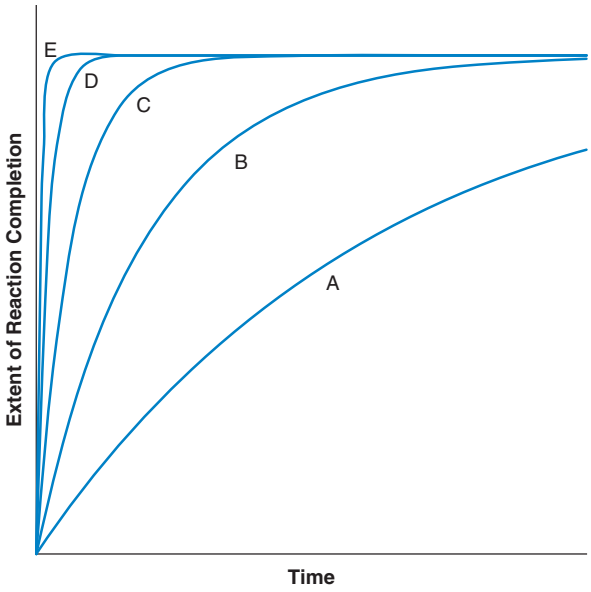


Fig. 6.2. For the same equilibrium constant, the approach to equilibrium is controlled by the kinetics of the reaction, this cannot be predicted *a priori*. Ionic reactions are often instantaneous. Besides these and reactions involving combustion, most other reactions take measurable time. From A–E, at each step, the reaction rate increases by a factor of 3, but the position of equilibrium is not altered. An accelerated reaction rate can be brought about by an appropriate catalyst. Heating will also typically increase the reaction rate, but it may also affect the position of the equilibrium.

You will notice that the equilibrium constant expression is the ratio in which the concentrations of the products appear in the numerator and the concentrations of the reactants appear in the denominator. This is quite arbitrary, but it is the accepted convention. Hence, a large equilibrium constant indicates the equilibrium lies far to the right.

A large equilibrium constant does not assure the reaction will proceed at an appreciable rate.

We should point out that although a particular reaction may have a rather large equilibrium constant, the reaction may proceed from *right* to *left* if sufficiently large concentrations of the *products* are initially present. Also, the equilibrium constant tells us nothing about how *fast* a reaction will proceed toward equilibrium. Some reactions, in fact, may be so slow as to be unmeasurable. The equilibrium constant merely tells us the tendency of a reaction to occur and in what direction, not whether it is fast enough to be feasible in practice. (See Chapter 22 on kinetic methods of analysis for the measurement of reaction rates and their application to analyses.)

For the reaction depicted in Equation 6.1, the rate at which equilibrium is approached will likely be different for either the forward or the reverse reaction. That is, if we start with a mixture of C and D, the rate at which equilibrium is approached may be much slower or faster than for the converse reaction.

Figure 6.2 illustrates the approach to equilibrium at different reaction rates.

6.2 Types of Equilibria

Equilibrium constants may be written for dissociations, associations, reactions, or distributions.

We can write equilibrium constants for virtually any type of chemical process. Some common equilibria are listed in Table 6.1. The equilibria may represent dissociation (acid/base, solubility), formation of products (complexes), reactions

Table 6.1
Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acid dissociation constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

(redox), a distribution between two phases (water and nonaqueous solvent—solvent extraction; adsorption from water onto a surface, as in chromatography, etc.). We will describe some of these equilibria below and in later chapters.

6.3 Gibbs Free Energy and the Equilibrium Constant

The tendency for a reaction to occur is defined thermodynamically from its change in **enthalpy** (ΔH) and **entropy** (ΔS). Enthalpy is the heat absorbed when an endothermic reaction occurs under constant pressure. When heat is given off (exothermic reaction), ΔH is negative. Entropy is a measure of the disorder, or randomness, of a substance or system.

A system will always tend toward lower energy and increased randomness, that is, lower enthalpy and higher entropy. For example, a stone on a hill will tend to roll spontaneously down the hill (lower energy state), and a box of marbles ordered by color will tend to become randomly ordered when shaken. The combined effect of enthalpy and entropy is given by the **Gibbs free energy**, G:

$$G = H - TS \tag{6.6}$$

where T is the absolute temperature in kelvin; G is a measure of the energy of the system, and a system spontaneously tends toward lower energy states. The change in energy of a system at a constant temperature is

$$\Delta G = \Delta H - T\Delta S \tag{6.7}$$

So a process will be *spontaneous when* ΔG *is negative*, will be spontaneous in the reverse direction when ΔG is positive, and will be at equilibrium when ΔG is zero. Hence, a reaction is favored by heat given off (negative ΔH), as in exothermic reactions, and by increased entropy (positive ΔS). Both ΔH and ΔS can be either positive or negative, and the relative magnitudes of each and the temperature will determine whether ΔG will be negative so that the reaction will be spontaneous.

Enthalpy or entropy change alone cannot decide if a process will be spontaneous. Many salts, NH_4Cl for example, spontaneously dissolve in water in an endothermic process (heat is absorbed, the solution gets cold). In such cases, the large positive entropy of dissolution exceeds the positive enthalpy change.

Standard enthalpy H°, standard entropy S°, and standard free energy G° represent the thermodynamic quantities for one mole of a substance at standard state (P = 1 atm, T = 298 K, unit concentration). Then,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6.8}$$

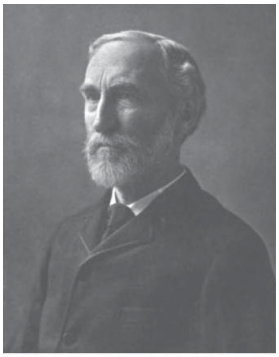
ΔG° is related to the equilibrium constant of a reaction by

$$\boxed{K = e^{-\Delta G^\circ/RT}} \tag{6.9}$$

or

$$\boxed{\Delta G^\circ = -RT \ln K = -2.303RT \log K} \tag{6.10}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}). Hence, if we know the standard free energy of a reaction, we can calculate the equilibrium constant. Obviously, the larger ΔG° (when negative), the larger will be K. Note that while ΔG° and ΔG give information about the spontaneity of a reaction, they say nothing about the *rate* at which it will occur. The reaction between hydrogen and oxygen to form water has a very large negative free energy change associated with it. But at room temperature, in the absence of a catalyst (or a spark!), these gases may coexist together for years without observable reaction.



J. Willard Gibbs (1839–1903) was the founder of chemical thermodynamics. He introduced the concept of free energy, now universally called Gibbs free energy in his honor. The Gibbs free energy relates the tendency of a physical or chemical system to simultaneously lower its energy and increase its disorder, or entropy, in a spontaneous natural process. Gibbs was awarded the first Ph.D. degree in engineering in the United States in 1863 by Yale University (his thesis was on the design of gearing). Albert Einstein, who relied on Gibb's studies of thermodynamics and discoveries in statistical mechanics for his own work, called Gibbs "the greatest mind in American history".

Everything in the universe tends toward increased disorder (increased entropy) and lower energy (lower enthalpy).

A spontaneous reaction results in energy given off and a lower free energy. At equilibrium, the free energy does not change.

A large equilibrium constant results from a large negative free energy change for the reaction in question.

6.4 Le Châtelier's Principle

We can shift an unfavorable equilibrium by increasing the reactant concentration.

The equilibrium concentrations of reactants and products can be altered by applying stress to the system, for example, by changing the temperature, the pressure, or the concentration of one of the reactants. The effects of such changes can be predicted from **Le Châtelier's principle**, which states that when stress is applied to a system at chemical equilibrium, the equilibrium will shift in a direction that tends to relieve or counteract that stress. The effects of temperature, pressure, and concentrations on chemical equilibria are considered below.

6.5 Temperature Effects on Equilibrium Constants

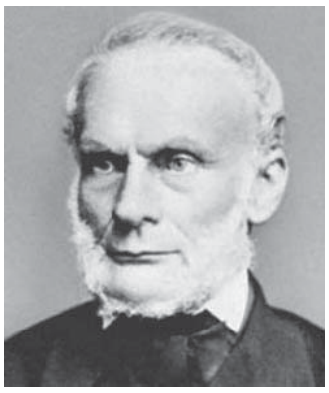
All equilibrium constants are temperature dependent, as are the rates of reactions.

French chemist Henry-Louise Le Châtelier (1850–1936), while working with thermodynamics, devised what became known as Le Châtelier's principle in 1884. This principle states that if a system is in a state of equilibrium and one of the conditions is changed, such as the pressure or temperature, the equilibrium will shift in such a way as to try to restore the original equilibrium condition.

As we have mentioned, temperature influences the individual rate constants for the forward and backward reactions and therefore the equilibrium constant (more correctly, temperature affects the free energy—see Equation 6.10). An increase in temperature will displace the equilibrium in the direction that results in absorbing heat, since this removes the source of the stress. So an endothermic forward reaction (which absorbs heat) will be displaced to the right, with an increase in the equilibrium constant. The reverse will be true for an exothermic forward reaction, which releases heat. An exothermic reaction needs to release heat to proceed, a process that will be hindered at higher temperature. The extent of the displacement will depend on the magnitude of the heat of reaction for the system.

Strictly speaking, enthalpy and entropy changes are not temperature independent. But in most cases it is a reasonable approximation that these are constant over a modest change in temperature, and the change in the equilibrium constant (K_1 at temperature T_1 and K_2 at temperature T_2) can be predicted by the Clausius-Clapeyron equation:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



Rudolf Julius Emanuel Clausius (1822–1888), German physicist and mathematician, was one of the pioneers of thermodynamics. He coined the word *entropy*.

In addition to influencing the position of equilibrium, temperature has a pronounced effect on the rates of the forward and backward reactions involved in the equilibrium, and so it influences the *rate* at which equilibrium is approached. This is because the number and the energy of collisions among the reacting species increase with increasing temperature. The rates of many endothermic reactions increase about two- to threefold for every 10°C rise in temperature. See Figure 6.2.

6.6 Pressure Effects on Equilibria

For solutions, pressure effects are usually negligible.

Pressure can have a large influence on the position of chemical equilibrium for reactions occurring in the gaseous phase. An increase in pressure favors a shift in the direction that results in a reduction in the volume of the system, for example, when one volume of nitrogen reacts with three volumes of hydrogen to produce two volumes of ammonia. But for reactions occurring in solutions, normal pressure changes have a negligible effect on the equilibrium because liquids cannot be compressed the way gases can. Note, however, that above a few atmospheres pressure, even "incompressible" fluids compress somewhat and one can learn about the electronic and mechanical changes to molecules by studying their spectroscopy under such conditions, for example, using high-pressure diamond cells.

6.7 Concentration Effects on Equilibria

Changes in concentration do not affect the equilibrium constant. They *do* affect the position of the equilibrium.

The value of an equilibrium constant is independent of the concentrations of the reactants and products. However, the *position* of equilibrium is very definitely influenced by the concentrations. The direction of change is readily predictable from Le Châtelier's principle. Consider the reaction of iron(III) with iodide:

$$3I^- + 2Fe^{3+} \rightleftharpoons I_3^- + 2Fe^{2+}$$

If the four components are in a state of equilibrium, as determined by the equilibrium constant, addition or removal of one of the components would cause the equilibrium to reestablish itself. For example, suppose we add more iron(II) to the solution. According to Le Châtelier's principle, the reaction will shift to the left to relieve the stress. Equilibrium will eventually be reestablished, and its position will still be defined by the same equilibrium constant.

6.8 Catalysts

Catalysts do not affect the equilibrium constant or the position at equilibrium.

Catalysts either speed up or retard[2] the rate at which an equilibrium is attained by affecting the rates of both the forward and the backward reactions. But catalysts affect both rates to the same extent and thus have no effect on the value of an equilibrium constant. See Figure 6.2.

See Chapter 22 for analytical uses of enzyme catalysts.

Catalysts are very important to the analytical chemist in a number of reactions that are normally too slow to be analytically useful. An example is the use of an osmium tetroxide catalyst to speed up the titration reaction between arsenic(III) and cerium(IV), whose equilibrium is very favorable but whose rate is normally too slow to be useful for titrations. The measurement of the change in the rate of a kinetically slow reaction in the presence of a catalyst can actually be used for determining the catalyst concentration. The same reaction between arsenic(III) and cerium(IV) is catalyzed also by iodide and the measurement of this reaction rate (through the disappearance of the yellow cerium(IV) color) constitutes the basis for what used to be the most widely used (and is still frequently used) method for measuring iodine, also called the Sandell-Kolthoff method. Modern methods used now for iodide include ion chromatography, ICP-MS, and ion-selective electrodes—see later chapters.

6.9 Completeness of Reactions

For quantitative analysis, equilibria should be at least 99.9% to the right for precise measurements. A reaction that is 75% to the right is still a "complete" reaction.

If the equilibrium of a reaction lies sufficiently to the right that the remaining amount of the substance being determined (reacted) is too small to be measured by the measurement technique, we say the reaction has gone to completion. If the equilibrium is not so favorable, then Le Châtelier's principle may be applied to make it so. We may either increase the concentration of a reactant or decrease the concentration of a product. Production of more product may be achieved by (1) allowing a gaseous product to escape, (2) precipitating the product, (3) forming a stable ionic complex of the product in solution, or (4) preferential extraction.

It is apparent from the above discussion that Le Châtelier's principle is the dominant concept behind most chemical reactions in the real world. It is particularly important in biochemical reactions, and external factors such as temperature can have a significant effect on biological equilibria. Catalysts (enzymes) are also key players in many biological and physiological reactions, as we shall see in Chapter 22.

[2]Such "negative catalysts" are generally called inhibitors.

6.10 Equilibrium Constants for Dissociating or Combining Species—Weak Electrolytes and Precipitates

Equilibrium constants are finite when dissociations are less than 100%.

When a substance dissolves in water, it will often partially or completely dissociate or ionize. Electrolytes that tend to dissociate only partially are called *weak electrolytes*, and those that tend to dissociate completely are *strong electrolytes*. For example, acetic acid only partially ionizes in water and is therefore a weak electrolyte. But hydrochloric acid is completely ionized and is therefore a strong electrolyte. (Acid dissociations in water are really proton transfer reactions: $HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$.) Some substances completely ionize in water but have limited solubility; we call these *slightly soluble substances*. Substances may combine in solution to form a dissociable product, for example, a complex. An example is the reaction of copper(II) with ammonia to form the $Cu(NH_3)_4^{2+}$ species.

A weak electrolyte is only partially dissociated. Many slightly soluble substances are strong electrolytes because the portion that dissolves is totally ionized.

The dissociation of weak electrolytes or the solubility of slightly soluble substances can be quantitatively described by equilibrium constants. Equilibrium constants for completely dissolved and dissociated electrolytes are effectively infinite. Consider the dissociating species AB:

$$AB \rightleftharpoons A + B \tag{6.11}$$

The equilibrium constant for such a dissociation can be written generally as

$$\boxed{\frac{[A][B]}{[AB]} = K_{eq}} \tag{6.12}$$

The larger K_{eq}, the greater will be the dissociation. For example, the larger the equilibrium constant of an acid, the stronger will be the acid.

Some species dissociate stepwise, and an equilibrium constant can be written for each dissociation step. A compound A_2B, for example, may dissociate as follows:

$$\boxed{A_2B \rightleftharpoons A + AB \quad K_1 = \frac{[A][AB]}{[A_2B]}} \tag{6.13}$$

$$\boxed{AB \rightleftharpoons A + B \quad K_2 = \frac{[A][B]}{[AB]}} \tag{6.14}$$

Successive stepwise dissociation constants become smaller.

The overall dissociation process of the compound is the sum of these two equilibria:

$$\boxed{A_2B \rightleftharpoons 2A + B \qquad K_{eq} = \frac{[A]^2[B]}{[A_2B]}} \tag{6.15}$$

If we multiply Equations 6.13 and 6.14 together, we arrive at the overall equilibrium constant:

$$\boxed{K_{eq} = K_1K_2 = \frac{[A][AB]}{[A_2B]} \cdot \frac{[A][B]}{[AB]} = \frac{[A]^2[B]}{[A_2B]}} \tag{6.16}$$

When chemical species dissociate in a stepwise manner like this, the successive equilibrium constants generally become progressively smaller. For a diprotic acid (e.g., HOOCCOOH), the dissociation of the second proton is inhibited relative to the

first ($K_2 < K_1$), because the negative charge on the monoanion makes it more difficult for the second proton to ionize. This effect is more pronounced the closer the proton sites are. Note that in equilibrium calculations we always use mol/L for solution concentrations.

If a reaction is written in the reverse, the same equilibria apply, but the equilibrium constant is inverted. Thus, in the above example, for $A + B \rightleftharpoons AB$, $K_{eq(reverse)} = [AB]/([A][B]) = 1/K_{eq(forward)}$. If K_{eq} for the forward reaction is 10^5, $K_{forward} = 1/K_{backward}$ then K_{eq} for the reverse reaction is 10^{-5}.

$K_{forward} = 1/K_{backward}$

Similar concepts apply for combining species, except, generally, the equilibrium constant will be greater than unity rather than smaller, since the reaction is favorable for forming the product (e.g., complex). We will discuss equilibrium constants for acids, complexes, and precipitates in later chapters.

6.11 Calculations Using Equilibrium Constants—Composition at Equilibrium?

Equilibrium constants are useful for calculating the concentrations of the various species in equilibrium, for example, the hydrogen ion concentration from the dissociation of a weak acid. In this section we present the general approach for calculations using equilibrium constants. The applications to specific equilibria are treated in later chapters dealing with these equilibria.

CHEMICAL REACTIONS

It is sometimes useful to know the concentrations of reactants and products in equilibrium in a chemical reaction. For example, we may need to know the amount of reactant for the construction of a titration curve or for calculating the potential of an electrode in the solution. These are, in fact, applications we consider in later chapters. Some example calculations will illustrate the general approach to solving equilibrium problems.

Example 6.1

The chemicals A and B react as follows to produce C and D:

$$A + B \rightleftharpoons C + D \qquad K = \frac{[C][D]}{[A][B]}$$

The equilibrium constant K has a value of 0.30. Assume 0.20 mol of A and 0.50 mol of B are dissolved in 1.00 L, and the reaction proceeds. Calculate the concentrations of reactants and products at equilibrium.

Solution

The initial concentration of A is 0.20 M and that of B is 0.50 M, while C and D are initially 0 M. After the reaction has reached equilibrium, the concentrations of A and B will be decreased and those of C and D will be increased. Let x represent the equilibrium concentration of C or the moles/liter of A and B reacting. Since we get one mole of D with each mole of C, the concentration of D will also be x. We may represent the *initial* concentration of A and B as the **analytical concentrations**, C_A and C_B. The **equilibrium concentrations** are [A] and [B]. The concentrations of A and B will each be diminished by x, that is, $[A] = C_A - x$ and $[B] = C_B - x$. So the equilibrium concentrations are

The equilibrium concentration is the initial (analytical) concentration minus the amount reacted.

This approach to to solving such problems is often called creating an "ICE" diagram. Initial, Change, and Equilibrium conditions are charted to help construct the equilibrium expression to be solved. See for example http://www.youtube.com/user/genchemconcepts#p/a/u/5/LZtVQnILdrE.

	[A]	[B]	[C]	[D]
Initial	0.20	0.50	0	0
Change (x = mmol/mL reacting)	$-x$	$-x$	$+x$	$+x$
Equilibrium	$0.20 - x$	$0.50 - x$	x	x

We can substitute these values in the equilibrium constant expression and solve for x:

$$\frac{(x)(x)}{(0.20-x)(0.50-x)} = 0.30$$

$$x^2 = (0.10 - 0.70x + x^2)0.30$$

$$0.70x^2 + 0.21x - 0.030 = 0$$

ICE diagram for Example 6.1

Concentration, *M*	[A]	[B]	[C]	[D]
Initial	***0.20***	***0.50***	***0.00***	***0.00***
Change	***–x***	***–x***	***+x***	***+x***
Equilibrium	***0.20–x***	***0.50–x***	***x***	***x***

This is a quadratic equation and can be solved algebraically for x using the quadratic formula given in Appendix B (see also Example 6.1 quadratic equation solution .xlsx on the **website** supplement for a quadratic equation solution calculator, also the Chapter 3 Solver **video** for solution of the quadratice equation):

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

$$= \frac{-0.21 \pm \sqrt{(0.21)^2 - 4(0.70)(-0.030)}}{2(0.70)}$$

$$= \frac{-0.21 \pm \sqrt{0.044 + 0.084}}{1.40} = 0.11\,M$$

$$[\mathrm{A}] = 0.20 - x = 0.09\,M$$

$$[\mathrm{B}] = 0.50 - x = 0.39\,M$$

$$[\mathrm{C}] = [\mathrm{D}] = x = 0.11\,M$$

In successive approximations, we begin by taking the analytical concentration as the equilibrium concentration, to calculate the amount reacted. Then we repeat the calculation after subtracting the calculated reacted amount, until it is constant.

Instead of using the quadratic equation, we could also use the **method of successive approximations**. In this procedure, we will first neglect x compared to the initial concentrations to simplify calculations, and calculate an initial value of x. Then we can use this first estimate of x to subtract from C_A and C_B to give an initial estimate of the equilibrium concentration of A and B, and calculate a new x. The process is repeated until x is essentially constant.

First calculation $\quad \dfrac{(x)(x)}{(0.20)(0.50)} = 0.30$

$$x = 0.173$$

The calculations converge more quickly if we keep an extra digit throughout.

Second calculation $\quad \dfrac{(x)(x)}{(0.20-0.173)(0.50-0.173)} = 0.30$

$$x = 0.051$$

Third calculation $\quad \dfrac{(x)(x)}{(0.20-0.051)(0.50-0.051)} = 0.30$

$$x = 0.14_2$$

Fourth calculation $$\frac{(x)(x)}{(0.20-0.142)(0.50-0.142)} = 0.30$$

$$x = 0.079$$

Fifth calculation $$\frac{(x)(x)}{(0.20-0.79)(0.50-0.079)} = 0.30$$

$$x = 0.12_4$$

Sixth calculation $$\frac{(x)(x)}{(0.20-0.124)(0.50-0.124)} = 0.30$$

$$x = 0.093$$

Seventh calculation $$\frac{(x)(x)}{(0.20-0.093)(0.50-0.093)} = 0.30$$

$$x = 0.11_4$$

Eighth calculation $$\frac{(x)(x)}{(0.20-0.114)(0.50-0.114)} = 0.30$$

$$x = 0.10_4$$

Ninth calculation $$\frac{(x)(x)}{(0.20-0.104)(0.50-0.104)} = 0.30$$

$$x = 0.10_7$$

Shorten the number of iterations by taking the average of the first two for the next.

We will take 0.11 as the equilibrium value of x since it essentially repeated the value of the seventh calculation. Note that in these iterations, x oscillates above and below the equilibrium value. The larger x solved for in a particular problem is compared to C, the larger will be the oscillations and the more iterations that will be required to reach an equilibrium value (as in this example—not the best for this approach). There is a more efficient way of completing the iteration. Take the average of the first and second for the third iteration, which should be close to the final value (in this case, 0.11_2). One or two more iterations will tell us we have reached the equilibrium value. Try it! ■

In Example 6.1, appreciable amounts of A remained, even though B was in excess, because the equilibrium constant was not very large. In fact, the equilibrium was only about halfway to the right since C and D were about the same concentration as A. In most reactions of analytical interest, the equilibrium constants are large, and the equilibrium lies far to the right. In these cases, the equilibrium concentrations of reactants that are not in excess are generally very small compared to the other concentrations. This simplifies our calculations.

EXCEL GOAL SEEK FOR ITERATIVE PROBLEM SOLVING

Microsoft Excel™ provides several powerful tools to perform iterative or "trial-and-error" solutions. Frequently only one parameter needs to be solved for in a problem; this is the case for most equilibrium calculations. There may be more than one reactant or product but a single reaction parameter is multiplied by stoichiometric coefficients to calculate change in concentrations of all the reactants and products. In this case, the "Goal Seek" function in Excel is ideal to use; it is already built-in to your Excel

software and nothing needs to be installed. Consider a slightly more challenging version of Example 6.1 where the reaction stoichiometry is

$$\begin{array}{ccccc} A & + & 3B & = & C + 2D \\ 0.2-x & & 0.5-x & & x \quad 2x \end{array}$$

the equilibrium constant being $\frac{[C][D]^2}{[A][B]^3} = 3.00$ and the initial concentrations of A and B being 0.20 and 0.50 *M*, while no C and D are initially present. We construct an ICE diagram on an Excel sheet. A screenshot below shows the formulas in the cells, rather than the values. (We have formatted the numbers in columns B to E to 2 decimals.) Note that a "reaction parameter," equivalent to x in the previous ICE diagram for Example 6.1, is set up in cell G2 with an initial value of 0. (Don't confuse [A] with the column B, etc., in setting formulas.) The changes in cells B4 to E4 are thus noted in terms of G2, and the equilibrium values in cells B5 to E5 are similarly noted in terms of initial values and G2. The equilibrium constant in cell C7 is accordingly expressed in terms of the equilibrium values.

	A	B	C	D	E	F	G
1	Concentration, M	[A]	[B]	[C]	[D]		Change
2							0
3	Initial	0.20	0.50	0.00	0.00		
4	Change	=-G2	=-3*G2	=G2	=2*G2		
5	Equilibrium	=B3+B4	=C3+C4	=D3+D4	=E3+E4		
6							
7	Equilibrium Constant		=D5*E5^2/(B5*C5^3)				

The actual spreadsheet will not show the formulas and will look like:

	A	B	C	D	E	F	G
1	Concentration, M	[A]	[B]	[C]	[D]		Change
2							0
3	Initial	0.20	0.50	0.00	0.00		
4	Change	0.00	0.00	0.00	0.00		
5	Equilibrium	0.20	0.50	0.00	0.00		
6							
7	Equilibrium Constant		0.00				

Now put your cursor on cell C7 (the equilibrium constant expression), which is known to be 3.00 but presently reads zero. Click on the data tab. [This and following instructions pertain to Excel 2010 and will be slightly different for other versions. However, the Goal Seek function exists in all versions of Excel and you can go to Excel Help (key F1) and type in Goal Seek; it will give you guidance on how to access this function on your version of Excel. In older versions, it may be under Tools.] Once the Data menu bar opens, locate the "What-If Analysis" submenu and click on it, a drop-down menu will open. Click on Goal Seek. There are three data entry boxes in the Goal Seek operation. These are: "Set Cell," "To Value," and "By changing Cell." Because you had your cursor on C7, the Goal Seek operation will already open with C7 in the "Set Cell" box. If this is not so, type in C7 or the location of your equilibrium constant expression, if you have decided to type it in some other cell. In the "To Value" box, type in the value of the equilibrium constant 3 and type in G2 in the "By changing Cell" box (or when you have clicked on this box, put your cursor on cell G2 and click). Click OK on the Goal Seek box. Voila! You have a solution with all the equilibrium values calculated.

	A	B	C	D	E	F	G
1	Concentration, M	[A]	[B]	[C]	[D]		Change
2							0.0939
3	Initial	0.20	0.50	0.00	0.00		
4	Change	-0.09	-0.28	0.09	0.19		
5	Equilibrium	0.11	0.22	0.09	0.19		
6							
7	Equilibrium Constant		3.00				

You can access the spreadsheets "Practice Goal Seek spreadsheet, Section 6.11, setup.xlsx" and "Practice Goal Seek spreadsheet, Section 6.11, answer.xlsx" in Chapter 6 of the text **website** (Goal Seek problems).

USING GOAL SEEK TO SOLVE AN EQUATION

Goal Seek can solve a single variable polynomial equation if there is a real unique solution to it. Solutions to a quadratic equation will be such a case. Consider that in Example 6.1 we were trying to solve the equation

$$0.70x^2 + 0.21x = 0.03$$

Consider an Excel spreadsheet in which in cell A2, we have the variable x that we wish to vary (presently just zero is entered) and cell B2 the expression of the polynomial we wish to solve is entered in terms of A2. First the formula version is illustrated; then what the spreadsheet will actually look like is shown.

	A	B	C
1	x	poly	
2	0	=.70*A2^2+0.21*A2	

	A	B
1	x	Poly
2	0	0

Next you click on B2, access Goal Seek, set cell B2 to the value of 0.03 and vary cell A2 to get to this goal. You will immediately be rewarded with the solution that $x = 0.10_5$ as shown below.

	A	B	C
1	x	Poly	
2	0.10466	0.029646	

Do note that a nth degree polynomial ultimately has n possible solutions, except that for a real problem only one of them is logically possible. It will be up to you decide if the solution being produced is logically tenable. For example, negative values of x or values greater than 0.2 are not logically possible in the present illustration.

The answer given here is close to the true value. But note that the target value did not quite converge to 0.03. This is a limitation of Goal Seek, and there is a way to get around it, as illustrated and explained below (Shortcomings of Excel-Based Approaches and How to Get Around Them), by multiplying the target equation by a large number, e.g., 10,000, and setting the target value 10,000 larger. Try it. If you do, the target value comes to 0.0300, and the x value is 0.01565, which agrees with

the Solver calculation given in the Chapter 3 **video** and the Example 6.1 Quadratic Equation solution given in the text **website**.

Example 6.2

Assume that in Example 6.1 the equilibrium constant was 2.0×10^{16} instead of 0.30. Calculate the equilibrium concentrations of A, B, C, and D (starting with 0.20 mol A and 0.50 mol B in 1.00 L).

Solution

If the equilibrium constant for a reaction is very large, x is very small compared to the analytical concentration, which simplifies calculations.

Since K is very large, the reaction of A with B will be virtually complete to the right, leaving only traces of A at equilibrium. Let x represent the equilibrium concentration of A. An amount of B equal to A will have reacted to form an equivalent amount of C and D (about 0.20 M for each). We can summarize the equilibrium concentrations as follows:

$$[\mathrm{A}] = x$$

$$[\mathrm{B}] = (0.50 - 0.20) + x = 0.30 + x$$

$$[\mathrm{C}] = 0.20 - x$$

$$[\mathrm{D}] = 0.20 - x$$

Or, looking at the equilibrium,

$$\begin{array}{ccccccccc} \mathrm{A} & + & \mathrm{B} & \rightleftharpoons & \mathrm{C} & + & \mathrm{D} \\ x & & 0.30 + x & & 0.20 - x & & 0.20 - x \end{array}$$

Basically, we have said that all of A is converted to a like amount of C and D, except for a small amount x. Now x will be very small compared to 0.20 and 0.30 and can be neglected. So we can say

$$[\mathrm{A}] = x$$

$$[\mathrm{B}] \approx 0.30$$

$$[\mathrm{C}] \approx 0.20$$

$$[\mathrm{D}] \approx 0.20$$

The only unknown concentration is [A]. Substituting these numbers in the equilibrium constant expression, we have

$$\frac{(0.20)(0.20)}{(x)(0.30)} = 2.0 \times 10^{16}$$

$$x = [\mathrm{A}] = 6.7 \times 10^{-18} M \text{ (usually analytically undetectable)}$$

■

Neglect x compared to C (product) if $C \leq 0.01 K_{eq}$ in a reaction.

In this case the calculation was considerably simplified by neglecting x in comparison to other concentrations. If x should turn out to be significant compared to these concentrations, then the solution should be reworked using the quadratic formula, or Goal Seek. **Generally, if the value of x is less than about 5% of the assumed concentration, it can be neglected**. In this case, the error in x itself is usually 5% or less. **This simplification will generally hold if the product concentration is less than 1% at K_{eq}, that is $\leq 0.01\ K_{eq}$.** However, once you have mastered using Excel, especially its Goal Seek and Solver functions discussed later in the book, (Solver-based

equilibrium calculations are also discussed in reference 8), you may find that it is just as simple or simpler to solve a problem without any approximation using Excel. This is because no judgments on what can or cannot be neglected is needed. A **video** illustrating the use of Goal Seek to solve an equilibrium problem is on the text **website**.

Video: Goal Seek Equilibrium

Example 6.3

A and B react as follows:

$$A + 2B \rightleftharpoons 2C \qquad K = \frac{[C]^2}{[A][B]^2}$$

Assume 0.10 mol of A is reacted with 0.20 mol of B in a volume of 1000 mL; $K = 1.0 \times 10^{10}$. What are the equilibrium concentrations of A, B, and C?

Solution

We have stoichiometrically equal amounts of A and B, so both are virtually all reacted, with trace amounts remaining. Let x represent the equilibrium concentration of A. At equilibrium, we have

A	+	2B	$\rightleftharpoons$	2C
x		$2x$		$0.20 - 2x \approx 0.20$

For each mole of A that either reacts (or is produced), we produce (or remove) two moles of C, and consume (or produce) two moles of B. Substituting into the equilibrium constant expression,

$$\frac{(0.20)^2}{(x)(2x)^2} = 1.0 \times 10^{10}$$

$$\frac{0.040}{4x^3} = 1.0 \times 10^{10}$$

$$x = [A] = \sqrt[3]{\frac{4.0 \times 10^{-2}}{4.0 \times 10^{10}}} = \sqrt[3]{1.0 \times 10^{-12}} = 1.0 \times 10^{-4} M$$

$$B = 2x = 2.0 \times 10^{-4} M$$

(analytically detectable, but not appreciable compared to the starting}?> concentration)

DISSOCIATION EQUILIBRIA

Calculations involving dissociating species are not much different from the example just given for chemical reactions.

Example 6.4

Calculate the equilibrium concentrations of A and B in a 0.10 M solution of a weak electrolyte AB with an equilibrium constant of 3.0×10^{-6}.

Solution

$$AB \rightleftharpoons A + B \qquad K_{eq} = \frac{[A][B]}{[AB]}$$

Both [A] and [B] are unknown and equal. Let x represent their equilibrium concentrations. The concentration of AB at equilibrium is equal to its initial analytical concentration minus x.

$$\begin{array}{ccccc} \text{AB} & & \rightleftharpoons & \text{A} + & \text{B} \\ 0.10 - x & & & x \quad & x \end{array}$$

In a dissociation, neglect x compared to the initial concentration C if $C \geq 100K_{eq}$ in a dissociation.

The value of K_{eq} is quite small, so we are probably justified in neglecting x compared to 0.10. Otherwise, we will have to use a quadratic equation. Substituting into the K_{eq} expression,

$$\frac{(x)(x)}{0.10} = 3.0 \times 10^{-6}$$

$$x = [\text{A}] = [\text{B}] = \sqrt{3.0 \times 10^{-7}} = 5.5 \times 10^{-4} M$$

After the calculation is done, check if the approximation you made was valid. Here the calculated value of x can indeed be neglected compared to 0.10. ■

SHORTCOMINGS OF EXCEL-BASED APPROACHES AND HOW TO GET AROUND THEM

Goal Seek and Solver functions in Excel attempt to achieve convergence to some specified value by varying the value(s) of some other parameters. Because of quirks built into the software, convergence to the specified value is judged in terms of absolute difference rather than relative difference. For example, if you are using Goal Seek to converge to a value of 3×10^{-6}, the software may regard that reaching zero is close enough. (If you were an accountant and counting pennies, this may indeed be close enough, but this is not the case in most scientific problems.) Now let us consider Example 6.4. Without any approximation, the equation that you need to solve is:

$$\frac{x^2}{0.10 - x} = 3.0 \times 10^{-6}$$

One advantage of solving such a problem in Excel is that we do not really need to make a nice equation in one line out of this; we can put in the variable x as being in the cell A2 and then write the expression on the left-hand side of the above equation in cell B2 as shown below.

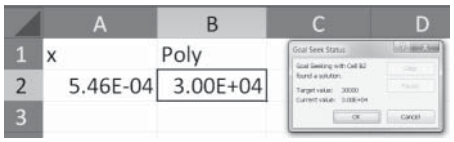
	A	B	C
1	x	Poly	
2	0.00E+00	=A2^2/(0.10-A2)	

If you now go through the Goal Seek exercise by setting cell B2 to 3E-6 (a shorthand notation for writing 3×10^{-6} in Excel) by changing cell A2, you will find that it says it found a solution but in fact it did not change anything! That is, the answer in cell A2 is 0.00E+00, still zero. This is because the software mistakenly believes that for your purposes 0 is close enough to 3×10^{-6}. Consider that we multiply both sides of the above equation with the same large number, say 10^{10}, so that the equation now is

$$10^{10} \times \frac{x^2}{0.10 - x} = 3.0 \times 10^{4}$$

In the Excel spreadsheet in cell B2 we have to put in a 1E10 multiplier before the rest of the expression. Of course, mathematically there is no difference between the two equations and solutions to either will produce the same correct value of x. From the software's point of view, however, you will now want the convergence value to be

3×10^4. If you go through the Goal Seek exercise again (setting the new expression in cell B2 to attain a value of 3E4 by varying A2), you will see that this time it does work, giving you the correct solution for x as 5.5E-4.



You can see the spreadsheet setup and the answer in the text **website** (Goal Seek problems).

6.12 The Common Ion Effect—Shifting the Equilibrium

Equilibria can be markedly affected by adding one or more of the species present, as is predicted from Le Châtelier's principle. Example 6.5 illustrates this principle.

Example 6.5

Assume that A and B are an ion pair, which can dissociate into A (a cation) and B (an anion). Recalculate the concentration of A in Example 6.4, assuming that the solution also contains 0.20 M B.

Solution

We can represent the equilibrium concentration as follows:

	[AB]	[A]	[B]
Initial	0.10	0	0.20
Change (x = mmol/mL of AB dissociated)	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	$0.20 + x$
	≈ 0.10		≈ 0.20

The value of x will be smaller now than before because of the common ion effect of B, so we can certainly neglect it compared to the initial concentrations. Substituting in the equilibrium constant expression,

$$\frac{(x)(0.20)}{(0.10)} = 3.0 \times 10^{-6}$$

$$x = 1.5 \times 10^{-6} M$$

The concentration of A was decreased nearly 400-fold. ■

Adjusting the pH is a common way of shifting the equilibrium.

The common ion effect can be used to make analytical reactions more favorable or quantitative. The adjustment of acidity, for example, is frequently used to shift equilibria. Titrations with potassium dichromate, for example, are favored in acid solution, since protons are consumed in the reaction. Titrations with iodine, a weak oxidizing agent, are usually done in slightly alkaline solution to shift the equilibrium toward completion of the reaction, for example, in titrating arsenic(III):

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2I^- + 2H^+$$

6.13 SYSTEMATIC APPROACH TO EQUILIBRIUM CALCULATIONS — HOW TO SOLVE ANY EQUILIBRIUM PROBLEM

Now that some familiarity has been gained with equilibrium problems, we will consider a systematic approach for calculating equilibrium concentrations that will work with all equilibria, no matter how complex. It consists of identifying the unknown concentrations involved and *writing a set of simultaneous equations equal to the number of unknowns*. Simplifying assumptions are made with respect to relative concentrations of species (not unlike the approach we have already taken) to shorten the solving of the equations. This approach involves writing expressions for **mass balance** of species and one for **charge balance** of species as part of our equations. We will first describe how to arrive at these expressions.

MASS BALANCE EQUATIONS

The principle of mass balance is based on the law of mass conservation, and it states that the number of atoms of an element remains constant in chemical reactions because no atoms are produced or destroyed. The principle is expressed mathematically by equating the concentrations, usually in molarities. The equations for all the pertinent chemical equilibria are written, from which appropriate relations between species concentrations are written.

Example 6.6

Write the equation of mass balance for a 0.100 M solution of acetic acid.

Solution

The equilibria are

$$HOAc \rightleftharpoons H^+ + OAc^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

In a mass balance, the analytical concentration is equal to the sum of the concentrations of the equilibrium species derived from the parent compound (or an appropriate multiple).

We know that the analytical concentration of acetic acid is equal to the sum of the equilibrium concentrations of all its species:

$$C_{HOAc} = [HOAc] + [OAc^-] = 0.100\,M$$

A second mass balance expression may be written for the equilibrium concentration of H^+, which is derived from both HOAc and H_2O. We obtain one H^+ for each OAc^- and one for each OH^-:

$$[H^+] = [OAc^-] + [OH^-]$$

Example 6.7

Write the equations of mass balance for a $1.00 \times 10^{-5} M [Ag(NH_3)_2]Cl$ solution.

Solution

The equilibria are

$$[Ag(NH_3)_2]Cl \rightarrow Ag(NH_3)_2^+ + Cl^-$$

$$Ag(NH_3)_2^+ \rightleftharpoons Ag(NH_3)^+ + NH_3$$

$$Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

The Cl^- concentration is equal to the concentration of the salt that dissociated, that is, $1.00 \times 10^{-5} M$. Likewise, the sum of the concentrations of all silver species is equal to the concentration of Ag in the original salt that dissociated:

$$C_{Ag} = [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] = [Cl^-] = 1.00 \times 10^{-5} M$$

We have the following nitrogen-containing species:

$$NH_4^+ \quad NH_3 \quad Ag(NH_3)^+ \quad Ag(NH_3)_2^+$$

The concentration of N from the last species is twice the concentration of $Ag(NH_3)_2^+$. For this species, the concentration of the nitrogen is twice the concentration of the $Ag(NH_3)_2^+$, since there are two NH_3 per molecule. Hence, we can write

$$C_{NH_3} = [NH_4^+] + [NH_3] + [Ag(NH_3)^+] + 2[Ag(NH_3)_2^+] = 2.00 \times 10^{-5} M$$

Finally, we can write

$$[OH^-] = [NH_4^+] + [H^+]$$

Some of the equilibria and the concentrations derived from them may be insignificant compared to others and may not be needed in subsequent calculations. ■

We have seen that several mass balance expressions may be written. Some may not be needed for calculations (we may have more equations than unknowns), or some may be simplified or ignored due to the small concentrations involved compared to others. This will become apparent in the equilibrium calculations below.

CHARGE BALANCE EQUATIONS

According to the **principle of electroneutrality**, all solutions are electrically neutral; that is, there is no solution containing a detectable excess of positive or negative charge because the sum of the positive charges equals the sum of negative charges. We may write a *single* charge balance equation for a given set of equilibria.

Example 6.8

Write a charge balance equation for a solution of H_2CO_3.

Solution

The equilibria are

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

In a charge balance, the sum of the charge concentration of cationic species equals the sum of charge concentration of the anionic species in equilibrium.

Dissociation of H_2CO_3 gives H^+ and two anionic species, HCO_3^- and CO_3^{2-}, and that of water gives H^+ and OH^-. The amount of H^+ from that portion of *completely* dissociated H_2CO_3 is equal to twice the amount of CO_3^{2-} formed, and from *partial* (first step) dissociation is equal to the amount of HCO_3^- formed. That is, for each CO_3^{2-} formed, there are $2\,H^+$; for each HCO_3^- formed, there is $1\,H^+$; and for each OH^- formed, there is $1\,H^+$. Now, for the singly charged species, the *charge*

The charge concentration is equal to the molar concentration times the charge of a species.

concentration is identical to the concentration of the *species*. But for CO_3^{2-}, the charge concentration is twice the concentration of the species, so we must multiply the CO_3^{2-} concentration by 2 to arrive at the charge concentration from it. According to the principle of electroneutrality, positive charge concentration must equal the negative charge concentration. Hence,

$$[H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]$$

Note that while there may be more than one source for a given species (H^+ in this case), the total charge concentrations from all sources is always equal to the net equilibrium concentration of the species multiplied by its charge.

Example 6.9

Here, we neglect the dissociation of water. However, to be comprehensive, you can always include the formation of H^+ and OH^- from water in the charge balance expression for an aqueous system. Incorporating ions derived from the dissociation of water becomes more important as the concentration of other ions in the solutions decrease, i.e., it is more important in very dilute solutions. The pH of 10^{-3} *M* HCl can be correctly calculated, for example without taking into account the dissociation of water but the pH of 10^{-6} *M* HCl cannot.

Write a charge balance expression for a solution containing KCl, $Al_2(SO_4)_3$, and KNO_3. Neglect the dissociation of water.

Solution

$$[K^+] + 3[Al^{3+}] = [Cl^-] + 2[SO_4^{2-}] + [NO_3^-]$$

Example 6.10

Write a charge balance equation for a saturated solution of $CdCO_3$.

Solution

The equilibria are

$$CdCO_3 \rightleftharpoons Cd^{2+} + CO_3^{2-}$$
$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$
$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Again, the charge concentration for the singly charged species (H^+, OH^-, HCO_3^-) will be equal to the concentrations of the species. But for Cd^{2+} and CO_3^{2-} the charge concentration will be twice their concentrations. We must again equate the positive and negative charge concentrations.

$$2[Cd^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]$$

Example 6.11

Write a charge balance equation for Example 6.7.

Solution

$$[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] + [NH_4^+] + [H^+] = [Cl^-] + [OH^-]$$

Since all are singly charged species, the charge concentrations are equal to the molar concentrations.

EQUILIBRIUM CALCULATIONS USING THE SYSTEMATIC APPROACH—THE STEPS

We may now describe the systematic approach for calculating equilibrium concentrations in problems involving several equilibria. The basic steps can be summarized as follows:

In the systematic approach, a series of equations equal in number to the number of unknown species is written. These are simultaneously solved, using approximations to simplify.

1. Write the chemical reactions appropriate for the system.
2. Write the equilibrium constant expressions for these reactions.
3. Write all the mass balance expressions.
4. Write the charge balance expression.
5. Count the number of chemical species involved and the number of *independent* equations (from steps 2, 3, and 4). If the number of equations is greater than or equal to the number of chemical species, then a solution is possible. At this point, it is possible to proceed to an answer.
6. Make simplifying assumptions concerning the relative concentrations of chemical species. At this point you need to think like a chemist so that the *math* will be simplified.
7. Calculate the answer.
8. Check the validity of your assumptions!

Let us examine one of the examples worked before, but using this approach.

Example 6.12

Repeat the problem stated in Example 6.4 using the systematic approach outlined above.

Chemical reactions

$$AB = A + B$$

Equilibrium constant expressions

Use equilibrium constant expressions plus mass and charge balance expressions to write the equations.

$$K_{eq} = \frac{[A][B]}{[AB]} = 3.0 \times 10^{-6} \quad (1)$$

Mass balance expressions

$$C_{AB} = [AB] + [A] = 0.10\ M \quad (2)$$

$$[A] = [B] \quad (3)$$

Remember that C represents the total analytical concentration of AB.

Charge balance expression

There is none because none of the species is charged.

Number of expressions versus number of unknowns

There are three unknowns ([AB], [A], and [B]) and three expressions (one equilibrium and two mass balance).

Use the same rules as before for simplifying assumptions ($C_A \geq 100K_{eq}$ for dissociations, $C \leq 0.01K_{eq}$ for reactions).

Simplifying assumptions: We want the equilibrium concentrations of A, B, and AB. Because K is small, very little AB will dissociate, so from (2):

$$[AB] = C_{AB} - [A] = 0.10 - [A] \approx 0.10\,M$$

Calculate

[AB] was found above.

[A] can be found from (1) and (3).

$$\frac{[A][B]}{0.10} = 3.0 \times 10^{-6}$$

$$[A] = \sqrt{3.0 \times 10^{-7}} = 5.5 \times 10^{-4} M$$

[B] can be found from (3):

$$[B] = [A] = 5.5 \times 10^{-4} M$$

Check

$$[AB] = 0.10 - 5.5 \times 10^{-4} = 0.10\,M \text{ (within significant figures)}$$

The systematic approach is applicable to multiple equilibria.

You see that the same answer was obtained as when the problem was worked intuitively as in Example 6.4. You may think that the systematic approach is excessively complicated and formal. For this extremely simple problem that may be a justified opinion. However, you should realize that the systematic approach will be applicable to *all* equilibrium calculations, regardless of the difficulty of the problem. You may find problems involving multiple equilibria and/or many species to be hopelessly complicated if you use only an intuitive approach. Nevertheless, you should also realize that a good intuitive "feel" for equilibrium problems is an extremely valuable asset. You should attempt to improve your intuition concerning equilibrium problems. Such intuition comes from experience gained by working a number of problems of different varieties. As you gain experience you will be able to shorten some of the formalism of the systematic approach, and you will find it easier to make appropriate simplifying assumptions. Although need for making approximations may no longer exist, the ability to set up the charge balance and mass balance equations is needed even if you use an Excel-based approach to solve the problem.

6.14 Some Hints for Applying the Systematic Approach for Equilibrium Calculations

Mass balances:

1. One will be for the total analytical concentration of the main parent species.
2. Others will be for species of interest, e.g., H^+ and other (dissociated) species in equilibrium.

Charge balances:

1. Charge balance equations are simply adding all cationic species on one side and all anionic species on the other, each multiplied by the respective charges.
2. Both mass and charge balance equations are rarely needed for solving the equilibrium calculations; in the case of ionic equilibria, charge balance equations are often easier to write.

Solving the equilibrium concentrations:

1. Using simplifying assumptions, at least one of the equilibrium species concentrations can be estimated.
2. From (substituting) this, the other species can be calculated.

Follow the rules given after Example 6.11.

Example 6.13

Repeat the problem outlined in Example 6.5 using the systematic approach. Assume the charge on A is +1, the charge on B is −1, and that the extra B (0.20 *M*) comes from MB; MB is completely dissociated.

Solution

Chemical reactions

$$AB = A^+ + B^-$$

$$MB \rightarrow M^+ + B^-$$

Equilibrium expressions

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = 3.0 \times 10^{-6} \quad (1)$$

Mass balance expressions

$$C_{AB} = [AB] + [A^+] = 0.10\ M \quad (2)$$

$$[B^-] = [A^+] + [M^+] = [A^+] + 0.20\ M \quad (3)$$

Charge balance expression

$$[A^+] + [M^+] = [B^-] \quad (4)$$

Number of expressions versus number of unknowns

There are three unknowns ([AB], $[A^+]$, and $[B^-]$; the concentration of M^+ is known to be 0.20 *M*) and three independent expressions (one equilibrium and two mass balance; the charge balance is the same as the second mass balance).

Both mass and charge balance equations are often not needed. Both are needed, however, to derive the shape of titration curve.

Simplifying assumptions

(i) Because K_{eq} is small, very little AB will dissociate, so from (2).

$$[AB] = 0.10 - [A^+] \approx 0.10M$$

(ii) $[A] \ll [M]$ so from (3) or (4):

$$[B^-] = 0.20 + [A^+] \approx 0.20\ M$$

Calculate

[A] is now found from (1):

$$\frac{[A^+](0.20)}{0.10} = 3.0 \times 10^{-6}$$

$$[A^+] = 1.5 \times 10^{-6} M$$

Check

(i) $[AB] = 0.10 - 1.5 \times 10^{-6} = 0.10\ M$

(ii) $[B] = 0.20 + 1.5 \times 10^{-6} = 0.20\ M$

SOLVING EXAMPLE 6.13 USING GOAL SEEK

Set up the spreadsheet using individual columns for $[A^+]$, $[B^-]$, $[M^+]$, [AB], and K_{eq}. The "formula view" of the spreadsheet then would look like:

	A	B	C	D	E	F
1	A	B	M	AB	K	
2	0.00E+00	=C2+A2	2.00E-01	=1.00E-01-A2	=1e10*A2*B2/D2	

Note the 1E10 multiplier so as to avoid the aforementioned pitfall in Excel. Now Goal Seek, setting E2 to 3E4 by varying A2 (which is equal to x), you will find that A2 will readily converge to 1.50E-6, see the text **website**.

We will in general use the approximation approaches given in Sections 6.10 and 6.11, which actually incorporate many of the equilibria and assumptions used in the systematic approach. The use of the systematic approach for problems involving multiple equilibria is discussed in Chapter 8.

We can now write some general rules for solving chemical equilibrium problems, using the approximation approach. These rules should be applicable to acid–base dissociation, complex formation, oxidation–reduction reactions, and others. That is, all equilibria can be treated similarly.

1. Write down the equilibria involved.
2. Write the equilibrium constant expressions and the numerical values.
3. From a knowledge of the chemistry involved, let x represent the equilibrium concentration of the species that will be unknown and small compared to other equilibrium concentrations; other species of unknown and small concentrations will be multiples of this.
4. List the equilibrium concentrations of all species, adding or subtracting the appropriate multiple of x from the analytical concentration where needed.
5. Make suitable approximations by neglecting x compared to finite equilibrium concentrations. This is generally valid if the finite concentration is about $100 \times K_{eq}$ or more. Also, if the calculated x is less than approximately 5% of the finite concentration, the assumption is valid.
6. Substitute the approximate representation of individual concentration into the equilibrium constant expression and solve for x.
7. If the approximations in step 5 are invalid, use the quadratic formula to solve for x or use an Excel-based approach.

The application of these rules will become more apparent in subsequent chapters when we deal with specific equilibria in detail.

6.15 Heterogeneous Equilibria—Solids Don't Count

Heterogeneous equilibria are slower than solution equilibria.

Equilibria in which all the components are in solution (a "homogeneous" medium) generally occur quite rapidly. If an equilibrium involves two phases ("heterogeneous"), the rate of approach to equilibrium will generally be substantially slower than in the case of solutions. An example is the dissolution of a poorly soluble solid or the formation of a precipitate, neither of these processes will be instantaneous.

The "concentration" of a pure solid or liquid is unity.

Another way in which heterogeneous equilibria differ from homogeneous equilibria is the manner in which the different constituents offset the equilibrium. Guldberg and Waage showed that when a solid is a component of a reversible chemical process, its active mass can be considered constant, regardless of how much of the solid is present. That is, when any amount of the solid is already present, adding more solid does not bring about a shift in the equilibrium. So the expression for the equilibrium constant need not contain any concentration terms for substances present as solids. That is, the standard state of a solid is taken as that of the solid itself, or unity. Thus, for the equilibrium

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

we write that

$$K_{eq} = [Ca^{2+}][F^-]^2$$

The same is true for pure liquids (undissolved) in equilibrium, such as mercury. The standard state of water is taken as unity in dilute *aqueous solutions*, and water does not appear in equilibrium constant expressions.

Consider a saturated solution of sugar with undissolved sugar remaining at the bottom. The relevant equilibrium constant is $Sugar_{solution}/Sugar_{solid}$. We know well that adding more solid sugar to a saturated solution will not increase the solution concentration further. If the equilibrium constant is indeed a constant, obviously adding more solid sugar to the system does not change the "concentration" of the solid sugar. Any amount of undissolved solid in the saturated solution system represents the same "concentration" of the solid.

6.16 Activity and Activity Coefficients—Concentration Is Not the Whole Story

The "effective concentration" of an ion is decreased by shielding it with other "inert" ions, and it represents the activity of the ion.

Generally, the presence of diverse salts (not containing ions common to the equilibrium involved) will cause an increase in dissociation of a weak electrolyte or in the solubility of a precipitate. Cations attract anions, and vice versa, and so the cations of the analyte

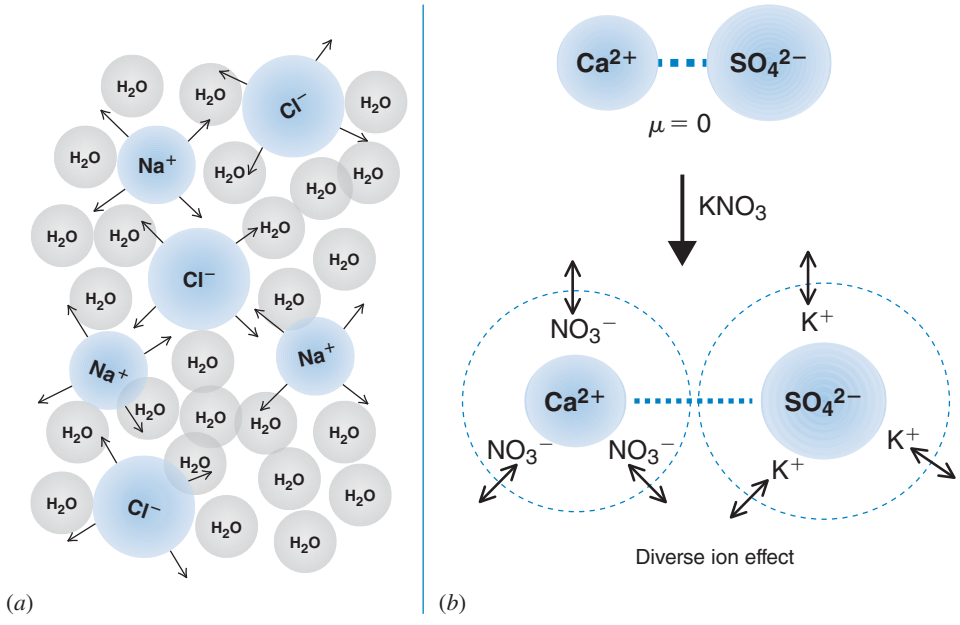


Fig. 6.3. (*a*) In solution, Na^+ and Cl^- from salt form an ion atmosphere where each ion type has more of the oppositely charged ions as nearest neighbors. The structure is very dynamic in nature (all species are rapidly shifting). (*b*) Addition of an inert salt, such as KNO_3, decreases the attraction between ion pairs by shielding and reducing the effective charge and thus increases the solubility of sparingly soluble salts such as $CaSO_4$ (see Section 6.16).

attract anions of the diverse electrolyte and the anions of the analyte are surrounded by the cations of the diverse electrolyte. The attraction of the ions participating in the equilibrium of interest by the dissolved electrolyte effectively shields them, *decreasing their effective concentration* and shifting the equilibrium. We say that an "ion atmosphere" is formed about the cation and anion of interest. As the charge on either the diverse salt or the ions of the equilibrium reaction is increased, the diverse salt effect generally increases. This effect on the equilibrium is not predicted by Le Châtelier's principle; but it is readily understood if you think in terms of the effective concentrations being changed.

Activities are important in potentiometric measurements. See Chapter 13.

This "effective concentration" of an ion in the presence of an electrolyte is called the **activity** of the ion. To quantitatively describe the effects of salts on equilibrium constants, one must use activities, not concentrations (see the diverse salt effect below). In potentiometric measurements, it is activity that is measured, not concentration (see Chapter 13). In this section we describe how to estimate activity.

THE ACTIVITY COEFFICIENT

G. N. Lewis introduced the thermodynamic concept of activity in 1908 in a paper entitled "The Osmotic Pressure of Concentrated Solutions and the Laws of Perfect Solutions."

The **activity** of an ion a_i is defined by

$$a_i = C_i f_i \tag{6.17}$$

where C_i is the concentration of the ion i and f_i is its **activity coefficient**. The concentration is usually expressed as molarity, and the activity has the same units as the concentration. The activity coefficient is dimensionless, but numerical values for activity coefficients do depend on the choice of standard state. The activity coefficient varies with the total number of ions in the solution and with their charge, and it is a correction for interionic attraction. *In dilute solution, less than* 10^{-4}M, *the activity coefficient of a simple electrolyte is near unity*, and activity is approximately equal to the concentration. As the concentration of an electrolyte increases, or as an extraneous salt is added, the activity coefficients of ions decrease, and the activity becomes less than the concentration. Note, however, that at much higher concentrations a different effect comes into play. Ions, especially cations, are hydrated in aqueous solution and the associated water of solvation becomes unavailable to function as solvent. This causes the activity coefficient to reach a minimum as a function of concentration and at very high concentrations; it has a value greater than unity.

IONIC STRENGTH

For ionic strengths less than 10^{-4}, activity coefficients are near unity. In 1921 Lewis and Randall first introduced the empirical concept of ionic strength and showed that in dilute solution, the logarithm of the activity coefficient is proportional to the square root of the ionic strength.

From the above discussion, we can see that the activity coefficient is a function of the total electrolyte concentration of the solution. The **ionic strength** is a measure of total electrolyte concentration and is defined by

$$\mu = \frac{1}{2}\sum C_i Z_i^2 \tag{6.18}$$

where μ is the ionic strength and Z_i is the charge on each individual ion. All cations and anions present in solution are included in the calculation. Obviously, for each positive charge there will be a negative charge.

Example 6.14

Calculate the ionic strength of a 0.2 *M* solution of KNO_3 and a 0.2 *M* solution of K_2SO_4.

Solution

For KNO_3,

$$\mu = \frac{C_{K^+}Z_{K^+}^2 + C_{NO_3^-}Z_{NO_3^-}^2}{2}$$

$$[K^+] = 0.2\ M \qquad [NO_3^-] = 0.2\ M$$

$$\mu = \frac{0.2 \times (1)^2 + 0.2 \times (1)^2}{2} = 0.2$$

Higher charged ions contribute more to the ionic strength.

For K_2SO_4,

$$\mu = \frac{C_{K^+}Z_{K^+}^2 + C_{SO_4^{2-}}Z_{SO_4^{2-}}^2}{2}$$

$$[K^+] = 0.4\ M \qquad [SO_4^{2-}] = 0.2\ M$$

So,

$$\mu = \frac{0.4 \times (1)^2 + 0.2 \times (2)^2}{2} = 0.6$$

Note that due to the doubly charged SO_4^{2-}, the ionic strength of the same molar concentration of K_2SO_4 is three times that of the KNO_3. ■

In 1923, Dutch physicist Petrus (Peter) Debye (1884–1966), together with his assistant Erich Hückel (1896–1980), developed the Debye-Hückel theory of electrolyte solutions, an improvement of Svante Arrhenius's theory of electrical conductivity in electrolytic solutions.

If more than one salt is present, then the ionic strength is calculated from the total concentration and charges of all the different ions. For any given electrolyte, the ionic strength will be proportional to the concentration. Strong acids that are completely ionized are treated in the same manner as salts. If the acids are partially ionized, then the concentration of the ionized species must be estimated from the ionization constant before the ionic strength is computed. Very weak acids can usually be considered to be nonionized and do not contribute to the ionic strength.

Peter J. W. Debye

Example 6.15

Calculate the ionic strength of a solution consisting of 0.30 *M* NaCl and 0.20 *M* Na_2SO_4.

$$\mu = \frac{C_{Na^+}Z_{Na^+}^2 + C_{Cl^-}Z_{Cl^-}^2 + C_{SO_4^{2-}}Z_{SO_4^{2-}}^2}{2}$$

$$= \frac{0.70 \times (1)^2 + 0.30 \times (1)^2 + 0.20 \times (2)^2}{2}$$

$$= 0.90$$

■

Erich A. A. J. Hückel

CALCULATION OF ACTIVITY COEFFICIENTS

In 1923, Debye and Hückel derived a theoretical expression for calculating activity coefficients. The original **Debye-Hückel** equation is given as Equation 6.19a below but it is of limited use as it can be used only in extremely dilute solutions:

$$-\log f_i = AZ_i^2\sqrt{\mu} \tag{6.19a}$$

This equation applies for ionic strengths up to 0.2.

They later provided a more useful equation, known as the **Extended Debye–Hückel equation**:

$$-\log f_i = \frac{AZ_i^2\sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} \tag{6.19b}$$

A and B are constants; the values are, respectively, 0.51 and 0.33 for water at 25°C. At other temperatures, the values can be computed from $A = 1.82 \times 10^6(\mathrm{DT})^{-3/2}$ and $B = 50.3(\mathrm{DT})^{-1/2}$ where D and T are the dielectric constant and the absolute temperature, respectively; a_i is the **ion size parameter**, which is the effective diameter of the hydrated ion in angstrom units, Å. An angstrom is 100 picometers (pm, 10^{-10} meter). A limitation of the Debye–Hückel equation is the accuracy to which a_i can be evaluated. For many singly charged ions, a_i is generally about 3 Å, and for practical purposes Equation 6.19b simplifies to

The estimation of the ion size parameter places a limit on the accuracy of the calculated activity coefficient.

This equation may be used for ionic strengths less than 0.01.

$$-\log f_i = \frac{0.51 Z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \tag{6.20}$$

See Reference 10 for a tabulation of a_i values.

For common multiply charged ions, a_i may become as large as 11 Å. But at ionic strengths less than 0.01, the second term of the denominator becomes small with respect to 1, so uncertainties in a_i become relatively unimportant, and Equation 6.20 can be applied at ionic strengths of 0.01 or less. Equation 6.19b can be applied up to ionic strengths of about 0.2. Reference 10 at the end of the chapter lists values for a_i for different ions and also includes a table of calculated activity coefficients, using Equation 6.19b, at ionic strengths ranging from 0.0005 to 0.1. This paper, with the complete list of ion size parameters, is available on the text **website**. Excel answers using Equations 6.19b and 6.20 for the following two problems are on the **website** (Spreadsheets). Table 6.2 above contains a list of ion size parameters for some common ions taken from this reference.

Table 6.2

Ion Size Parameters for Common Ions

Ion	Ion size parameter Å (Angstroms)
H^+	9
$(C_3H_7)_4N^+$	8
$(C_3H_7)_3NH^+, \{OC_6H_2(NO_3)_3\}^-$	7
$Li^+, C_6H_5COO^-, (C_2H_5)_4N^+$	6
$CHCl_2COO^-, (C_2H_5)_3NH^+$	5
$Na^+, IO_3^-, HSO_3^-, (CH_3)_3NH^+, C_2H_5NH_3^+$	4–4.5
$K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-$	3
$Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+$	2.5
Mg^{2+}, Be^{2+}	8
$Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}$	6
$Sr^{2+}, Ba^{2+}, Cd^{2+}, H_2C(COO)_2^{2-}$	5
$Hg_2^{2+}, SO_4^{2-}, CrO_4^{2-}$	4
$Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}$	9
$Citrate^{3-}$	5
$PO_4^{3-}, Fe(CN)_6^{3-}, \{CO(NH_3)_6\}^{3+}$	4
$Th^{4+}, Zr^{4+}, Ce^{4+}$	11
$Fe(CN)_6^{4-}$	**5**

Taken from Kielland, Reference 10 (See the text **website** for an arrangement of inorganic and organic ions.)

Example 6.16

Calculate the activity coefficients for K^+ and SO_4^{2-} in a 0.0020 *M* solution of potassium sulfate.

Solution

The ionic strength is 0.0060, so we can apply Equation 6.20:

$$-\log f_{K^+} = \frac{0.51(1)^2\sqrt{0.0060}}{1+\sqrt{0.0060}} = 0.037$$

$$f_{K^+} = 10^{-0.037} = 10^{-1} \times 10^{0.963} = 0.918$$

$$-\log f_{SO_4^{2-}} = \frac{0.51(2)^2\sqrt{0.0060}}{1+\sqrt{0.0060}} = 0.14_7$$

$$f_{SO_4^{2-}} = 10^{-0.14_7} = 10^{-1} \times 10^{0.85_3} = 0.71_3$$

Example 6.17

Calculate the activity coefficients for K^+ and SO_4^{2-} in a 0.020 *M* solution of potassium sulfate.

Solution

The ionic strength is 0.060, so we would use Equation 6.19b. From Table 6.2, we find that $a_{K^+} = 3$ Å and $a_{SO_4^{2-}} = 4.0$ Å. For K^+, we can use Equation 6.20:

$$-\log f_{K^+} = \frac{0.51(1)^2\sqrt{0.060}}{1+\sqrt{0.060}} = 0.10_1$$

$$f_{K^+} = 10^{-0.101} = 10^{-1} \times 10^{0.899} = 0.79_4$$

For SO_4^{2-}, use Equation 6.19b:

$$-\log f_{SO_4^{2-}} = \frac{0.51(2)^2\sqrt{0.060}}{1+0.33 \times 4.0\sqrt{0.060}} = 0.37_8$$

$$f_{SO_4^{2-}} = 10^{-1} \times 10^{0.62_2} = 0.41_9$$

This latter compares with a calculated value of 0.39_6 using Equation 6.20. Note the decrease in the activity coefficients compared to 0.002 *M* K_2SO_4, especially for the SO_4^{2-} ion.

Spreadsheets for calculating activity coefficients using Equations 6.19b and 6.20 are given in the textbook's **website** for Chapter 6.

For higher ionic strengths, a number of empirical equations have been developed. One of the more useful is the **Davies modification** (see Reference 9):

$$-\log f_i = 0.51 Z_i^2 \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\,\mu \right) \tag{6.21}$$

Use this equation for ionic strengths of 0.2–0.5. It gives higher activity coefficients compared to the Extended Debye–Hückel equation.

It is valid up to ionic strengths of about 0.5.

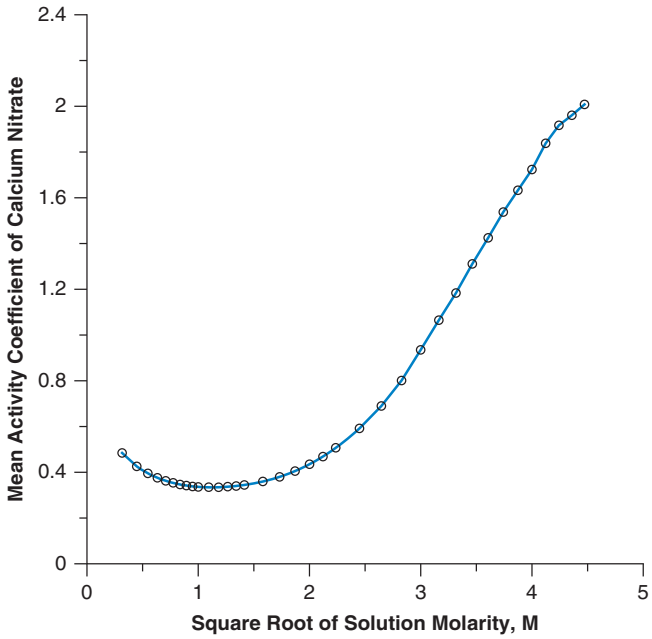


Fig. 6.4. Mean ionic activity coefficient of calcium nitrate as a function of concentration. Data taken from R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.* **70** (1948) 1870.

A 0.01 *M* solution of HCl prepared in 8 *M* NaCl has an activity about 100 times that in water! Its pH is actually 0.0. See F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **30**, (1958) 1247 and G. D. Christian, *CRC Crit. Rev. in Anal. Chem.*, **5**(2) (1975) 119–153.

At very high electrolyte concentrations, activity coefficients increase and become greater than unity. Note that Equation 6.21 does predict this; the last term causes an increase in the activity coefficient as μ increases. This is because the activity of the solvent, water, decreases and the water that is tied in the primary solvation shell of the ions (cations are especially hydrated) are not available to function as solvent. Consider that if the solvation number of Na^+ is 4 (meaning that 4 molecules of water are attached to each sodium ion), an 8 molal NaCl solution has 32 of the 55.5 moles of the water already tied up with the sodium, the effective amount of water remaining to function as solvent is only 43% of that in a very dilute solution. The effective concentration is thus 2.4× higher. This change in concentration is ultimately reflected in an increased activity coefficient. Unfortunately, the real situation is more complex than this because water becomes so scarce at very high concentrations, solvation numbers are not constant and they also begin to decrease from their values in more dilute solutions. For more detailed discussion of activity coefficients in concentrated solutions, see the paper by Stokes and Robinson cited in Figure 6.4.

The Stokes-Robinson equation, which works for AB and AB_2 type electrolytes up to several molar in concentration, is given by:

$$-\log f_{\pm} = \frac{0.51 Z_A Z_B \sqrt{\mu}}{1 + 0.33 a_t \sqrt{\mu}} + \frac{n}{\nu} \log a_w + \log(1 - 0.018)(n - \nu)m \qquad (6.22)$$

where $f_{\pm}$ is the mean activity coefficient of the positive and the negative ion (this is a geometric mean), Z_A and Z_B are respectively the charge on ion A and ion B, a_w is the activity of water (the ratio of vapor pressure of the solution to that of pure water), m is the molality of the solution, n is the hydration number per solute molecule, and ν is the number of species formed from each solute molecule, e.g., for $Ca(NO_3)_2$, this is 3.

We can draw some general conclusions about the estimation of activity coefficients.

The greater the charge on diverse ions, the greater their effect on the activity.

The activity of nonelectrolytes is the same as the concentration, up to ionic strengths of 1.

1. The activity coefficients of ions of a given charge magnitude are approximately the same in solutions of a given ionic strength, and this activity coefficient is the same regardless of their individual concentrations.

2. The behavior of ions become less ideal as the charge magnitude increases, resulting in less confidence in calculated activity coefficients.
3. The calculated activity coefficient of an ion in a mixed electrolyte solution will be less accurate than in a single-electrolyte solution.
4. The activity coefficients of nonelectrolytes (uncharged molecules) can generally be considered equal to unity in ionic strengths up to 0.1, and deviations from this approximation are only moderate in ionic strengths as high as 1. Undissociated acids, HA, are nonelectrolytes whose activity coefficients can be taken as unity. However, in highly concentrated electrolytes, the activity coefficients of nonelectrolytes do exceed unity, again because solvent becomes unavailable. This is the basis of "salting out" a nonelectrolyte from solution, often used in organic synthesis.

Salting out can be useful in analytical chemistry as well. It is possible to add sufficient $CaCl_2$ to a mixture of water and acetone containing an organic chelate of cobalt that the water will all be taken up and separate as a highly concentrated $CaCl_2$ solution layer, distinct from the acetone layer bearing the Co chelate. See C.E. Matkovich and G. D. Christian *Anal. Chem.* **45** (1973) 1915.

A final comment about activity coefficients: Kenneth S. Pitzer recast activity coefficient corrections using quantum mechanics, and provides rigorous treatment of concentrated solutions. See Reference 11.

6.17 The Diverse Ion Effect: The Thermodynamic Equilibrium Constant and Activity Coefficients

We mentioned at the beginning of the last section on activity that the presence of diverse salts will generally increase the dissociation of weak electrolytes due to a shielding (or decrease in the activity) of the ionic species produced upon dissociation. We can quantitatively predict the extent of the effect on the equilibrium by taking into account the activities of the species in the equilibrium.

In our consideration of equilibrium constants thus far, we have assumed no diverse ion effect, that is, an ionic strength of zero and an activity coefficient of 1. Equilibrium constants should more exactly be expressed in terms of activities rather than concentrations. Consider the dissociation of AB. The **thermodynamic equilibrium constant** (i.e., the equilibrium constant extrapolated to the case of infinite dilution) K_{eq}° is

Thermodynamic equilibrium constants hold at all ionic strengths.

For a qualitative picture see panel (*b*), Figure 6.3

$$K_{eq}^{\circ} = \frac{a_A \cdot a_B}{a_{AB}} = \frac{[A]f_A \cdot [B]f_B}{[AB]f_{AB}} \tag{6.23}$$

Since the **concentration equilibrium constant** $K_{eq} = [A][B]/[AB]$, then

$$K_{eq}^{\circ} = K_{eq}\frac{f_A \cdot f_B}{f_{AB}} \tag{6.24}$$

or

$$K_{eq} = K_{eq}^{\circ}\frac{f_{AB}}{f_A \cdot f_B} \tag{6.25}$$

Concentration equilibrium constants must be corrected for ionic strength.

The numerical value of K_{eq}° holds for all activities. $K_{eq} = K_{eq}^{\circ}$ at zero ionic strength, but at appreciable ionic strengths, a value for K_{eq} must be calculated for each ionic strength using Equation 6.25. The equilibrium constants listed in Appendix C are for zero ionic strength; that is, they are really thermodynamic equilibrium constants. (For some reaction systems, experimental K_{eq} values are available at different ionic strengths

and can be used for equilibrium calculations at the listed ionic strength, using molar concentrations without having to calculate activity coefficients. For example, chemical oceanography is of sufficient importance that all relevant equilibrium constants uniquely applicable to a seawater matrix are available.)

Example 6.18

The weak electrolyte AB dissociates to A^+ and B^-, with a thermodynamic equilibrium constant K°_{eq} of 2×10^{-8} in the presence of a diverse salt of ionic strength 0.1. If the activity coefficients of A^+ and B^- are 0.6 and 0.7, respectively, at $\mu = 0.1$: (a) Calculate the molar equilibrium constant K_{eq} in terms of concentration. (b) Calculate the percent dissociation of a $1.0 \times 10^{-4} M$ solution of AB in water.

Solution

(a)

$$AB \rightleftharpoons A^+ + B^-$$

$$K_{eq} = \frac{[A^+][B^-]}{[AB]}$$

$$K^\circ_{eq} = \frac{a_{A^+} \cdot a_{B^-}}{a_{AB}} = \frac{[A^+]f_{A^+} \cdot [B^-]f_{B^-}}{[AB]f_{AB}}$$

The activity coefficient of a neutral species is unity, so

$$K^\circ_{eq} = \frac{[A^+][B^-]}{[AB]} \cdot f_{A^+} \cdot f_{B^-} = K_{eq} f_{A^+} \cdot f_{B^-}$$

$$K_{eq} = \frac{K^\circ_{eq}}{f_{A^+} \cdot f_{B^-}} = \frac{2 \times 10^{-8}}{(0.6)(0.7)} = 5 \times 10^{-8}$$

(b)

$$\begin{array}{ccccc} AB & \rightleftharpoons & A^+ & + & B^- \\ 1 \times 10^{-4} - x & & x & & x \end{array}$$

In water, $f_{A^+} = f_{B^-} \approx 1$ (since $\mu < 10^{-4}$), $x \ll 10^{-4}$

$$\frac{[A^+][B^-]}{[AB]} = 2 \times 10^{-8}$$

$$\frac{(x)(x)}{1.0 \times 10^{-4}} = 2 \times 10^{-8}$$

$$x = 1.4 \times 10^{-6} M$$

$$\% \text{ dissociated} = \frac{1.4 \times 10^{-6} M}{1.0 \times 10^{-4} M} \times 100\% = 1.4\%$$

For 0.1 M salt,

$$\frac{[A^+][B^-]}{[AB]} = 5 \times 10^{-8}$$

$$\frac{(x)(x)}{1.0 \times 10^{-4}} = 5 \times 10^{-8}$$

$$x = 2.2 \times 10^{-6}$$

$$\% \text{ dissociated} = \frac{2.2 \times 10^{-6}}{1.0 \times 10^{-4}} \times 100\% = 2.2\%$$

which represents a 57% increase in dissociation.

We will generally ignore diverse salt effects.

Calculations using the diverse ion effect are illustrated in Chapter 7 for acid dissociation and in Chapter 10 for precipitate solubilities. For illustrative purposes throughout this book, we will in general neglect the diverse ion effects on equilibria. In most cases, we are interested in *relative* changes in equilibrium concentrations, and the neglect of activities will not change our arguments.

Electrostatic effects are important in the behavior of charged molecules such as proteins, DNA and other charged biopolymers, how ions move in capillary electrophoresis, and the behavior of glass and ion selective electrodes, to name a few areas. Read Professor's Favorite Musings: Where Do Activity Coefficients Come From? The thoughts of Professor Michael D. Morris, University of Michigan, on this topic are on the text **website**.

Problems

EQUILIBRIUM CALCULATIONS

1. A and B react as follows: $A + B \rightleftharpoons C + D$. The equilibrium constant is 2.0×10^3. If 0.30 mol of A and 0.80 mol of B are mixed in 1 L, what are the concentrations of A, B, C, and D after reaction?

2. A and B react as follows: $A + B \rightleftharpoons 2C$. The equilibrium constant is 5.0×10^6. If 0.40 mol of A and 0.70 mol of B are mixed in 1 L, what are the concentrations of A, B, and C after reaction? (See the text **website** for a **video** using Goal Seek to solve this problem.)

Video: Goal Seek Problem 6.2

3. The dissociation constant for salicylic acid, $C_6H_4(OH)COOH$, is 1.0×10^{-3}. Calculate the percent dissociation of a $1.0 \times 10^{-3} M$ solution. There is one dissociable proton. (See also Excel Problem 26 below.)

4. The dissociation constant for hydrocyanic acid, HCN, is 7.2×10^{-10}. Calculate the percent dissociation of a $1.0 \times 10^{-3} M$ solution.

5. Calculate the percent dissociation of the salicylic acid in Problem 3 if the solution also contained $1.0 \times 10^{-2} M$ sodium salicylate (the salt of salicylic acid).

6. Hydrogen sulfide, H_2S, dissociates stepwise, with dissociation constants of 9.1×10^{-8} and 1.2×10^{-15}, respectively. Write the overall dissociation reaction and the overall equilibrium constant.

7. Fe^{2+} and $Cr_2O_7^{2-}$ react as follows: $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightleftharpoons 6\,Fe^{3+} + 2Cr^{3+} + 7H_2O$. The equilibrium constant for the reaction is 1×10^{57}. Calculate the equilibrium concentrations of the iron and chromium species if 10 mL each of 0.02 *M* $K_2Cr_2O_7$ in 1.14 *M* HCl and 0.12 *M* $FeSO_4$ in 1.14 *M* HCl are reacted.

SYSTEMATIC APPROACH TO EQUILIBRIUM CALCULATIONS

8. Write charge balance expressions for (a) a saturated solution of Bi_2S_3; (b) a solution of Na_2S.

9. Write the equations of mass balance and electroneutrality for a 0.100 *M* $[Cd(NH_3)_4]Cl_2$ solution.

10. Prove the following relations using the principles of electroneutrality and mass balance:

(a) $[NO_2^-] = [H^+] - [OH^-]$ for 0.2 *M* HNO_2 solution

(b) $[CH_3COOH] = 0.2 - [H^+] + [OH^-]$ for 0.2 *M* CH_3COOH solution

(c) $[H_2C_2O_4] = 0.1 - [H^+] + [OH^-] - [C_2O_4^{2-}]$ for 0.1 *M* $H_2C_2O_4$ solution

(d) $[HCN] = [OH^-] - [H^+]$ for 0.1 *M* KCN solution

(e) $[H_2PO_4^-] = \dfrac{[OH^-] - [H^+] - [HPO_4^{2-}] - 3[H_3PO_4]}{2}$ for 0.1 *M* Na_3PO_4 solution

(f) $[HSO_4^-] = 0.2 - [H^+] - [OH^-]$ for 0.1 *M* H_2SO_4 solution (assume that the dissociation of H_2SO_4 to H^+ and HSO_4^- is quantitative)

11. Write equations of mass balance for an aqueous saturated solution of BaF_2 containing the species F^-, HF, HF_2^-, and Ba^{2+}.

12. Write an equation of mass balance for an aqueous solution of $Ba_3(PO_4)_2$.
13. Calculate the pH of a 0.100 *M* solution of acetic acid using the charge/mass balance approach.

IONIC STRENGTH

14. Calculate the ionic strengths of the following solutions: (a) 0.30 *M* NaCl; (b) 0.30 *M* Na_2SO_4; (c) 0.30 *M* NaCl and 0.20 *M* K_2SO_4; (d) 0.20 *M* $Al_2(SO_4)_3$ and 0.10 *M* Na_2SO_4.
15. Calculate the ionic strengths of the following solutions: (a) 0.20 *M* $ZnSO_4$; (b) 0.40 *M* $MgCl_2$; (c) 0.50 *M* $LaCl_3$; (d) 1.0 *M* $K_2Cr_2O_7$; (e) 1.0 *M* $Tl(NO_3)_3$ + 1.0 *M* $Pb(NO_3)_2$.

ACTIVITY

See the text **website**, Spreadsheet Problems, for Excel answers to problems 16–19.

16. Calculate the activity coefficients of the sodium and chloride ions for a 0.00100 *M* solution of NaCl.
17. Calculate the activity coefficients of each ion in a solution containing 0.0020 *M* Na_2SO_4 and 0.0010 *M* $Al_2(SO_4)_3$.
18. Calculate the activity of the NO_3^- ion in a solution of 0.0020 *M* KNO_3.
19. Calculate the activity of the CrO_4^{2-} ion in a 0.020 *M* solution of Na_2CrO_4.
20. 2.5 *M* sulfuric acid (H_2SO_4) has a density of 1.15. The relative humidity over such a solution is 88.8%. If you assume that each proton is solvated by 4 molecules of water, what will be the mean activity coefficient according to Equation 6.22?

THERMODYNAMIC EQUILIBRIUM CONSTANTS

21. Write thermodynamic equilibrium constant expressions for the following:
    (a) $HCN \rightleftharpoons H^+ + CN^-$
    (b) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
22. Calculate the pH of a solution of 5.0×10^{-3} *M* benzoic acid (a) in water and (b) in the presence of 0.05 *M* K_2SO_4.

EXCEL EXERCISES

See the text **website**, Spreadsheet Problems, for Excel solutions to these problems.

23. Write a spreadsheet program for calculating activity coefficients using Equation 6.20. Then compare it with the one on the text's **website**. Do a calculation with both to check the accuracy.
24. Calculate the activity coefficients for K^+ and SO_4^{2-} in Example 6.16 using the website spreadsheet for Equation 6.20. Compare your results with the manually calculated values in the example.
25. Calculate the activity coefficients in Example 6.17 using the website spreadsheets for Equations 6.19b and 6.20. Compare your results with the manually calculated values in the example.
26. Use Excel Goal Seek to calculate the concentration, *x*, in Problem 3 above. (The problem requires use of the quadratic equation.)
27. Solve Problems 16 to 19 above using Excel.

Recommended References

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Chapter Seven
ACID–BASE EQUILIBRIA

Chapter 7 URLs

Police arrested two kids yesterday, one was drinking battery acid, the other was eating fireworks. They charged one and let the other one off.

—Tommy Cooper

Saying sulfates do not cause acid rain is the same as saying that smoking does not cause lung cancer.

—Drew Lewis

Learning Objectives

WHAT ARE SOME OF THE KEY THINGS WE WILL LEARN FROM THIS CHAPTER?

- Acid–base theories, p. 223
- Acid–base equilibria in water, p. 225 (key equations: 7.11, 7.13, 7.19)
- Weak acids and bases, p. 232
- Salts of weak acids and bases, p. 234 (key equations: 7.27, 7.29, 7.32, 7.36, 7.39)
- Buffers, p. 238 (key equations: 7.45, 7.58)
- Polyprotic acids—α values, pp. 245, 248 (key equations: 7.74–7.77)
- Using spreadsheets to prepare α vs. pH plots, p. 251
- Salts of polyprotic acids, p. 255 (key equations: 7.96, 7.97, 7.99, 7.100)
- Logarithmic concentration diagrams, p. 266
- pH calculator programs, p. 269

Sir Humphry Davy (1778–1829). Best known for his discovery of several alkali and alkaline earth metals and for establishing chlorine and iodine as elements. Berzelius called Davy's 1806 Bakerian lecture *On Some Chemical Agencies of Electricity* as one of the highpoints ever to have enriched the theories of chemistry.

The acidity or basicity of a solution is frequently an important factor in chemical reactions. The use of buffers to maintain the solution pH at a desired level is very important. In addition, fundamental acid–base equilibria are important in understanding acid–base titrations and the effects of acids on chemical species and reactions, for example, the effects of complexation or precipitation. In Chapter 6, we described the fundamental concept of equilibrium constants. In this chapter, we consider in more detail various acid–base equilibrium calculations, including *weak acids* and *bases*, hydrolysis of *salts of weak acids and bases*, buffers, polyprotic acids and their salts, and *physiological buffers*. Acid–base theories and the basic pH concept are reviewed first.

7.1 The Early History of Acid—Base Concepts

The word *acid* derives from Latin *acere*, meaning sour. Bases were referred to as *alkali* in early history and that word derives from Arabic *al-qili*, the ashes of the plant saltwort, rich in sodium carbonate. In the mid seventeenth century it was recognized that acids and bases (called *alkali* in early history) tend to neutralize each other (known as the Silvio-Tachenio theory) but the concepts were vague. Acids, for example, were thought to be substances that would cause limestone to effervesce and alkalis as those that would effervesce with acids. In 1664 Robert Boyle published in *The*

Experimental History of Colours that extracts of certain plants such as red roses and Brazil wood changed color reversibly as the solution was made alternately acidic and basic. Many other plant and flower extracts were shown subsequently to behave in a similar fashion. In 1675, Boyle objected to the vagueness of the Silvio–Tachenio theory and largely because of his efforts, a set of definitions emerged about acids that sought to incorporate their known properties: acids taste sour, cause limestone to effervesce, turn blue plant dyes to red, and precipitate sulfur from alkaline solutions. Alkalies are substances that are slippery to the touch and can reverse the effect of acids. Almost a hundred years elapsed before Antoine-Laurent Lavoisier formed his own opinion of how acids come to be. Based primarily on his observations on combustion and respiration, in which carbon is converted to carbon dioxide (the acidic nature of carbon dioxide dissolved in water was already obvious), he named the gas recently (1774) discovered by Joseph Priestley, so essential for combustion or respiration, as oxygen (from Greek, meaning *acid former*), since he surmised it was what created the acidic product.

Alessandro Volta announced the electric pile—an early type of battery—in 1800. Humphry Davy started playing with electricity immediately thereafter. Through electrolysis he discovered several new elements. In 1807 he electrolyzed fused potash and then soda—substances that many thought to be elements—and isolated potassium and sodium. He also similarly isolated magnesium, calcium, strontium, and barium. Davy recognized that these alkali and alkaline earth metals combine with oxygen and form already known oxides that are highly basic, which challenged Lavoisier's theory that oxygen was the acidifying element. He went on to establish that hydrochloric acid, not "oxymuriatic acid" as Lavoisier called it, was acidifying; by electrolysis he isolated hydrogen and one other element, chlorine (that he so named in 1810), which until then was believed to be a compound containing oxygen. Rather than oxygen, Davy suggested in 1815 that hydrogen may be the acidifying element. All substances that contain hydrogen, however, are not acids. It would wait for Justus von Liebig, to identify an acid in 1838 as a compound of hydrogen where the hydrogen can be replaced by a metal.

Justus Von Liebig (1803–1873) was a German chemist who profoundly enriched agricultural and biological chemistry. Liebig first recognized nitrogen as an essential plant nutrient and is hence often called the father of the fertilizer industry. Liebig first advocated experimentally centered teaching of chemistry. He was also the first to attempt to systematize organic chemistry.

Svante Arrhenius (1859–1927) submitted a 150-page dissertation in 1884 on electrolytic conductivity to Uppsala for the doctorate. It did not impress the professors, and he received a fourth class degree, but upon his defense it was reclassified as third class. Nineteen years later, extensions of this very work would earn him the 1903 Nobel Prize in Chemistry.

The Arrhenius theory is restricted to aqueous solutions. See *J. Am. Chem. Soc.*, **34** (1912) 353 for his personal observations of the difficulty Arrhenius had in the acceptance of his theory.

7.2 Acid–Base Theories—Not All Are Created Equal

Several acid–base theories have been proposed to explain or classify acidic and basic properties of substances. You are probably most familiar with the **Arrhenius theory**, which is applicable only to water. Other theories are more general and are applicable to other solvents or even the gas phase. We describe the common acid–base theories here.

ARRHENIUS THEORY—H^+ AND OH^-

Arrhenius, as a graduate student, introduced a dramatically new theory that an **acid** is any substance that ionizes (partially or completely) in water to give *hydrogen ions* (which associate with the solvent to give hydronium ions, H_3O^+):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

A **base** ionizes in water to give *hydroxide ions*. Weak (partially ionized) bases generally ionize as follows:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

while strong bases such as metal hydroxides (e.g., NaOH) dissociate as

$$M(OH)_n \rightarrow M^{n+} + nOH^-$$

This theory is obviously restricted to water as the solvent.

THEORY OF SOLVENT SYSTEMS—SOLVENT CATIONS AND ANIONS

Franklin and Germann's theory is similar to the Arrhenius theory but is applicable also to other ionizable solvents.

In 1905, Franklin was working in liquid NH_3 as solvent and noticed the similarity with acid-base behavior in water. In 1925, Germann, working with liquid $COCl_2$ as solvent observed the similarities as well and formulated a general solvent system concept of acids and bases. This theory recognizes the ionization of a solvent to give a cation and an anion; for example, $2H_2O \rightleftharpoons H_3O^+ + OH^-$ or $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$. An **acid** is defined as a solute that yields the characteristic *cation of the solvent* while a **base** is a solute that yields the characteristic *anion of the solvent*. Thus, NH_4Cl (which produces ammoniated NH_4^+, i.e., $[NH_4(NH_3)^+]$, and Cl^-) is a strong acid in liquid ammonia (similar to HCl in water: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$) while $NaNH_2$ is a strong base in ammonia (similar to NaOH in water); both of these compounds ionize to give the characteristic solvent cation and anion, respectively. Ethanol ionizes as follows: $2C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$. Hence, sodium ethoxide, $NaOC_2H_5$, is a strong base in this solvent.

BRØNSTED—LOWRY THEORY—TAKING AND GIVING PROTONS

The Brønsted–Lowry theory assumes a transfer of protons from an acid to a base, i.e., conjugate pairs.

Thomas M. Lowry (1874–1936). In 1923, Lowry and Brønsted independently described the theory that is named after them.

The theory of solvent systems is suitable for ionizable solvents, but it is not applicable to acid–base reactions in nonionizable solvents such as benzene or dioxane. In 1923, Brønsted and Lowry independently described what is now known as the **Brønsted–Lowry** theory. This theory states that an **acid** is any substance that can *donate a proton*, and a **base** is any substance that can *accept a proton*. Thus, we can write a "half-reaction"a

$$\text{acid} = H^+ + \text{base} \tag{7.1}$$

The acid and base of a half-reaction are called **conjugate pairs**. Free protons do not exist in solution, and there must be a proton acceptor (base) before a proton donor (acid) will release its proton. That is, there must be a combination of two half-reactions. Another way to look at it is that an acid is an acid because it can lose a proton. However, it cannot exhibit its acidic behavior unless there is a base present to accept the proton. It is like being wealthy on a deserted island with no one to accept your money. Some acid–base reactions in different solvents are illustrated in Table 7.1. In the first example, acetate ion is the conjugate base of acetic acid and ammonium ion is the conjugate acid of ammonia. The first four examples represent ionization of an acid or a base in a solvent, while the others represent a neutralization reaction between an acid and a base in the solvent.

It is apparent from the above definition that a substance cannot act as an acid unless a base is present to accept the protons. Thus, acids will undergo complete

Table 7.1

Brønsted Acid–Base Reactions: Conjugate acid base pairs are denoted in the same color

Solvent	$Acid_1$	+	$Base_2$	→	$Acid_2$	+	$Base_1$
NH_3 (liq.)	HOAc		NH_3		NH_4^+		OAc^-
H_2O	HCl		H_2O		H_3O^+		Cl^-
H_2O	NH_4^+		H_2O		H_3O^+		NH_3
H_2O	H_2O		OAc^-		HOAc		OH^-
H_2O	HCO_3^-		OH^-		H_2O		CO_3^{2-}
C_2H_5OH	NH_4^+		$C_2H_5O^-$		C_2H_5OH		NH_3
C_6H_6	H picrate		$C_6H_5NH_2$		$C_6H_5NH_3^+$		$picrate^-$

or partial ionization in basic solvents such as water, liquid ammonia, or ethanol, depending on the basicity of the solvent and the strength of the acid. But in neutral or "inert" solvents, ionization is insignificant. However, ionization in the solvent is not a prerequisite for an acid–base reaction, as in the last example in the table, where picric acid reacts with aniline.

LEWIS THEORY—TAKING AND GIVING ELECTRONS

Also in 1923, G. N. Lewis introduced the electronic theory of acids and bases. In the **Lewis** theory, an acid is a substance that can accept an electron pair and a base is a substance that can donate an electron pair. The latter frequently contains an oxygen or a nitrogen as the electron donor. Thus, nonhydrogen-containing substances are included as acids. Examples of acid–base reactions in the Lewis theory are as follows:

The Lewis theory assumes a donation (sharing) of electrons from a base to an acid.

$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H{:}NH_3^+$$

$$AlCl_3 + :O(R)(R) \rightarrow Cl_3Al{:}OR_2$$

$$O(H)(H){:} + H^+ \rightarrow H_2O{:}H^+$$

$$H^+ + :OH^- \rightarrow H{:}OH$$

In the second example, aluminum chloride is an acid and ether is a base.

Gilbert N. Lewis (1875–1946) developed theories of covalent bonding, leading to the Lewis electronic theory of acids and bases.

7.3 Acid–Base Equilibria in Water

We see from the above that when an acid or base is dissolved in water, it will dissociate, or **ionize**, the amount of ionization being dependent on the strength of the acid or the base. A "strong" electrolyte is completely dissociated, while a "weak" electrolyte is partially dissociated. Table 7.2 lists some common electrolytes, some strong and some weak. Other weak acids and bases are listed in Appendix C.

Hydrochloric acid is a strong acid, and in water, its ionization is complete:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \tag{7.2}$$

An equilibrium constant for Equation 7.2 would have a value of infinity. The proton H^+ exists in water as a hydrated ion, the **hydronium ion**, H_3O^+. Higher hydrates probably exist, particularly $H_9O_4^+$. The hydronium ion is written as H_3O^+ for convenience and to emphasize Brønsted behavior.

Acetic acid[1] is a weak acid, which ionizes only partially in water (a few percent):

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^- \tag{7.3}$$

We can write an **equilibrium constant** for this reaction:

$$K_a^\circ = \frac{a_{H_3O^+} \cdot a_{OAc^-}}{a_{HOAc} \cdot a_{H_2O}} \tag{7.4}$$

[1] We shall use the symbol OAc^- to represent the acetate ion $CH_3{-}\overset{\overset{O}{\|}}{C}{-}O^-$.

Table 7.2
Some Strong Electrolytes and Some Weak Electrolytes

Strong	Weak
HCl	CH_3COOH (acetic acid)
$HClO_4$	NH_3
H_2SO_4[a]	C_6H_5OH (phenol)
HNO_3	$HCHO_2$ (formic acid)
NaOH	$C_6H_5NH_2$ (aniline)
	CH_3COONa

[a]The first proton is completely ionized in dilute solution, but the second proton is partially ionized ($K_2 = 10^{-2}$).

where K_a° is the **thermodynamic acidity constant** (see Section 6.16) and a is the **activity** of the indicated species. Salt cations or anions may also partially react with water after they are dissociated. For example, acetate ion is formed from dissociated acetate salts, to give HOAc.

The activity can be thought of as representing the *effective* concentration of an ion (described in Chapter 6). The effects of protons in reactions are often governed by their activities, and it is the activity that is measured by the widely used pH meter (Chapter 13). Methods for predicting numerical values of activity coefficients were described in Chapter 6.

In dilute solutions, the activity of water remains essentially constant, and is taken as unity at standard state. Therefore, Equation 7.4 can be written as

$$K_a^\circ = \frac{a_{H_3O^+} \cdot a_{OAc^-}}{a_{HOAc}} \tag{7.5}$$

Autoprotolysis is the self-ionization of a solvent to give a characteristic cation and anion, e.g., $2CH_3OH \rightleftharpoons CH_3OH^+ + CH_3O^-$.

Pure water ionizes slightly, or undergoes **autoprotolysis**:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \tag{7.6}$$

The equilibrium constant for this is

$$K_w^\circ = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O^2}} \tag{7.7}$$

Again, the activity of water is constant in dilute solutions (its concentration is essentially constant at ~55.5 M), so

$$K_w^\circ = a_{H_3O^+} \cdot a_{OH^-} \tag{7.8}$$

where K_w° is the **thermodynamic autoprotolysis**, or **self-ionization, constant**.

We will use H^+ in place of H_3O^+, for simplicity. Also, molar concentrations will generally be used instead of activities.

Calculations are simplified if we neglect activity coefficients. This simplification results in only slight errors for dilute solutions, and we shall use molar concentrations in all our calculations. This will satisfactorily illustrate the equilibria involved. Most of the solutions we will be concerned with are rather dilute, and we will frequently be interested in relative changes in pH (and large ones) in which case small errors are insignificant. We will simplify our expressions by using H^+ in place of H_3O^+. This is not inconsistent since the waters of solvation associated with other ions or molecules (e.g., metal ions) are not generally written and H_3O^+ is not an accurate representation of the actual species present; typically the proton in dilute aqueous solution has at least four water molecules in its solvation shell.

Molar concentration will be represented by square brackets [ ] around the species. Simplified equations for the above reactions are

$$HCl \rightarrow H^+ + Cl^- \tag{7.9}$$

$$HOAc \rightleftharpoons H^+ + OAc^- \tag{7.10}$$

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]} \tag{7.11}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{7.12}$$

$$K_w = [H^+][OH^-] \tag{7.13}$$

K_a and K_w are the **molar equilibrium constants**.

K_w is exactly 1.00×10^{-14} at 24°C and even at 25°C, to a smaller number of significant figures, it is still accurately represented as 1.0×10^{-14}. The product of the hydrogen ion concentration and the hydroxide ion concentration in aqueous solution is *always* equal to 1.0×10^{-14} at room temperature:

Chemists (and especially students!) are lucky that nature made K_w an even unit number at room temperature. Imagine doing pH calculations with a K_w like 2.39×10^{-13}. However, see Section 7.5 where you must indeed do this for other temperatures.

$$[H^+][OH^-] = 1.0 \times 10^{-14} \tag{7.14}$$

In pure water, then, the concentrations of these two species are equal since there are no other sources of H^+ or OH^- except H_2O dissociation:

$$[H^+] = [OH^-]$$

Therefore,

$$[H^+][H^+] = 1.0 \times 10^{-14}$$

$$[H^+] = 1.0 \times 10^{-7}\ M \equiv [OH^-]$$

If an acid is added to water, we can calculate the hydroxide ion concentration if we know the hydrogen ion concentration from the acid. *But when the hydrogen ion concentration from the acid is very small, 10^{-6} M or less, the contribution to $[H^+]$ from the ionization of water cannot be neglected.*

Example 7.1

A 1.0×10^{-3} *M* solution of hydrochloric acid is prepared. What is the hydroxide ion concentration?

Solution

Since hydrochloric acid is a strong electrolyte and is completely ionized, the H^+ concentration is 1.0×10^{-3} *M*. Thus,

$$(1.0 \times 10^{-3})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = 1.0 \times 10^{-11}\ M$$

7.4 The pH Scale

The concentration of H^+ or OH^- in aqueous solution can vary over extremely wide ranges, from 1 *M* or greater to 10^{-14} *M* or less. To construct a plot of H^+ concentration against some variable would be very difficult if the concentration changed from, say, 10^{-1} *M* to 10^{-13} *M*. This range is common in a titration. It is more convenient to

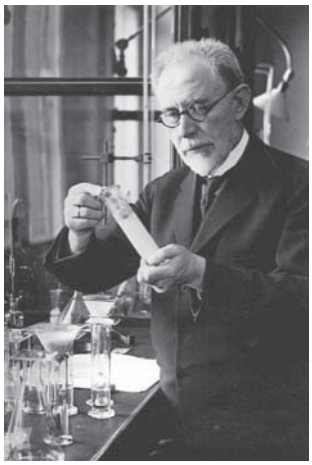
pScales are used to compress and more conveniently express a range of numbers that span several decades in magnitude.

pH is really $-\log a_{H^+}$. This is what a pH meter (glass electrode) measures—see Chapter 13.

compress the acidity scale by placing it on a logarithm basis. The **pH** of a solution was defined by Sørenson as

$$\boxed{\text{pH} = -\log[\text{H}^+]} \tag{7.15}$$

The minus sign is used because most of the concentrations encountered are less than 1 *M*, and so this designation gives a positive number. (More strictly, pH is now defined as $-\log a_{H^+}$, but we will use the simpler definition of Equation 7.15.) In general, **pAnything = − log Anything**, and this method of notation will be used later for other numbers that can vary by large amounts, or are very large or small (e.g., equilibrium constants).



Carlsberg Laboratory archives
In 1909, Søren Sørenson, head of the chemistry department at Carlsberg Laboratory (Carlsberg Brewery) invented the term *pH* to describe this effect and defined it as $-\log[\text{H}^+]$. The term *pH* refers simply to "the power of hydrogen." In 1924, he realized that the pH of a solution is a function of the "activity" of the H^+ ion, and published a second paper on the subject, defining it as $\text{pH} = -\log a_{\text{H}^+}$.

Example 7.2

Calculate the pH of a 2.0×10^{-3} *M* solution of HCl.

Solution

HCl is completely ionized, so

$$[\text{H}^+] = 2.0 \times 10^{-3}\ M$$

$$\text{pH} = -\log(2.0 \times 10^{-3}) = 3 - \log\ 2.0 = 3 - 0.30 = 2.70$$

A similar definition is made for the hydroxide ion concentration:

$$\boxed{\text{pOH} = -\log[\text{OH}^-]} \tag{7.16}$$

Equation 7.13 can be used to calculate the hydroxyl ion concentration if the hydrogen ion concentration is known, and vice versa. The equation in logarithm form for a more direct calculation of pH or pOH is

$$-\log\ K_w = -\log[\text{H}^+][\text{OH}^-] = -\log[\text{H}^+] - \log\,[\text{OH}^-] \tag{7.17}$$

A 1 *M* HCl solution has a pH of 0 and pOH of 14. A 1 *M* NaOH solution has a pH of 14 and a pOH of 0.

$$\boxed{\text{p}K_w = \text{pH} + \text{pOH}} \tag{7.18}$$

At 25°C,

$$\boxed{14.00 = \text{pH} + \text{pOH}} \tag{7.19}$$

Example 7.3

Calculate the pOH and the pH of a 5.0×10^{-2} *M* solution of NaOH at 25°C.

Solution

$$[\text{OH}^-] = 5.0 \times 10^{-2}\ M$$

$$\text{pOH} = -\log(5.0 \times 10^{-2}) = 2 - \log\ 5.0 = 2 - 0.70 = 1.30$$

$$\text{pH} + 1.30 = 14.00$$

$$\text{pH} = 12.70$$

or

$$[H^+] = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13}\ M$$

$$pH = -\log(2.0 \times 10^{-13}) = 13 - \log\ 2.0 = 13 - 0.30 = 12.70$$

Example 7.4

Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution of pH 3.00 and 3.0 mL of a strong base of pH 10.00.

Keep track of millimoles!

Solution

$$[H^+] \text{ of acid solution} = 1.0 \times 10^{-3}\ M$$

$$\text{mmol } H^+ = 1.0 \times 10^{-3}\ M \times 2.0 \text{ mL} = 2.0 \times 10^{-3} \text{ mmol}$$

$$\text{pOH of base solution} = 14.00 - 10.00 = 4.00$$

$$[OH^-] = 1.0 \times 10^{-4}\ M$$

$$\text{mmol } OH^- = 1.0 \times 10^{-4}\ M \times 3.0 \text{ mL} = 3.0 \times 10^{-4} \text{ mmol}$$

There is an excess of acid.

$$\text{mmol } H^+ = 0.0020 - 0.0003 = 0.0017 \text{ mmol}$$

$$\text{Total Volume} = (2.0 + 3.0) \text{ mL} = 5.0 \text{ mL}$$

$$[H^+] = 0.0017 \text{ mmol}/5.0 \text{ mL} = 3.4 \times 10^{-4}\ M$$

$$pH = -\log\ 3.4 \times 10^{-4} = 4 - 0.53 = 3.47$$

Example 7.5

The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution.

Remember, this answer is reported to two significant figures (2.1×10^{-10} M) because the mantissa of the pH value (9.67) has two significant figures.

Solution

$$-\log[H^+] = 9.67$$

$$[H^+] = 10^{-9.67} = 10^{-10} \times 10^{0.33}$$

$$[H^+] = 2.1 \times 10^{-10}\ M$$

When $[H^+] = [OH^-]$, then a solution is said to be **neutral**. If $[H^+] > [OH^-]$, then the solution is **acidic**. And if $[H^+] < [OH^-]$, the solution is **alkaline**. The hydrogen ion and hydroxide ion concentrations in pure water at 25°C are each $10^{-7}\ M$, and the pH of water is 7. A pH of 7 is therefore neutral. Values of pH that are greater than this are alkaline, and pH values less than this are acidic. The reverse is true of pOH values. A pOH of 7 is also neutral. Note that the product of $[H^+]$ and $[OH^-]$ is always 10^{-14} at 25°C, and the sum of pH and pOH is always 14. If the temperature is other than 25°C, then K_w is different from 1.0×10^{-14}, and a neutral solution will have other than $10^{-7}\ M$ H^+ and OH^- (see below).

$[H^+] = 10^{-pH}$.

Some mistakenly believe that it is impossible to have a **negative pH**. There is no theoretical basis for this. A negative pH only means that the hydrogen ion

A 10 *M* HCl solution should have a pH of −1 and pOH of 15.

concentration is greater than 1 M. In actual practice, a negative pH is uncommon for two reasons. First, even strong acids may become partially undissociated at high concentrations. For example, 100% H_2SO_4 is so weakly dissociated that it can be stored in iron containers; more dilute H_2SO_4 solutions would contain sufficient protons from dissociation to attack and dissolve the iron. The second reason has to do with the *activity*, which we have chosen to neglect for dilute solutions. Since pH is really $-\log a_{H^+}$ (this is what a pH meter reading is a measure of), a solution that is 1.1 M in H^+ may actually have a positive pH because the activity of the H^+ is less than 1.0 M.[2] This is because at these high concentrations, the activity coefficient is less than unity (although at still higher concentrations the activity coefficient may become greater than unity—see Chapter 6). Nevertheless, there is mathematically no basis for not having a negative pH (or a negative pOH), although it may be rarely encountered in situations relevant to analytical chemistry.

The pH of 10^{-9} M HCl is *not* 9!

If the concentration of an acid or base is much less than 10^{-7} M, then its contribution to the acidity or basicity will be negligible compared with the contribution from water. The pH of a 10^{-8} M sodium hydroxide solution would therefore not differ significantly from 7. If the concentration of the acid or base is around 10^{-7} M, then its contribution is not negligible and neither is that from water; hence the sum of the two contributions must be taken.

Example 7.6

Calculate the pH and pOH of a 1.0×10^{-7} M solution of HCl.

Solution

Equilibria:

$$HCl \rightarrow H^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$[H^+]_{H_2Odiss.} = [OH^-]_{H_2Odiss.} = x$$

Since the hydrogen ions contributed from the ionization of water are not negligible compared to the HCl added,

$$[H^+] = C_{HCl} + [H^+]_{H_2Odiss.}$$

Then,

$$([H^+]_{HCl} + x)(x) = 1.0 \times 10^{-14}$$

$$(1.00 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

$$x^2 + 1.00 \times 10^{-7}x - 1.0 \times 10^{-14} = 0$$

Using the quadratic equation to solve [see Appendix B] or the use of Excel Goal Seek (Section 6.11),

$$x = \frac{-1.00 \times 10^{-7} \pm \sqrt{1.0 \times 10^{-14} + 4(1.0 \times 10^{-14})}}{2} = 6.2 \times 10^{-8} M$$

[2] As will be seen in Chapter 13, it is also difficult to *measure* the pH of a solution having a negative pH or pOH because high concentrations of acids or bases tend to introduce an error in the measurement by adding a significant and unknown liquid-junction potential in the measurements.

Therefore, the *total* H^+ concentration $= (1.00 \times 10^{-7} + 6.2 \times 10^{-8}) = 1.62 \times 10^{-7}\ M$:

$$\text{pH} = -\log 1.62 \times 10^{-7} = 7 - 0.21 = 6.79$$

$$\text{pOH} = 14.00 - 6.79 = 7.21$$

or, since $[OH^-] = x$,

$$\text{pOH} = -\log(6.2 \times 10^{-8}) = 8 - 0.79 = 7.21$$

Note that, owing to the presence of the added H^+, the ionization of water is suppressed by 38% by the common ion effect (Le Châtelier's principle). At higher acid (or base) concentrations, the suppression is even greater and the contribution from the water becomes negligible. The contribution from the autoionization of water can be considered negligible if the concentration of protons or hydroxyl ions from an acid or base is $10^{-6}M$ *or greater*.

We usually neglect the contribution of water to the acidity in the presence of an acid since its ionization is suppressed in the presence of the acid.

The calculation in this example is more academic than practical because *carbon dioxide from the air dissolved in water substantially exceeds these concentrations,* being about $1.2 \times 10^{-5}\ M$ carbonic acid. Since carbon dioxide in water forms an acid, extreme care would have to be taken to remove and keep this from the water, to have a solution of $10^{-7}\ M$ acid. ■

7.5 pH at Elevated Temperatures: Blood pH

It is a convenient fact of nature for students and chemists who deal with acidity calculations and pH scales in aqueous solutions at room temperature that pK_w is an integer number. At 100°C, for example, $K_w = 5.5 \times 10^{-13}$, and a *neutral solution* has

$$[H^+] = [OH^-] = \sqrt{5.5 \times 10^{-13}} = 7.4 \times 10^{-7}\ M$$

$$\text{pH} = \text{pOH} = 6.13$$

$$pK_w = 12.26 = \text{pH} + \text{pOH}$$

A neutral solution has pH < 7 above room temperature.

Not all measurements or interpretations are done at room temperature, however, and the temperature dependence of K_w must be taken into account (recall from Chapter 6 that equilibrium constants are temperature dependent). An important example is the pH of the body. The pH of blood at body temperature (37°C) is 7.35 to 7.45. This value represents a slightly more alkaline solution relative to neutral water than the same value would be at room temperature. At 37°C, $K_w = 2.5 \times 10^{-14}$ and $pK_w = 13.60$. The pH (and pOH) of a neutral solution is 13.60/2 = 6.80. The hydrogen ion (and hydroxide ion) concentration is $\sqrt{2.5 \times 10^{-14}} = 1.6 \times 10^{-7}\ M$. Since a neutral solution at 37°C would have pH 6.8, a blood pH of 7.4 is more alkaline at 37°C by 0.2 pH units than it would be at 25°C. This is important when one considers that a change of 0.3 pH units in the body is extreme.

The hydrochloric acid concentration in the stomach is about 0.1 to 0.02 *M*. Since $\text{pH} = -\log[H^+]$, the pH at 0.02 *M* would be 1.7. It will be the same *regardless of the temperature* since the hydrogen ion concentration is the same (neglecting solvent volume changes), and the same pH would be measured at either temperature. But, while the pOH would be 14.0 − 1.7 = 12.3 at 25°C, it is 13.6 − 1.7 = 11.9 at 37°C.

The pH of blood must be measured at body temperature to accurately reflect the status of blood buffers.

Not only does the temperature affect the ionization of water in the body and therefore change the pH of neutrality, it also affects the ionization constants of the acids and bases from which the buffer systems in the body are derived. As we shall see later in the chapter, this influences the pH of the buffers, and so a blood pH of 7.4

measured at 37°C will not be the same when measured at room temperature, in contrast to the stomach pH, whose value was determined by the concentration of a strong acid. For this reason, measurement of blood pH for diagnostic purposes is generally done at 37°C (see Chapter 13).

7.6 Weak Acids and Bases—What Is the pH?

We have limited our calculations so far to strong acids and bases in which ionization is assumed to be complete. Since the concentration of H^+ or OH^- is determined readily from the concentration of the acid or base, the calculations are straightforward. As seen in Equation 7.3, weak acids (or bases) are only partially ionized. While mineral (inorganic) acids and bases such as HCl, $HClO_4$, HNO_3, and NaOH are strong electrolytes that are totally ionized in water; most organic acids and bases, as found in clinical applications, are weak.

The ionization constant can be used to calculate the amount ionized and, from this, the pH. The acidity constant for acetic acid at 25°C is 1.75×10^{-5}:

$$\frac{[H^+][OAc^-]}{[HOAc]} = 1.75 \times 10^{-5} \tag{7.20}$$

When acetic acid ionizes, it dissociates to equal portions of H^+ and OAc^- by such an amount that the computation on the left side of Equation 7.20 will always be equal to 1.75×10^{-5}:

$$HOAc \rightleftharpoons H^+ + OAc^- \tag{7.21}$$

If the original concentration of acetic acid is C and the concentration of ionized acetic acid species (H^+ and OAc^-) is x, then the final concentration for each species at equilibrium is given by

$$\begin{array}{ccccc} HOAc & \rightleftharpoons & H^+ & + & OAc^- \\ (C-x) & & x & & x \end{array} \tag{7.22}$$

Example 7.7

Calculate the pH and pOH of a 1.00×10^{-3} M solution of acetic acid.

Solution

$$HOAc \rightleftharpoons H^+ + OAc^-$$

The concentrations of the various species in the form of an ICE table are as follows:

	[HOAc]	$[H^+]$	$[OAc^-]$
Initial	1.00×10^{-3}	0	0
Change (x = mmol/mL HOAc ionized)	$-x$	$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$	x	x

From Equation 7.20

$$\frac{(x)(x)}{1.00 \times 10^{-3} - x} = 1.75 \times 10^{-5}$$

The solution is that of a quadratic equation. If less than about 10 or 15% of the acid is ionized, the expression may be simplified by neglecting x compared with C (10^{-3} M in this case). This is an arbitrary (and not very demanding) criterion. The simplification applies if K_a *is smaller than about* $0.01C$, that is, smaller than 10^{-4} at $C = 0.01$ M, 10^{-3} at $C = 0.1$ M, and so forth. Under these conditions, the error in calculation is 5% or less (results come out too high), and within the probable accuracy of the equilibrium constant. Our calculation simplifies to

If $C_{HA} > 100K_a$, x can be neglected compared to C_{HA}.

$$\frac{x^2}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4}\ M \equiv [H^+]$$

Therefore,

$$pH = -\log(1.32 \times 10^{-4}) = 4 - \log 1.32 = 4 - 0.12 = 3.88$$

$$pOH = 14.00 - 3.88 = 10.12$$

The simplification in the calculation does not lead to serious errors, particularly since equilibrium constants are often not known to a high degree of accuracy (frequently no better than ±10%). In the above example, solution of the quadratic equation results in $[H^+] = 1.26 \times 10^{-4}$ M (5% less) and pH = 3.91. This pH is within 0.03 unit of that calculated using the simplification, which is near the limit of accuracy to which pH measurements can be made. It is almost certainly as close a calculation as is justified in view of the experimental errors in K_a or K_b values and the fact that we are using concentrations rather than activities in the calculations. In our calculations, we also neglected the contribution of hydrogen ions from the ionization of water (which was obviously justified); this is generally permissible except for very dilute ($<10^{-6}$ M) or very weak ($K_a < 10^{-12}$) acids.

The absolute accuracy of pH measurements is no better than 0.02 pH units. See Chapter 13.

Similar equations and calculations hold for weak bases. It should be noted, however, a computational tool like Goal Seek or Excel Solver can solve quadratic (or higher-order) equations so easily that increasingly it is easier to solve the original equation without approximation than to reflect on whether the approximation may be valid. A Goal Seek solution of Example 7.7 can be found in the **website** section of this chapter.

Example 7.8

The basicity constant K_b for ammonia is 1.75×10^{-5} at 25°C. (It is only coincidental that this is equal to K_a for acetic acid.) Calculate the pH and pOH for a 1.00×10^{-3} M solution of ammonia.

Solution

$$\underset{(1.00 \times 10^{-3} - x)}{NH_3} + H_2O \rightleftharpoons \underset{x}{NH_4^+} + \underset{x}{OH^-}$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5}$$

The same rule applies for the approximation applied for a weak acid. Thus,

$$\frac{(x)(x)}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4}\ M = [OH^-]$$

$$pOH = -\log 1.32 \times 10^{-4} = 3.88$$

$$pH = 14.00 - 3.88 = 10.12$$

For an Excel Goal Seek solution of Example 7.8 without approximation, see the chapter's **website**. ■

PROFESSOR'S FAVORITE WAY

Contributed by Professor W. Rudolph Seitz, University of New Hampshire

HANDLING BASES AS THEIR CONJUGATE ACIDS

Many tabulations of ionization constants of acids and bases list only acidity constants. That is, bases are listed in the form of their conjugate acid (see Equation 7.1). Table C.2b in Appendix C lists the corresponding acid formulas and acidity constants for the bases listed in Table C.2a. The amino groups of amine compounds are protonated (+1 charge) and can be treated as any other weak acid to give the corresponding conjugate base.

So, one can consider that there are two types of monoprotic acids, one that is uncharged (HA), e.g., HOAc, and one that has plus charge (HA^+), e.g., NH_4^+. Similarly, there are three types of diprotic acids, with charges of 0 (H_2A), e.g., oxalic acid $H_2C_2O_4$, 1 + (H_2A^+), e.g., glycinium ion $^+NH_3CH_2COOH$ and 2 + (H_2A^{2+}), e.g., the ethylenediammonium ion, $^+NH_3C_2H_4NH_3^+$. Hence, the protonated form of ammonia is NH_4^+, and the corresponding acidity constant is 5.71×10^{-10}. In order to calculate the pH of an ammonia solution (as in Example 7.8), then, the K_b of the conjugate base form of the acid NH_4^+ is calculated from $K_b = K_w/K_a$($K_b = 1.00 \times 10^{-14}/5.71 \times 10^{-10} = 1.75 \times 10^{-5}$).

For a diprotic acid–base pair like ethylenediamine, $NH_2C_2H_4NH_2$, and its acid forms, the protonated forms are $^+NH_3C_2H_4NH_3^+$ and $NH_2C_2H_4NH_3^+$ (each protonated amine group has a +1 charge). The protonated amine groups dissociate stepwise to give $NH_2C_2H_4NH_3^+$ and $NH_2C_2H_4NH_2$, with $K_{a1} = 1.41 \times 10^{-7}$ and $K_{a2} = 1.18 \times 10^{-10}$. For the conjugate base forms, $K_{b1} = K_w/K_{a2}$ and $K_{b2} = K_w/K_{a1}$). Since K_{a1} is larger than K_{a2}, then K_{b2} is smaller than K_{b1}.

In this book, while dealing with α-values and in all the Excel exercises, we have followed this approach: considered all problems in terms of acid dissociation constants. It is suggested that you do so as well. ■

7.7 Salts of Weak Acids and Bases — They Aren't Neutral

The hydrolysis of OAc^- is no different than the "ionization" of NH_3 in Example 7.8.

The salt of a weak acid, for example, NaOAc, is a strong electrolyte, like (almost) all salts, and completely ionizes. In addition, the anion of the salt of a weak acid is a **Brønsted base**, which will accept protons. It partially hydrolyzes in water (a Brønsted acid) to form hydroxide ion and the corresponding undissociated acid. For example,

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^- \qquad (7.23)$$

The HOAc here is undissociated and therefore does not contribute to the pH. This ionization is also known as **hydrolysis** of the salt ion. Because it hydrolyzes, sodium acetate is a weak base (the conjugate base of acetic acid). The ionization constant for Equation 7.23 is equal to the basicity constant of the salt anion. The weaker the

conjugate acid, the stronger the conjugate base, that is, the more strongly the salt will combine with a proton, as from the water, to shift the ionization in Equation 7.23 to the right. *Equilibria for these Brønsted bases are treated identically to the weak bases we have just considered*. We can write an equilibrium constant:

$$K_{\mathrm{H}} = K_b = \frac{[\mathrm{HOAc}][\mathrm{OH}^-]}{[\mathrm{OAc}^-]} \tag{7.24}$$

K_{H} is called the **hydrolysis constant** of the salt and is the same as the basicity constant. We will use K_b to emphasize that these salts are treated the same as for any other weak base.

The value of K_b can be calculated from K_a of acetic acid and K_w if we multiply both the numerator and denominator by $[\mathrm{H}^+]$:

$$K_b = \frac{[\mathrm{HOAc}]}{[\mathrm{OAc}^-]} \cdot \frac{[\mathrm{OH}^-][\mathrm{H}^+]}{[\mathrm{H}^+]} \tag{7.25}$$

The quantity inside the dashed line is K_w and the remainder is $1/K_a$. Hence,

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10} \tag{7.26}$$

We see from the small K_b that the acetate ion is quite a weak base with only a small fraction of ionization. *The product of K_a of any weak acid and K_b of its conjugate base is always equal to K_w*:

$$\boxed{K_a K_b = K_w} \tag{7.27}$$

You will understand that this is merely a restatement of what was stated in the previous section in treating a base in terms of its conjugate acid. The product of the acid dissociation constant of any acid and the base dissociation constant of its conjugate base is K_w.

For any salt of a weak acid HA that hydrolyzes in water,

$$\mathrm{A}^- + \mathrm{H_2O} \rightleftharpoons \mathrm{HA} + \mathrm{OH}^- \tag{7.28}$$

$$\boxed{\frac{[\mathrm{HA}][\mathrm{OH}^-]}{[\mathrm{A}^-]} = \frac{K_w}{K_a} = K_b} \tag{7.29}$$

The pH of such a salt (a Brønsted base) is calculated in the same manner as for any other weak base. When the salt hydrolyzes, it forms an equal amount of HA and OH^-. If the original concentration of A^- is C_{A^-}, then

$$\begin{array}{ccccc} \mathrm{A}^- & + \mathrm{H_2O} & \rightleftharpoons & \mathrm{HA} & + \mathrm{OH}^- \\ (C_{\mathrm{A}^-} - x) & & & x & x \end{array} \tag{7.30}$$

The quantity x can be neglected compared to C_{A^-} if $C_{\mathrm{A}^-} > 100K_b$, which will generally be the case for such weakly ionized bases.

We can solve for the OH^- concentration using Equation 7.30:

$$\frac{[\mathrm{OH}^-][\mathrm{OH}^-]}{C_{\mathrm{A}^-}} = \frac{K_w}{K_a} = K_b \tag{7.31}$$

Compare this with the algebraic setup in Example 7.8. They are identical:

$$\boxed{[\mathrm{OH}^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{\mathrm{A}^-}} = \sqrt{K_b \cdot C_{\mathrm{A}^-}}} \tag{7.32}$$

This equation holds only if $C_{A^-} > 100K_b$, and x can be neglected compared to C_{A^-}. If this is not the case, then the quadratic formula must be solved as for other bases in this situation.

Example 7.9

Calculate the pH of a 0.10 M solution of sodium acetate.

Solution

Compare this base "ionization" with that of NH_3, Example 7.8.

Write the equilibria

$$NaOAc \rightarrow Na^+ + OAc^- \text{ (ionization)}$$

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^- \text{ (hydrolysis)}$$

Write the equilibrium constant

$$\frac{[HOAc][OH^-]}{[OAc^-]} = K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of HOAc and OH^- at equilibrium. Then, at equilibrium,

$$[HOAc] = [OH^-] = x$$

$$[OAc^-] = C_{OAc^-} - x = 0.10 - x$$

Since $C_{OAc^-} \gg K_b$, neglect x compared to C_{OAc^-}. Then,

$$\frac{(x)(x)}{0.10} = 5.7 \times 10^{-10}$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.10} = 7.6 \times 10^{-6}\ M$$

Compare this last step with Equation 7.32. Also, compare the entire setup and solution with those in Example 7.8. The HOAc formed is undissociated and does not contribute to the pH:

$$[OH^-] = 7.6 \times 10^{-6}\ M$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{7.6 \times 10^{-6}} = 1.3 \times 10^{-9}\ M$$

$$pH = -\log 1.3 \times 10^{-9} = 9 - 0.11 = 8.89$$

For an Excel Goal Seek solution of Example 7.9 without approximation, see the text **website**. ■

Similar equations can be derived for the cations of salts of weak bases (the salts are completely dissociated). These are **Brønsted acids** and ionize (hydrolyze) in water:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+ \tag{7.33}$$

The B is undissociated and does not contribute to the pH. The acidity constant is

$$K_H = K_a = \frac{[B][H_3O^+]}{[BH^+]} \tag{7.34}$$

The acidity constant (hydrolysis constant) can be derived by multiplying the numerator and denominator by $[OH^-]$:

$$K_a = \frac{[B]\,\boxed{[H_3O^+]}}{[BH^+]} \cdot \frac{\boxed{[OH^-]}}{[OH^-]} \tag{7.35}$$

Again, the quantity inside the dashed lines is K_w, while the remainder is $1/K_b$. Therefore,

$$\boxed{\frac{[B][H_3O^+]}{[BH^+]} = \frac{K_w}{K_b} = K_a} \tag{7.36}$$

and for NH_4^+,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10} \tag{7.37}$$

We could, of course, have derived K_a from Equation 7.27. It is again coincidence that the numerical value of K_a for NH_4^+ equals K_b for OAc^-.

The salt of a weak base ionizes to form equal amounts of B and H_3O^+ (H^+ if we disregard hydronium ion formation as was done previously). We can therefore solve for the hydrogen ion concentration (by assuming $C_{BH^+} > 100K_a$):

$$\frac{[H^+][H^+]}{C_{BH^+}} = \frac{K_w}{K_b} = K_a \tag{7.38}$$

$$\boxed{[H^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{BH^+}} = \sqrt{K_a \cdot C_{BH^+}}} \tag{7.39}$$

Again, this equation only holds if $C_{BH^+} > 100K_a$. Otherwise, the quadratic formula must be solved.

Note: One can obtain K_a directly from a list of acidity constants, as in Table C2.b in Appendix C for the acid equilibrium as given in Equation 7.33; substituting in Equation 7.34 and solving for the hydrogen ion concentration gives Equation 7.39.

Example 7.10

Calculate the pH of a 0.25 *M* solution of ammonium chloride.

Solution

Write the equilibria

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \quad \text{(ionization)}$$
$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \quad \text{(hydrolysis)}$$
$$(NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+)$$

Write the equilibrium constant

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} = K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of $[NH_4OH]$ and $[H^+]$ at equilibrium. Then, at equilibrium,

$$[NH_4OH] = [H^+] = x$$

$$[NH_4{}^+] = C_{NH_4{}^+} - x = 0.25 - x$$

Since $C_{NH_4{}^+} \gg K_a$, neglect x compared to $C_{NH_4{}^+}$. Then,

$$\frac{(x)(x)}{0.25} = 5.7 \times 10^{-10}$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.25} = 1.2 \times 10^{-5}\ M$$

Compare this last step with Equation 7.39. Also, compare the entire setup and solution with those in Example 7.7. The NH_4OH formed is undissociated and does not contribute to the pH:

$$[H^+] = 1.2 \times 10^{-5}\ M$$

$$\text{pH} = -\log(1.2 \times 10^{-5}) = 5 - 0.08 = 4.92$$

For an Excel Goal Seek solution of Example 7.8 without approximation, see the chapter's **website**. See also the **video** illustrating the use of Goal Seek to calculate the pH of an NH_4F solution.[3] ■

Video: Goal Seek pH NH_4F

7.8 Buffers—Keeping the pH Constant (or Nearly So)

A **buffer** is defined as a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted. While carrying out a reaction, this is very useful for maintaining the pH within an optimum range. A buffer solution consists of a mixture of a weak acid and its conjugate base, or a weak base, and its conjugate acid at predetermined concentrations or ratios. That is, we have a mixture of a weak acid and its salt or a weak base and its salt. Consider an acetic acid–acetate buffer. The equilibrium that governs this system is

$$HOAc \rightleftharpoons H^+ + OAc^-$$

But now, since we have added a supply of acetate ions to the system (e.g., from sodium acetate), the hydrogen ion concentration is no longer equal to the acetate ion concentration. The hydrogen ion concentration is

$$[H^+] = K_a \frac{[HOAc]}{[OAc^-]} \tag{7.40}$$

Taking the negative logarithm of each side of this equation, we have

$$-\log[H^+] = -\log K_a - \log \frac{[HOAc]}{[OAc^-]} \tag{7.41}$$

$$\text{pH} = \text{p}K_a - \log \frac{[HOAc]}{[OAc^-]} \tag{7.42}$$

Upon inverting the last log term, it becomes positive:

$$\text{pH} = \text{p}K_a + \log \frac{[OAc^-]}{[HOAc]} \tag{7.43}$$

The pH of a buffer is determined by the ratio of the conjugate acid–base pair concentrations.

This form of the ionization constant equation is called the **Henderson–Hasselbalch**

[3] This is an unedited student video and contains some errors of statement, e,g., it talks about K_a of NH_3 whereas it should really refer to it as K_a of $NH_4{}^+$; it mistakenly states that bases like to take up electrons whereas bases of course like to take up hydrogen ions, etc. But despite these errors of statement, it is a nicely set up example of a correctly solved problem that shows the use of Excel Goal Seek!

equation. It is useful for calculating the pH of a weak acid solution containing its salt. A general form can be written for a weak acid HA that ionizes to its salt, A^-, and H^+:

$$HA \rightleftharpoons H^+ + A^- \tag{7.44}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{7.45}$$

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \tag{7.46}$$

$$pH = pK_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]} \tag{7.47}$$

Example 7.11

Calculate the pH of a buffer prepared by adding 10 mL of 0.10 *M* acetic acid to 20 mL of 0.10 *M* sodium acetate.

Solution

We need to calculate the concentration of the acid and salt in the solution. The final volume is 30 mL:

$$M_1 \times mL_1 = M_2 \times mL_2$$

For HOAc,

$$0.10 \text{ mmol/mL} \times 10 \text{ mL} = M_{HOAc} \times 30 \text{ mL}$$

$$M_{HOAc} = 0.033 \text{ mmol/mL}$$

For OAc^-,

$$0.10 \text{ mmol/mL} \times 20 \text{ mL} = M_{OAc^-} \times 30 \text{ mL}$$

$$M_{OAc^-} = 0.067 \text{ mmol/mL}$$

Some of the HOAc dissociates to $H^+ + OAc^-$, and the equilibrium concentration of HOAc would be the amount added (0.033 *M*) minus the amount dissociated, while that of OAc^- would be the amount added (0.067 *M*) plus the amount of HOAc dissociated. However, *the amount of acid dissociated is very small*, particularly in the presence of the added salt (ionization suppressed by the common ion effect), and can be neglected. Hence, we can assume the added concentrations to be the equilibrium concentrations:

The ionization of the acid is suppressed by the salt and can be neglected.

$$pH = -\log K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$pH = -\log(1.75 \times 10^{-5}) + \log \frac{0.067 \text{ mmol/mL}}{0.033 \text{ mmol/mL}}$$

$$= 4.76 + \log 2.0$$

$$= 5.06$$

We could have shortened the calculation by recognizing that in the log term the volumes cancel. So we can take the ratio of millimoles only:

We can use millimoles of acid and salt in place of molarity. Because the terms appear in a ratio, as long as the units are the same, they will cancel out. But it has to relate to moles or molarity, not mass.

$$mmol_{HOAc} = 0.10 \text{ mmol/mL} \times 10 \text{ mL} = 1.0 \text{ mmol}$$

$$mmol_{OAc^-} = 0.10 \text{ mmol/mL} \times 20 \text{ mL} = 2.0 \text{ mmol}$$

$$H = 4.76 + \log \frac{2.0 \text{ mmol}}{1.0 \text{ mmol}} = 5.06$$

■

The mixture of a weak acid and its salt may also be obtained by mixing an excess of weak acid with some strong base to produce the salt by neutralization, or by mixing an excess of salt with strong acid to produce the weak acid component of the buffer.

Example 7.12

Calculate the pH of a solution prepared by adding 25 mL of 0.10 *M* sodium hydroxide to 30 mL of 0.20 *M* acetic acid (this would actually be a step in a typical titration).

Solution

Keep track of millimoles of reactants!

$$\text{mmol HOAc} = 0.20\ M \times 30\ \text{mL} = 6.0\ \text{mmol}$$

$$\text{mmol NaOH} = 0.10\ M \times 25\ \text{mL} = 2.5\ \text{mmol}$$

These react as follows:

$$\text{HOAc} + \text{NaOH} \rightleftharpoons \text{NaOAc} + \text{H}_2\text{O}$$

After reaction,

$$\text{mmol NaOAc} = 2.5\ \text{mmol}$$

$$\text{mmol HOAc} = 6.0 - 2.5 = 3.5\ \text{mmol}$$

$$\text{pH} = 4.76 + \log \frac{2.5}{3.5} = 4.61$$

■

The **buffering mechanism** for a mixture of a weak acid and its salt can be explained as follows. The pH is governed by the logarithm of the ratio of the salt and acid:

$$\text{pH} = \text{constant} + \log \frac{[\text{A}^-]}{[\text{HA}]} \tag{7.48}$$

Dilution does not change the ratio of the buffering species.

If the solution is diluted, the ratio remains constant, and so the pH of the solution does not change.[4] If a small amount of a strong acid is added, it will combine with an equal amount of the A^- to convert it to HA. That is, in the equilibrium $HA \rightleftharpoons H^+ + A^-$, Le Châtelier's principle dictates added H^+ will combine with A^- to form HA, with the equilibrium lying far to the left if there is an excess of A^-. The change in the ratio $[A^-]/[HA]$ is small and hence the change in pH is small. If the acid had been added to an unbuffered solution (e.g., a solution of NaCl), the pH would have decreased markedly. If a small amount of a strong base is added, it will combine with part of the HA to form an equivalent amount of A^-. Again, the change in the ratio is small.

The buffering capacity increases with the concentrations of the buffering species.

The amount of acid or base that can be added without causing a large change in pH is governed by the **buffering capacity** of the solution. This is determined by the concentrations of HA and A^-. The higher their concentrations, the more acid or base the solution can tolerate. The buffer intensity or buffer index of a solution is defined as

$$\beta = dC_\text{B}/d\text{pH} = -dC_\text{HA}/d\text{pH} \tag{7.49}$$

where dC_B and dC_HA represent the number of moles per liter of strong base or acid, respectively, needed to bring about a pH change of dpH. Although the terms *buffer intensity* and *buffer capacity* are often used interchangeably, the buffer capacity is the integrated form of buffer intensity (e.g., the amount of strong acid/base needed to

[4] In actuality, the pH will *increase* slightly because the activity coefficient of the salt has been increased by decreasing the ionic strength. The activity of an uncharged molecule (i.e., undissociated acid) is equal to its molarity (see Chapter 6), and so the ratio increases, causing a slight increase in pH. See the end of the chapter.

change the pH by a certain finite amount) and is always a positive number. The larger it is, the more resistant the solution is to pH change. For a simple monoprotic weak acid/conjugate base buffer solutions of concentration greater than 0.001 *M*, the buffer intensity is approximated by:

$$\beta = 2.303 \frac{C_{HA} C_{A^-}}{C_{HA} + C_{A^-}} \tag{7.50}$$

where C_{HA} and C_{A^-} represent the analytical concentrations of the acid and its salt, respectively. Thus, if we have a mixture of 0.10 mol/L acetic acid and 0.10 mol/L sodium acetate, the buffer intensity is

See Chapter 8, Section 8.11 for a derivation of buffer intensity.

$$\beta = 2.303 \frac{0.10 \times 0.10}{0.10 + 0.10} = 0.050 \text{ mol/L per pH}$$

If we add 0.0050 mol/L solid sodium hydroxide, the change in pH is

$$d\text{pH} = dC_B/\beta = 0.0050/0.050 = 0.10 = \Delta\text{pH}$$

In addition to concentration, the buffer intensity is governed by the *ratio* of HA to A^-. It is *maximum* when the ratio is unity, that is, when the pH = pK_a:

The buffer intensity is maximum at pH = pK_a.

$$\text{pH} = \text{p}K_a + \log \frac{1}{1} = \text{p}K_a \tag{7.51}$$

This corresponds to the midpoint of a titration of a weak acid. In general, provided the concentration is not too dilute, the buffering capacity is satisfactory over a *pH range of* p$K_a \pm 1$. We will discuss the buffering capacity in more detail in Chapter 8, when the titration curves of weak acids are discussed.

Example 7.13: Professor's Favorite Example

Contributed by Professor Kris Varazo, Francis Marion University, Florence, South Carolina

Calculating the pH of a buffer when strong acid or base is added

As an example, suppose you have 100 mL of a buffer containing 0.100 *M* acetic acid and 0.0500 *M* sodium acetate. Calculate the pH of the buffer when 3.00 mL of 1.00 *M* HCl is added to it.

As a first step, calculate the pH of the buffer before adding the strong acid using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

All we need to determine the pH of this buffer is the pK_a of acetic acid, which is 4.76:

$$\text{pH} = 4.76 + \log \frac{0.0500}{0.100} = 4.46$$

Remember that adding acid to a solution will necessarily lower the pH, so we should expect the pH of the buffer to be lower than 4.46. The best way to solve this problem is to calculate the moles of acetic acid, moles of sodium acetate, and added moles of HCl:

$$100 \text{ mL} \times \frac{0.100 \text{ moles}}{1000 \text{ mL}} = 0.0100 \text{ moles acetic acid}$$

$$100 \text{ mL} \times \frac{0.0500 \text{ moles}}{1000 \text{ mL}} = 0.00500 \text{ moles sodium acetate}$$

$$3.00 \text{ mL} \times \frac{1.00 \text{ moles}}{1000 \text{ mL}} = 0.00300 \text{ moles hydrochloric acid}$$

Note that we expressed molarity in moles per 1000 mL instead of liters. Even though the Henderson–Hasselbalch equation uses molar concentrations, there is only one volume of buffer solution, so we can simply use the mole values we just calculated. We also need to know the chemical reaction occurring when strong acid is added to the buffer:

$$A^- + H^+ \rightarrow HA$$

The reaction says that the acetate ion in the buffer will react with the added strong acid, and the moles of acetate will decrease and the moles of acetic acid will increase. How much will the decrease and increase be? It is equal to the amount of strong acid added. We can now write the Henderson–Hasselbalch equation and account for the decrease in moles of acetate and increase in moles of acetic acid:

$$\text{pH} = pK_a + \log \frac{(\text{moles } A^- - \text{moles } H^+\text{added})}{(\text{moles HA} + \text{moles } H^+\text{added})} \tag{7.52}$$

$$\text{pH} = 4.76 + \log \frac{(0.00500 - 0.00300)}{(0.0100 + 0.00300)}$$

$$\text{pH} = 4.22$$

The new pH of the buffer is lower than the original value, and it makes sense because adding strong acid to a solution, even a buffer, will cause the pH to decrease. This approach also works in reverse, when you add a strong base to a buffer. In this case, the pH of the buffer will increase, and the relevant chemical reaction is:

$$HA + OH^- \rightarrow H_2O + A^-$$

This time the moles of acetic acid will decrease and the moles of acetate will increase. The Henderson–Hasselbalch equation can be written in the following form to solve for the pH:

$$\text{pH} = pKa + \log \frac{(\text{moles } A^- + \text{moles } OH^-\text{added})}{(\text{moles HA} - \text{moles } OH^-\text{added})} \tag{7.53}$$

Note that a buffer can resist a pH change, even when there is added an amount of strong acid or base greater (in moles) than the equilibrium amount of H^+ or OH^- (in moles) in the buffer. For example, in Example 7.13, the pH of the buffer is 4.46 and $[H^+] = 3.5 \times 10^{-5}\ M$, and millimoles $H^+ = (3.5 \times 10^{-5}\text{mmol/mL})(100\text{ mL}) = 3.5 \times 10^{-3}\text{mmol}$ (in equilibrium with the buffer components). We added 3.00 mmol H^+, far in excess of this. However, due to the reserve of buffer components (OAc^- to react with H^+ in this case), the added H^+ is consumed so that the pH remains relatively constant, *so long as we do not exceed the amount of buffer reserve*.

Similar calculations apply for mixtures of a weak base and its salt. We can consider the equilibrium between the base B and its conjugate acid BH^+ and write a K_a for the conjugate (Brønsted) acid:

$$BH^+ \rightleftharpoons B + H^+ \tag{7.54}$$

$$K_a = \frac{[B][H^+]}{[BH^+]} = \frac{K_w}{K_b} \tag{7.55}$$

The logarithmic Henderson–Hasselbalch form is derived exactly as above:

$$[H^+] = K_a \cdot \frac{[BH^+]}{[B]} = \frac{K_w}{K_b} \cdot \frac{[BH^+]}{[B]} \tag{7.56}$$

$$-\log[H^+] = -\log\ K_a - \log \frac{[BH^+]}{[B]} = -\log \frac{K_w}{K_b} - \log \frac{[BH^+]}{[B]} \tag{7.57}$$

$$\text{pH} = pK_a + \log\frac{[\text{B}]}{[\text{BH}^+]} = (\text{p}K_w - \text{p}K_b) + \log\frac{[\text{B}]}{[\text{BH}^+]} \quad (7.58)$$

$$\text{pH} = \text{p}K_a + \log\frac{[\text{proton acceptor}]}{[\text{proton donor}]} = (\text{p}K_w - \text{p}K_b) + \log\frac{[\text{proton acceptor}]}{[\text{proton donor}]} \quad (7.59)$$

Since $\text{pOH} = \text{p}K_w - \text{pH}$, we can also write, by subtracting either Equation 7.58 or Equation 7.59 from $\text{p}K_w$,

$$\text{pOH} = pK_b + \log\frac{[\text{BH}^+]}{[\text{B}]} = \text{p}K_b + \log\frac{[\text{proton donor}]}{[\text{proton acceptor}]} \quad (7.60)$$

A mixture of a weak base and its salt acts as a buffer in the same manner as a weak acid and its salt. When a strong acid is added, it combines with some of the base B to form the salt BH^+. Conversely, a base combines with BH^+ to form B. Since the change in the ratio will be small, the change in pH will be small. Again, the buffering capacity is maximum at a pH equal to $\text{p}K_a = 14 - \text{p}K_b$ (or at $\text{pOH} = \text{p}K_b$), with a useful range of $\text{p}K_a \pm 1$. Although we show the calculations in terms of pK_b as well, we recommend that you do all calculations using the pK_a of the conjugate acid; consistency keeps you in the comfort zone.

$\text{p}K_a = 14 - \text{p}K_b$ for a weak base. The alkaline buffering capacity is maximum at $\text{pOH} = \text{p}K_b (\text{pH} = \text{p}K_a)$.

When a buffer is diluted, the pH will not change appreciably because the ratio [proton donor] / [proton acceptor] will remain the same.[5]

Example 7.14

Calculate the volume of concentrated ammonia and the weight of ammonium chloride you would have to take to prepare 100 mL of a buffer at pH 10.00 if the final concentration of salt is to be 0.200 *M*.

Solution

We want 100 mL of 0.200 *M* NH_4Cl. Therefore, mmol NH_4Cl = 0.200 mmol/mL × 100 mL = 20.0 mmol

$$\text{mg NH}_4\text{Cl} = 20.0 \text{ mmol} \times 53.5 \text{ mg/mmol} = 1.07 \times 10^3 \text{mg}$$

Therefore, we need 1.07 g NH_4Cl. We calculate the concentration of NH_3 by

$\text{p}K_a$ can be obtained directly from K_a given in Table C.2b in Appendix C.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$= (14.00 - \text{p}K_b) + \log\frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$10.0 = (14.00 - 4.76) + \log\frac{[\text{NH}_3]}{0.200 \text{ mmol/mL}}$$

$$\log\frac{[\text{NH}_3]}{0.200 \text{ mmol/mL}} = 0.76$$

$$\frac{[\text{NH}_3]}{0.200 \text{ mmol/mL}} = 10^{0.76} = 5.8$$

$$[\text{NH}_3] = (0.200)(5.8) = 1.1_6 \text{ mmol/mL}$$

[5] Buying one bottle of buffer and keeping on diluting and reusing it is not a good business plan, however. As you dilute, you lose buffering capacity. If you get it really dilute, dissolution of atmospheric CO_2 and autoionization of water will affect the buffer pH.

The molarity of concentrated ammonia is 14.8 M. Therefore, remember, $C_1V_1 = C_2V_2$,

$$100 \text{ mL} \times 1.1_6 \text{ mmol/mL} = 14.8 \text{ mmol/mL} \times \text{mL NH}_3$$

$$\text{mL NH}_3 = 7.8 \text{ mL}$$

Example 7.15

How many grams ammonium chloride and how many milliliters 3.0 M sodium hydroxide should be added to 200 mL water and diluted to 500 mL to prepare a buffer of pH 9.50 with a salt concentration of 0.10 M?

Solution

We need the ratio of $[NH_3]/[NH_4^+]$. From Example 7.14.

$$\text{pH} = \text{p}K_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.24 + \log \frac{[NH_3]}{[NH_4^+]}$$

$$9.50 = 9.24 + \log \frac{[NH_3]}{[NH_4^+]}$$

$$\log \frac{[NH_3]}{[NH_4^+]} = 0.26$$

$$\frac{[NH_3]}{[NH_4^+]} = 10^{0.26} = 1.8$$

The final concentration of NH_4^+ is 0.10 M, so

$$[NH_3] = (1.8)(0.10) = 0.18\ M$$

$$\text{mmol NH}_4^+ \text{ in final solution} = 0.10\ M \times 500 \text{ mL} = 50 \text{ mmol}$$

$$\text{mmol NH}_3 \text{ in final solution} = 0.18\ M \times 500 \text{ mL} = 90 \text{ mmol}$$

The NH_3 is formed by reacting an equal number of millimoles of NH_4Cl with NaOH. Therefore, a total of $50 + 90 = 140$ mmol NH_4Cl must be taken:

$$\text{mg NH}_4\text{Cl} = 140 \text{ mmol} \times 53.5 \text{ mg/mmol} = 7.49 \times 10^3 \text{ mg} = 7.49 \text{ g}$$

The volume of NaOH needed to react with NH_4^+ to give 90 millimoles of NH_3 is:

$$3.0\ M \times x \text{ mL} = 90 \text{ mmol}$$

$$x = 30 \text{ mL NaOH}$$

Video: Goal Seek pH mixture

Select a buffer with a pK_a value near the desired pH.

Buffer salts do not hydrolyze appreciably.

See Chapter 13 for a list of NIST standard buffers.

We see that a buffer solution for a given pH is prepared by choosing a weak acid (or a weak base) and its salt, with a pK_a *value near the pH that we want*. There are a number of such acids and bases, and any pH region can be buffered by a proper choice of these. A weak acid and its salt give the best buffering in acid solution, and a weak base and its salt give the best buffering in alkaline solution. Some useful buffers for measurements in physiological solutions are described below. National Institute of Standards and Technology (NIST) buffers used for calibrating pH electrodes are described in Chapter 13.

You may have wondered why, in buffer mixtures, the salt does not react with water to hydrolyze as an acid or base. This is because the reaction is suppressed by the presence of the acid or base. In Equation 7.28, the presence of appreciable amounts of

either HA or OH^- will suppress the ionization almost completely. In Equation 7.33, the presence of either B or H_3O^+ will suppress the ionization.

Goal Seek may be used to calculate the pH of mixtures of acids and bases, as in preparing buffers illustrated above. See the text website for an example **video** for calculating the pH of a mixture of carbonic acid and sodium hydroxide: Goal Seek pH mixture.

7.9 Polyprotic Acids and Their Salts

Many acids or bases are polyfunctional, that is, have more than one ionizable proton or hydroxide ion. These substances ionize stepwise, and an equilibrium constant can be written for each step. Consider, for example, the ionization of phosphoric acid:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_{a1} = 1.1 \times 10^{-2} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \tag{7.61}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_{a2} = 7.5 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \tag{7.62}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad K_{a3} = 4.8 \times 10^{-13} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \tag{7.63}$$

The stepwise K_a values of polyprotic acids get progressively smaller as the increased negative charge makes dissociation of the next proton more difficult.

Recall from Chapter 6 that the overall ionization is the sum of these individual steps and the overall ionization constant is the product of the individual ionization constants:

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

$$K_a = K_{a1}K_{a2}K_{a3} = 4.0 \times 10^{-22} = \frac{[H^+]^3[PO_4^{3-}]}{[H_3PO_4]} \tag{7.64}$$

The individual pK_a values are 1.96, 7.12, and 12.32, respectively, for pK_{a1}, pK_{a2}, and pK_{a3}. In order to make precise pH calculations, the contributions of protons from each ionization step must be taken into account. Exact calculation is difficult and requires a tedious iterative procedure since $[H^+]$ is unknown in addition to the various phosphoric acid species. See, for example, References 8 and 11 for calculations. Excel or other spreadsheet-based calculations can be simple. This is illustrated later.

In most cases, approximations can be made so that each ionization step can be considered individually. If the difference between successive ionization constants is more than 10^3, each proton can be differentiated in a titration, that is, each is titrated separately to give stepwise pH breaks in the titration curve. (If an ionization constant is less than about 10^{-9}, then the ionization is too small for a pH break to be exhibited in the titration curve—for example, the third proton for H_3PO_4.) When the individual pK_a's are separated by three units or more, calculations are simplified because *the system can be considered as simply a mixture of three weak acids of equal concentration that largely do not interact with each other.*

We can titrate the first two protons of H_3PO_4 separately. The third is too weak to titrate.

BUFFER CALCULATIONS FOR POLYPROTIC ACIDS

The anion on the right side in each ionization step can be considered the salt (conjugate base) of the acid from which it is derived. That is, in Equation 7.61, $H_2PO_4^-$ is the salt of the acid H_3PO_4. In Equation 7.62, HPO_4^{2-} is the salt of the acid $H_2PO_4^-$, and in Equation 7.63, PO_4^{3-} is the salt of the acid HPO_4^{2-}. So each of these pairs constitutes a buffer system, and orthophosphate buffers can be prepared over a wide pH range.

We can prepare phosphate buffers with pH centered around 1.96 (pK_{a1}), 7.12 (pK_{a2}), and 12.32 (pK_{a3}).

The optimum buffering capacity of each pair occurs at a pH corresponding to its pK_a. The $HPO_4^{2-}/H_2PO_4^-$ couple is an effective buffer system in the blood (see below).

Example 7.16

The pH of blood is 7.40. What is the ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ in the blood (assume 25°C)?

Solution

$$\text{pH} = \text{p}K_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

$$\text{p}K_{a2} = 7.12$$

Therefore,

$$\text{pH} = 7.12 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$7.40 = 7.12 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{(7.40-7.12)} = 10^{0.28} = 1.9$$

DISSOCIATION CALCULATIONS FOR POLYPROTIC ACIDS

Because the individual ionization constants are sufficiently different, *the pH of a solution of H_3PO_4 can be calculated by treating it just as we would any weak acid*. The H^+ from the first ionization step effectively suppresses the other two ionization steps, so that the H^+ contribution from them is negligible compared to the first ionization. The quadratic equation must, however, be solved because K_{a1} is relatively large.

Example 7.17

Calculate the pH of a 0.100 *M* H_3PO_4 solution.

Solution

$$\begin{array}{ccccc} H_3PO_4 & \approx & H^+ & + & H_2PO_4^- \\ 0.100 - x & & x & & x \end{array}$$

From Equation 7.61,

$$\frac{(x)(x)}{0.100 - x} = 1.1 \times 10^{-2}$$

In order to neglect x, C should be $\geq 100K_a$. Here, it is only 10 times as large. Therefore, use the quadratic equation to solve:

$$x^2 + 0.011x - 1.1 \times 10^{-3} = 0$$

Treat H_3PO_4 as a monoprotic acid. But x can't be neglected compared to C.

$$x = \frac{-0.011 \pm \sqrt{(0.011)^2 - 4(-1.1 \times 10^{-3})}}{2}$$

$$x = [H^+] = 0.028\ M$$

The acid is 28% ionized:

$$\text{pH} = -\log 2.8 \times 10^{-2} = 2 - 0.45 = 1.55$$

We can determine if our assumption that the only important source of protons is H_3PO_4 was a realistic one. $H_2PO_4^-$ would be the next most likely source of protons. From Equation 7.62, $[HPO_4^{2-}] = K_{a2}\,[H_2PO_4^-]/[H^+]$. Assuming the concentrations of $H_2PO_4^-$ and H^+ as a first approximation are 0.028 *M* as calculated, then $[HPO_4^{2-}] \approx K_{a2} = 7.5 \times 10^{-8}$ *M*. This is very small compared to 0.028 *M* $H_2PO_4^-$, and so further dissociation is indeed insignificant. We were justified in our approach.

7.10 Ladder Diagrams

Professor's Favorite Example

Contributed by Professor Galena Talanova, Howard University

What is the dominant species at a given pH?

A simple way to visualize what is the dominant species at a given pH is to construct what David Harvey of Depauw University (http://acad.depauw.edu/~harvey/ASDL2008/introduction.html) calls **Ladder Diagrams**. We draw a vertical axis in pH with horizontal bars for the different pK_a's present in the system, as illustrated in Figure 7.1 below.

Referring to Figure 7.1(a), the unionized acid HOAc dominates below a pH of 4.76 (the pK_a value of HOAc) while above this value the OAc^- anion is dominant. Referring to Figure 7.1(b), one can consider that all three acid–base systems can be simultaneously or individually present. For the HF–F^- system depicted in blue, HF dominates at pH values below its pK_a of 3.17 and above this F^- dominates. Similarly H_2S and NH_4^+ dominate at pH values below 6.88 and 9.25, respectively, while HS^- and NH_3 dominates at respective pH values above that. Such diagrams also indicate what species will be dominant in a mixed system at a given pH: at a pH of 6 for

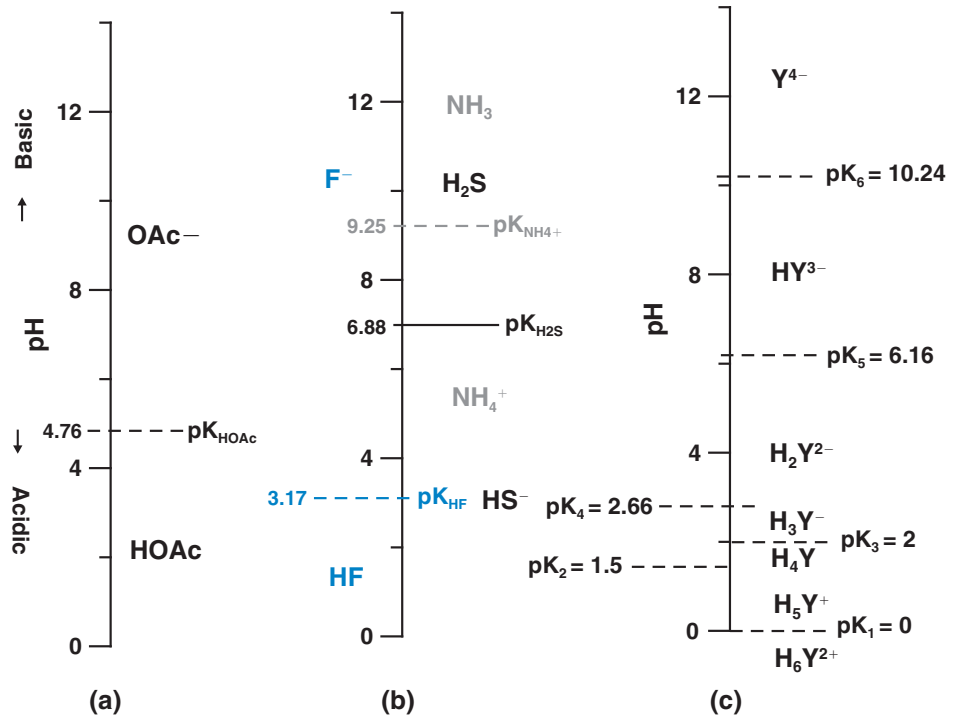


Fig. 7.1. Ladder diagrams depicting systems containing (a) acetic acid and acetate, (b) ammonium and ammonia, hydrofluoric acid and fluoride, (di)hydrogen sulfide and hydrosulfide, and (c) diprotonated ethylenediaminetetraacetic acid (EDTA) (H_6Y^{2+}) and the other six species obtained by successive deprotonation.

example, we will expect F^-, NH_4^+, and H_2S to be the dominant species relative to their respective conjugate acid/base. Finally, Figure 7.1(c) shows the case for EDTA, this represents a hexaprotic acid system; the free acid is actually the diprotonated form H_6Y^{2+} and it exists in dominant form only in extremely strongly acid solutions (pH < 0). The respective zones in which the other individual species dominate (e.g., Y^{4-} is dominant at pH > 10). More details and example problems are given in a PowerPoint file (ch7 7.10 ladder diagrams.ppt) available in the text **website**. ■

7.11 FRACTIONS OF DISSOCIATING SPECIES AT A GIVEN pH: α VALUES — HOW MUCH OF EACH SPECIES?

Often, it is of interest to know the distribution of the different species of a polyprotic acid as a function of pH, that is, at known hydrogen ion concentration as in a buffered solution.

Consider, for example, the dissociation of phosphoric acid. The equilibria are given in Equations 7.61 to 7.63. All the four phosphoric acid species coexist in equilibrium with one another, although the concentrations of some may be very small at a given pH. By changing the pH, the equilibria shift; the relative concentrations change. It is possible to derive general equations for calculating the fraction of the acid that exists in a given form, from the given hydrogen ion concentration.

For a given total **analytical concentration** of phosphoric acid, $C_{H_3PO_4}$, we can write

H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} all exist together in equilibrium. The pH determines the fraction of each.

$$C_{H_3PO_4} = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] \tag{7.65}$$

where the terms on the right-hand side of the equation represent the **equilibrium concentrations** of the individual species. We presumably know the initial total concentration $C_{H_3PO_4}$ and wish to find the fractions or concentrations of the individual species at equilibrium.

We define

$$\alpha_0 = \frac{[H_3PO_4]}{C_{H_3PO_4}} \qquad \alpha_1 = \frac{[H_2PO_4^-]}{C_{H_3PO_4}} \qquad \alpha_2 = \frac{[HPO_4^{2-}]}{C_{H_3PO_4}}$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{C_{H_3PO_4}} \qquad \alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 = 1$$

where the α's are the **fractions** of each species present at equilibrium. Note that the subscripts denote the number of dissociated protons or the charge on the species. We can use Equation 7.65 and the equilibrium constant expressions 7.61 through 7.63 to obtain an expression for $C_{H_3PO_4}$ in terms of the desired species. This is substituted into the appropriate equation to obtain α in terms of $[H^+]$ and the equilibrium constants. In order to calculate α_0, for example, we can rearrange Equations 7.61 through 7.63 to solve for all the species except $[H_3PO_4]$ and substitute into Equation 7.65:

$$[PO_4^{3-}] = \frac{K_{a3}[HPO_4^{2-}]}{[H^+]} \tag{7.66}$$

$$[HPO_4^{2-}] = \frac{K_{a2}[H_2PO_4^-]}{[H^+]} \tag{7.67}$$

$$[H_2PO_4^-] = \frac{K_{a1}[H_3PO_4]}{[H^+]} \tag{7.68}$$

We want all these to contain only $[H_3PO_4]$ (and $[H^+]$, the variable). We can substitute Equation 7.68 for $[H_2PO_4^-]$ in Equation 7.67:

$$[HPO_4^{2-}] = \frac{K_{a1}K_{a2}[H_3PO_4]}{[H^+]^2} \tag{7.69}$$

And we can substitute Equation 7.69 into Equation 7.66 for $[HPO_4^{2-}]$:

$$[PO_4^{3-}] = \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3} \tag{7.70}$$

Finally, we can substitute 7.68 through 7.70 in Equation 7.65:

$$C_{H_3PO_4} = \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3} + \frac{K_{a1}K_{a2}[H_3PO_4]}{[H^+]^2} + \frac{K_{a1}[H_3PO_4]}{[H^+]} + [H_3PO_4] \tag{7.71}$$

We can divide each side of this expression by $[H_3PO_4]$ to obtain $1/\alpha_0$:

$$\frac{C_{H_3PO_4}}{[H_3PO_4]} = \frac{1}{\alpha_0} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}}{[H^+]} + 1 \tag{7.72}$$

Taking the reciprocal of both sides

$$\alpha_0 = \frac{1}{(K_{a1}K_{a2}K_{a3}/[H^+]^3) + (K_{a1}K_{a2}/[H^+]^2) + (K_{a1}/[H^+]) + 1} \tag{7.73}$$

multiplying both the numerator and denominator on the right with $[H^+]^3$, we have:

$$\boxed{\alpha_0 = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}} \tag{7.74}$$

Use this equation to calculate the fraction of H_3PO_4 in solution.

Similar approaches can be taken to obtain expressions for the other α's. For α_1, for example, the equilibrium constant expressions would be solved for all species in terms of $[H_2PO_4^-]$ and substituted into Equation 7.65 to obtain an expression for $C_{H_3PO_4}$ containing only $[H_2PO_4^-]$ and $[H^+]$, from which α_1 is calculated. The results for the other α's are

$$\boxed{\alpha_1 = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}} \tag{7.75}$$

$$\boxed{\alpha_2 = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}} \tag{7.76}$$

$$\boxed{\alpha_3 = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}} \tag{7.77}$$

Derive these equations in Problem 62.

Note that all have the *same denominator* and that *the sum of the numerators equals the denominator*. For α_0, the first term in the denominator becomes the numerator; for α_1, the second term in the denominator becomes the numerator; for α_2, the third term becomes the numerator, and so on. See Problem 63 for a more detailed derivation of the other α's.

In general, an n-protic acid ($n = 1, 2, 3$, respectively, for HOAc, $H_2C_2O_4$, H_3PO_4, etc.) will have $n + 1$ species other than H^+ derived from the acid (e.g., $H_2C_2O_4$,

$HC_2O_4^-$, and $C_2O_4^{2-}$) and thus, $n + 1$ α-values. The denominator in the α-values, Q_n, will consist in each case of $n + 1$ terms:

$$Q_n = \sum_{i=0}^{i=n} [H^+]^{n-i} K_{a0} \ldots K_{ai} \tag{7.78}$$

where K_{a0} is taken to be 1. Thus

$$Q_1 = [H^+] + K_a \tag{7.79}$$

$$Q_2 = [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2} \tag{7.80}$$

$$Q_3 = [H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3} \tag{7.81}$$

$$Q_4 = [H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4} \tag{7.82}$$

While Equation 7.78 may look complicated, it is easy to remember the pattern represented by Equations 7.79 through 7.82. You start with $[H^+]^n$ where n is the number of dissociable proton and then replace an H^+ with a K_a term, beginning with K_{a1} until you run out of both. For α_0 to α_n, remember that the first term in the Q expression becomes the numerator for α_0, the second term for α_1 and so on. Thus, α_1 for a monoprotic acid $\alpha_{1,m}$ is:

$$\alpha_{1,m} = K_a/Q_1 = \frac{K_a}{[H^+] + K_a} \tag{7.83}$$

and α_3 for a tetraprotic acid $\alpha_{3,te}$ is:

$$\begin{aligned}\alpha_{3,te} &= K_{a1}K_{a2}K_{a3}[H^+]/Q_4 \\ &= K_{a1}K_{a2}K_{a3}[H^+]/([H^+]^4 + K_{a1}[H^+]^3 + K_{a1}K_{a2}[H^+]^2 \\ &\quad + K_{a1}K_{a2}K_{a3}[H^+] + K_{a1}K_{a2}K_{a3}K_{a4})\end{aligned} \tag{7.84}$$

Example 7.18

Calculate the equilibrium concentration of the different species in a 0.10 M phosphoric acid solution at pH 3.00 ($[H^+] = 1.0 \times 10^{-3}$ M).

Solution

Substituting into Equation 7.79,

$$\alpha_0 = \frac{(1.0 \times 10^{-3})^3}{(1.0 \times 10^{-3})^3 + (1.1 \times 10^{-2})(1.0 \times 10^{-3})^2 + (1.1 \times 10^{-2})(7.5 \times 10^{-8})(1.0 \times 10^{-3}) + (1.1 \times 10^{-2})(7.5 \times 10^{-8})(4.8 \times 10^{-13})}$$

$$= \frac{1.0 \times 10^{-9}}{1.2 \times 10^{-8}} = 8.3 \times 10^{-2}$$

$$[H_3PO_4] = C_{H_3PO_4}\,\alpha_0 = 0.10 \times 8.3 \times 10^{-2} = 8.3 \times 10^{-3}\ M$$

Similarly,

$$\alpha_1 = 0.92$$

$$[H_2PO_4^-] = C_{H_3PO_4}\,\alpha_1 = 0.10 \times 0.92 = 9.2 \times 10^{-2}\ M$$

$$\alpha_2 = 6.9 \times 10^{-5}$$

$$[HPO_4^{2-}] = C_{H_3PO_4}\,\alpha_2 = 0.10 \times 6.9 \times 10^{-5} = 6.9 \times 10^{-6}\,M$$

$$\alpha_3 = 3.3 \times 10^{-14}$$

$$[PO_4^{3-}] = C_{H_3PO_4}\,\alpha_3 = 0.10 \times 3.3 \times 10^{-14} = 3.3 \times 10^{-15}\,M$$

We see that at pH 3, the majority (92%) of the phosphoric acid exists as $H_2PO_4^-$ and 8.3% exists as H_3PO_4. Only 3.3×10^{-12}% exists as PO_4^{3-}! ■

We can prepare a spreadsheet to calculate the fraction of each species as a function of pH. Formulas and calculations are shown in the spreadsheet[6], and Figure 7.2 shows the corresponding α versus pH plot. The K_a values are entered in cells B4, D4, and F4. The pH values are entered in column A. All the formulas needed for each cell are listed at the bottom of the spreadsheet, and they are initially entered in the boldfaced cells. The formula for calculating the corresponding hydrogen ion concentration (used in the α calculation) is entered in cell B6. The formula for the denominator used for each α calculation is entered in cell C6. Note that the constants are entered as absolute values, while the hydrogen ion concentration is computed from the specific pH values entered in column A. The formulas for the three α calculations are entered in cells D6, E6, and F6. All formulas are copied down to row 34.

The overlapping curves represent buffer regions. The pH values where α_1 and α_2 are 1 represent the end points in titrating H_3PO_4.

See Section 7.16 for a way of representing these plots as straight lines (log–log plots).

Referring to Figure 7.2.xlsx that is available to you from the website (the screenshot is reproduced as Figure 7.3), we want to plot α_0, α_1, α_2, and α_3 (which appear in the columns D:G, titled a_0, a_1, a_2, and a_3) as a function of pH (column A).The most expedient way to accomplish this is to leave the x-data (pH) where it is in column A and move the three sets of y-data we want to plot in contiguous columns. We therefore select the $[H^+]$ and denominator (Q) data (B5:C34) that we do not wish to plot and cut and paste (Ctrl-X, Ctrl V) beginning in cell H5. We select B5:C34 again and delete the empty space (Alt-E D, Shift cells left). Now highlight all the data

By far the best way to understand Excel-related text is to have the relevant Excel file open on your computer while you read this text.

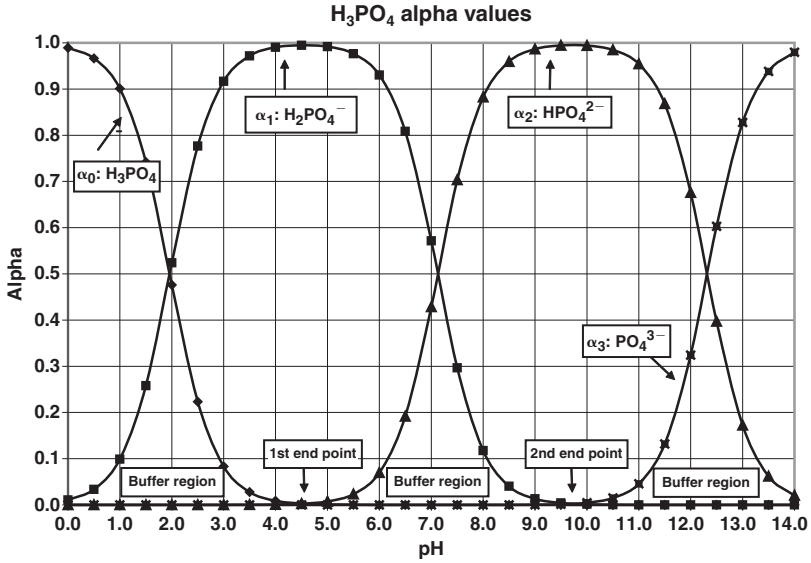


Fig. 7.2. Fractions of H_3PO_4 species as a function of pH. (Buffer region designation suggestions courtesy of Professor Galina Talanova, Howard University)

[6]The "standard view" of any Excel spreadsheet consists of the numbers entered in a cell or the results of the formula entered into a cell. It does not normally show the formula contained in the cell until your cursor is on the cell and then it displays the formula in the formula bar. At any time, you can change the "standard view" into "formula view" by pressing the Ctrl and ‘ (accent key) together.

	A	B	C	D	E	F	G
1	**Calculation of alpha values for H_3PO_4 vs. pH.**						
2	Alpha (α_i) denominator = $[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}$						
3	Numerators: $\alpha_0 = [H^+]^3$; $\alpha_1 = K_{a1}[H^+]^2$; $\alpha_2 = K_{a1}K_{a2}[H^+]$; $\alpha_3 = K_{a1}K_{a2}K_{a3}$						
4	K_{a1}=	1.10E-02	K_{a2}=	7.50E-08	K_{a3}=	4.80E-13	
5	**pH**	**$[H^+]$**	**Denominator**	α_0	α_1	α_2	α_3
6	0.0	**1**	**1.01E+00**	**9.89E−01**	**1.09E−02**	**8.16E−10**	**3.92E−22**
7	0.5	0.316228	3.27E-02	9.66E-01	3.36E-02	7.97E-09	1.21E-20
8	1.0	0.1	1.11E-03	9.01E-01	9.91E-02	7.43E-08	3.57E-19
9	1.5	0.031623	4.26E-05	7.42E-01	2.58E-01	6.12E-07	9.29E-18
10	2.0	0.01	2.10E-06	4.76E-01	5.24E-01	3.93E-06	1.89E-16
11	2.5	0.003162	1.42E-07	2.23E-01	7.77E-01	1.84E-05	2.80E-15
12	3.0	0.001	1.20E-08	8.33E-02	9.17E-01	6.87E-05	3.30E-14
13	3.5	0.000316	1.13E-09	2.79E-02	9.72E-01	2.30E-04	3.50E-13
14	4.0	0.0001	1.11E-10	9.00E-03	9.90E-01	7.43E-04	3.56E-12
15	4.5	3.16E-05	1.11E-11	2.86E-03	9.95E-01	2.36E-03	3.58E-11
16	5.0	0.00001	1.11E-12	9.02E-04	9.92E-01	7.44E-03	3.57E-10
17	5.5	3.16E-06	1.13E-13	2.81E-04	9.77E-01	2.32E-02	3.52E-09
18	6.0	0.000001	1.18E-14	8.46E-05	9.30E-01	6.98E-02	3.35E-08
19	6.5	3.16E-07	1.36E-15	2.32E-05	8.08E-01	1.92E-01	2.91E-07
20	7.0	1E-07	1.93E-16	5.19E-06	5.71E-01	4.29E-01	2.06E-06
21	7.5	3.16E-08	3.71E-17	8.53E-07	2.97E-01	7.03E-01	1.07E-05
22	8.0	1E-08	9.35E-18	1.07E-07	1.18E-01	8.82E-01	4.24E-05
23	8.5	3.16E-09	2.72E-18	1.16E-08	4.05E-02	9.59E-01	1.46E-04
24	9.0	1E-09	8.36E-19	1.20E-09	1.32E-02	9.86E-01	4.73E-04
25	9.5	3.16E-10	2.62E-19	1.21E-10	4.19E-03	9.94E-01	1.51E-03
26	10.0	1E-10	8.30E-20	1.20E-11	1.33E-03	9.94E-01	4.77E-03
27	10.5	3.16E-11	2.65E-20	1.19E-12	4.15E-04	9.85E-01	1.49E-02
28	11.0	1E-11	8.65E-21	1.16E-13	1.27E-04	9.54E-01	4.58E-02
29	11.5	3.16E-12	3.00E-21	1.05E-14	3.66E-05	8.68E-01	1.32E-01
30	12.0	1E-12	1.22E-21	8.19E-16	9.01E-06	6.76E-01	3.24E-01
31	12.5	3.16E-13	6.57E-22	4.81E-17	1.67E-06	3.97E-01	6.03E-01
32	13.0	1E-13	4.79E-22	2.09E-18	2.30E-07	1.72E-01	8.28E-01
33	13.5	3.16E-14	4.22E-22	7.49E-20	2.61E-08	6.18E-02	9.38E-01
34	14.0	1E-14	4.04E-22	2.47E-21	2.72E-09	2.04E-02	9.80E-01
35	Formulas for cells in **boldface**:						
36	**Cell B6** = $[H^+]$ =	10^-A6					
37	**Cell C6**=denom.=	B6^3+$B$4*B6^2+$B$4*$D$4*B6+$B$4*$D$4*$F$4					
38	**Cell D6** = α_0 =	B6^3/C6					
39	**Cell E6** = α_1 =	($B$4*B6^2)/C6					
40	**Cell F6** = α_2 =	($B$4*$D$4*B6)/C6					
41	**Cell G6** = α_3 =	($B$4*$D$4*$F$4)/C6					
42	Copy each formula down through Cell 34						
43	Plot A6:A34 vs. D6:D34, E6:E34, F6:F34, and G6:G34 (series 1, 2, 3, and 4)						

Fig. 7.3. Screenshot of the file Figure 7.2.xlsx (the spreadsheet itself is available in the text **website**).

columns we wish to plot (A5:E34) and click on **Insert—Charts- Scatter**. You can choose the scatter plot shown in column 1, row 2 in the drop-down menu if you just want to see the line plot. Otherwise the scatter plot shown in column 2, row 1 if you want to see the specific points plotted as in Figure 7.2. The plot appears. You can move it to a separate sheet (by right-clicking on the frame of the chart, selecting **Move Chart**, **New Sheet**, and **OK**). Play with the Chart layout on the menu bar: You can click on **Layout 3** (the grid line and linear fit layout), the linear fits are irrelevant here can be subsequently deleted by clicking on the fit lines and deleting them, leaving the gridlines. You can also click on the axes and chart titles, and change them to what you want them to read, etc.

The plot generated by the procedure above is given in Figure 7.2. This figure illustrates how the ratios of the four phosphoric acid species change as the pH is adjusted, for example, in titrating H_3PO_4 with NaOH. While some appear to go to zero concentration above or below certain pH values, they are not really zero,

but diminishingly small. For example, we saw in Example 7.18 that at pH 3.00, the concentration of the PO_4^{3-} ion for 0.1 M H_3PO_4 is only 3.3×10^{-15} M, but it is indeed present in equilibrium. The pH regions where two curves overlap (with appreciable concentrations) represent regions in which buffers may be prepared using those two species. For example, mixtures of H_3PO_4 and $H_2PO_4^-$ can be used to prepare buffers around pH 2.0 ± 1, mixtures of $H_2PO_4^-$ and HPO_4^{2-} around pH 7.1 ± 1, and mixtures of HPO_4^{2-} and PO_4^{3-} around pH 12.3 ± 1. The pH values at which the fraction of a species is essentially 1.0 correspond to the end points in the titration of phosphoric acid with a strong base, that is, $H_2PO_4^{2-}$ at the first end point (pH 4.5), HPO_4^{2-} at the second end point (pH 9.7).

Equation 7.71 could be used for a rigorous calculation of the hydrogen ion concentration from dissociation of a phosphoric acid solution at a given H_3PO_4 concentration (no other added H^+), but this involves tedious iterations. As a first approximation, $[H^+]$ could be calculated from K_{a1} as in Example 7.17, assuming that only the first dissociation step of phosphoric acid was significant. (This is, in fact, what we did in that example.) The first calculated $[H^+]$ could then be substituted in Equation 7.71 to calculate a second approximation of $[H_3PO_4]$, which would be used for a second iterative calculation of $[H^+]$ using K_{a1}, and so forth, until the concentration was constant. A simpler way is to use Excel and Goal Seek as illustrated in Example 7.19 below.

A useful applet developed by Professor Constantinos Efstathiou at the University of Athens allows easy plotting of distribution diagrams of mono- to tetraprotic acids: http://www.chem.uoa.gr/applets/AppletAcid/Appl_Distr2.html. Check out the phosphoric acid one and compare with Figure 7.1, and the EDTA (H_4A) one with Figure 9.1 in Chapter 9. You can change the pK_a values to see how the plots change. The applet also plots log distribution diagrams for the acids (Section 7.16 below). You can also change the K_a values in the spreadsheet Figure 7.2.xlsx to see how the distribution will change.

Example 7.19 The Method of Charge Balance. Calculation of pH in a Phosphoric Acid System

Calculate the pH of 0.050 M H_3PO_4 using Excel and Goal Seek. What will be the pH if you add 0.11 mole of NaOAc and 0.02 mole of K_2HPO_4 to 1 L of this of this solution?

The charge balance method invokes that the sum of the positive charges in any solution equals the sum of negative charges. So for a solution containing only phosphoric acid, the relevant charge balance equation is:

$$[H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] \qquad (7.85)$$

Note that the multipliers of 2 and 3 need, respectively, to be applied to the concentrations of HPO_4^{2-} and PO_4^{3-} because these ions, respectively, carry 2 and 3 units of charge. Putting all terms on one side, expressing $[OH^-]$ as $K_w/[H^+]$ and expressing the various phosphate species concentrations in terms of their α-values, we have:

$$[H^+] - K_w/[H^+] - C_p(\alpha_1 + 2\alpha_2 + 3\alpha_3) = 0 \qquad (7.86)$$

where C_p is the concentration of the total phosphate species, in this case the concentration of H_3PO_4 taken. The Example 7.19.xlsx spreadsheet is available in your text **website**. In cells B1:B5, we have, respectively, written down the values of K_{a1}, K_{a2}, K_{a3}, C_p, and K_w. It is unfortunate that many of the symbols we traditionally use in chemical problems aren't allowed by Excel as KA1, etc. It actually refers to the cell

in column KA and row 1. Similarly C and R refer to columns and rows and are not allowed to be used for any other meaning. Thus, for our purposes, we have named K_{a1}, K_{a2}, K_{a3}, and C_p as KAA, KAB, KAC, and CP and written these names in column A next to the numeric values in column bar. Next we want to permanently ascribe these names to the specific numbers, so that every time we write KAA, Excel will know that we are referring to the value of KAA, 1.1×10^{-2}. To do this, we put our cursor on cell B2. In the top right corner on the formula bar normally it would say B2, when we put our cursor on cell B2. But notice that it says KAA. This is because we have given the number in cell B2 the name KAA. We did this (Excel 2010 only—previous versions have a different procedure) by putting the cursor on cell B2, clicking on the name box (top left corner of formula bar), typing KAA and hitting enter. Verify that cell B2 has the name KAA by moving to some other cell and coming back to cell B2 and noticing that the name box says KAA. (Practice on another spreadsheet naming cells.) For convenience, we have named cells B3:B5 in a similar manner as KAB, KAC, CP, and KW.

Now two rows below this, we have set up column headings as pH, H^+, OH^-, Q3, Alpha1, Alpha2, Alpha3, and Equation. In cell A8, under pH is the value we will be trying to calculate. Presently you can enter any guess value for pH that you might think is reasonable, any value between 0 and 14; it is not important. For now let us enter 0. Also, go ahead and name the cell pH (we do not really need to do this, we can keep on referring to it as cell A8, but it is fun to give names to the cells to designate what they are). In cell B8, under H^+ we want to calculate the corresponding value of $[H^+]$. Excel does not *a priori* know the relationship between pH and $[H^+]$. Since we know that $[H^+]$ can be expressed as 10^{-pH}, we enter in cell B8, $= 10^{-pH}$. (If we did not name cell A8 as pH, we would have had to write in cell B8 $= 10^{-A8}$.) Again, while this is not essential, for convenience, we name cell B8 as H. In cell C8, to calculate the value of $[OH^-]$, we enter $=$ KW/H. For good measure, we name cell C8 as OH. Next under heading Q_3, we have to put in the expression of Equation 7.81, using current names and so we enter in cell D8:

$$= H\text{^}3 + KAA^*H\text{^}2 + KAA^*KAB^*H + KAA^*KAB^*KAC$$

and name the cell Q (we can name it Q or Q three, but not Q3, remember?). Similarly, we enter the alpha formulas in Equations 7.75 through 7.77 in cells E8:G8 and also name them, respectively, ALFA1, ALFA2, and ALFA3. For example, we have entered in cell F8

$$= KAA^*KAB^*H/Q$$

Finally,we are ready to write our Equation 7.86 in cell H8 as:

$$= (1E10) * (H\text{-}OH\text{-}CP * (ALFA1 + 2^*ALFA2 + 3^*ALFA3))$$

You will note that the expression following the 1E10 multiplier (remember this is to stop Excel from believing prematurely that it has found a solution) is the expression in Equation 7.86. All we have to do now is to invoke Goal Seek (Data/What-If Analysis/Goal Seek), type in H8 in the Set Cell box, in "To Value" box type 0 (Equation 7.86), and "By changing cell" box enter pH (or A8). You instantly get your solution, the pH is 1.73. In the "Equation" cell (H8), there is merit to squaring the entire parenthetical expression because this makes it have only positive values. This is not important when we are solving a single problem, but it is important when we solve multiple problems at a time; we will discuss this in greater depth in a later section.

Now let us solve the second part of the problem in which we put into this solution in addition 0.11 *M* NaOAc, 0.02 *M* K_2HPO_4. Introducing another acid-base system would normally seem to be a formidable problem. Actually it is not. We have to do only a modest amount of additional work on the existing spreadsheet to solve this problem. The worked-out solution appears in the spreadsheet Example 7.19b.xlsx on

the text **website**, but let us presently modify the Example 7.19.xlsx spreadsheet we have been working on.

First, we need to understand the changes. We have added sodium (0.11 *M*, we will call this CNA), potassium ($2 \times 0.02 = 0.04$ *M*, we will call this CK) and acetate species (a total of 0.11 *M*, we will call this COAC). The concentration of our total phosphate species has increased from 0.050 *M* to 0.070 *M* and we need to define the dissociation constant for acetic acid (1.75E-5; we shall call this KOAC). The addition of the new species requires that we modify Equation 7.85 to be:

$$[H^+] + [Na^+] + [K^+] = [OH^-] + [OAc^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] \tag{7.87}$$

If we define Q_1 to be the relevant denominator for the acetate system (see Equation 7.79), then α_1 for the acetate system (ALFA1OAC, the name ALFA1 is already taken by the phosphate system—the two α_1 values for these acetate and phosphate systems are *not* the same—although they are in the same solution and are subject to the same pH, the K_a-values for the two systems are different) will be given by Equation 7.83 and we can write Equation 7.87 as:

$$[H^+] + [Na^+] + [K^+] - K_w/[H^+] - C_{OAc}\alpha_{1OAC} - C_p(\alpha_1 + 2\alpha_2 + 3\alpha_3) = 0 \tag{7.88}$$

Now going back to the spreadsheet, in cells D1:D4 we put in the values for KOAC, CNA, CK, and COAC, and give these cells the corresponding names.We put the cursor on column H and insert two more columns (Alt-I and C, twice in succession) so we can create headings Q1 and Alpha1OAc. In these two cells we respectively enter, for Q1, = H + KOAC in cell H8 and name it Qone. For Alpha1OAc (cell I8), we enter = KOAC/Q one and also name the cell ALFA1OAC. Now it is a matter of modifying the equation in cell J8 as:

$$= (10000000000) * (H + CK + CNA - OH - COAC * ALFA1OAC - CP$$
$$* (ALFA1 + 2^*ALFA2 + 3^*ALFA3))$$

Once again, invoke Goal Seek and ask it to set cell J8 to value 0 by changing the cell pH and you immediately have your answer, the pH is 5.17. ■

7.12 SALTS OF POLYPROTIC ACIDS—ACID, BASE, OR BOTH?

Salts of acids such as H_3PO_4 may be acidic or basic. The protonated salts possess both acidic and basic properties ($H_2PO_4^-$, HPO_4^{2-}), while the unprotonated salt is simply a Brønsted base that hydrolyzes (PO_4^{3-}).

1. Amphoteric Salts. $H_2PO_4^-$ possesses both acidic and basic properties. That is, it is **amphoteric**. It ionizes as a weak acid and it also is a Brønsted base that hydrolyzes:

$H_2PO_4^-$ acts as both an acid and a base. See the end of Section 7.16 for how to estimate the extent of each reaction using log–log diagrams.

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 7.5 \times 10^{-8} \tag{7.89}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \quad K_b = \frac{K_w}{K_{a1}} = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]}$$
$$= \frac{1.00 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.1 \times 10^{-13} \tag{7.90}$$

The solution could, hence, be either alkaline or acidic, depending on which ionization is more extensive. Since K_{a2} for the first ionization is nearly 10^5 greater than K_b for the second ionization, the solution in this case will obviously be acidic.

An expression for the hydrogen ion concentration in a solution of an ion such as $H_2PO_4^-$ can be obtained as follows. The total hydrogen ion concentration is equal to the amounts produced from the ionization equilibrium in Equation 7.89 and the ionization of water, less the amount of OH^- produced from the hydrolysis in Equation 7.90. We can write, then,

$$C_{H^+} = [H^+]_{total} = [H^+]_{H_2O} + [H^+]_{H_2PO_4^-} - [OH^-]_{H_2PO_4^-} \tag{7.91}$$

or

$$[H^+] = [OH^-] + [HPO_4^{2-}] - [H_3PO_4] \tag{7.92}$$

We have included the contribution from water since it will not be negligible if the pH of the salt solution happens to be near 7—although in this particular case, the solution will be acid, making the water ionization negligible.

We can solve for $[H^+]$ by substituting expressions in the right-hand side of Equation 7.92 from the equilibrium constant expressions 7.61 and 7.62 and K_w to eliminate all but $[H_2PO_4^-]$, the experimental variable, and $[H^+]$:

$$[H^+] = \frac{K_w}{[H^+]} + \frac{K_{a2}[H_2PO_4^-]}{[H^+]} - \frac{[H_2PO_4^-][H^+]}{K_{a1}} \tag{7.93}$$

from which (by multiplying each side of the equation by $[H^+]$, collecting the terms containing $[H^+]^2$ on the left side, and solving for $[H^+]^2$)

$$[H^+]^2 = \frac{K_w + K_{a2}[H_2PO_4^-]}{1 + \frac{[H_2PO_4^-]}{K_{a1}}} \tag{7.94}$$

$$[H^+] = \sqrt{\frac{K_{a1}K_w + K_{a1}K_{a2}[H_2PO_4^-]}{K_{a1} + [H_2PO_4^-]}} \tag{7.95}$$

That is, for the general case HA^-,

For HA^{2-}, substitute $[HA^{2-}]$ for $[HA^-]$, K_{a2} for K_{a1}, and K_{a3} for K_{a2}.

$$[H^+] = \sqrt{\frac{K_{a1}K_w + K_{a1}K_{a2}[HA^-]}{K_{a1} + [HA^-]}} \tag{7.96}$$

This equation is valid for any salt HA^- derived from an acid H_2A (or for HA^{2-} derived from H_2A^-, etc.) where $[H_2PO_4^-]$ is replaced by $[HA^-]$.

If we assume that the equilibrium concentration $[HA^-]$ is equal to the concentration of salt added, that is, that the extent of ionization and hydrolysis is fairly small, then this value along with the constants can be used for the calculation of $[H^+]$. This assumption is reasonable if the two equilibrium constants (K_{a1} and K_b) involving the salt HA^- are small and the solution is not too dilute. In many cases, $K_{a1}K_w \ll K_{a1}K_{a2}[HA^-]$ in the numerator and can be neglected. This is the equation we would have obtained if we had neglected the dissociation of water. Furthermore, if $K_{a1} \ll [HA^-]$ in the denominator, the equation simplifies to

For HA^{2-}, $[H^+] = \sqrt{K_{a2}K_{a3}}$.

$$[H^+] = \sqrt{K_{a1}K_{a2}} \tag{7.97}$$

Therefore, if the assumptions hold, the pH of a solution of $H_2PO_4^-$ is independent of its concentration! This approximation is adequate for our purposes. The equation

generally applies if there is a large difference between K_{a1} and K_{a2}. For the case of $H_2PO_4^-$, then,

$$[H^+] \approx \sqrt{K_{a1}K_{a2}} = \sqrt{1.1 \times 10^{-2} \times 7.5 \times 10^{-8}} = 2.9 \times 10^{-5}\ M \qquad (7.98)$$

and the pH is approximately independent of the salt concentration (pH ≈ 4.54). This would be the approximate pH of an NaH_2PO_4 solution.

Similarly, HPO_4^{2-} is both an acid and a base. The K values involved here are K_{a2} and K_{a3} of H_3PO_4 ($H_2PO_4^- \equiv H_2A$ and $HPO_4^{2-} \equiv HA^-$). Since $K_{a2} >> K_{a3}$, the pH of a Na_2HPO_4 solution can be calculated from

$$[H^+] \approx \sqrt{K_{a2}K_{a3}} = \sqrt{7.5 \times 10^{-8} \times 4.8 \times 10^{-13}} = 1.9 \times 10^{-10} \qquad (7.99)$$

and the calculated pH is 9.72. Because the pH of amphoteric salts of this type is essentially independent of concentration, the salts are useful for preparing solutions of known pH for standardizing pH meters. For example, potassium acid phthalate, $KHC_8H_4O_2$, gives a solution of pH 4.0 at 25°C. However, these salts are poor buffers against acids or bases; their pH does not fall in the buffer region but occurs at the end point of a titration curve, where the pH can change markedly if either acid or base is added, although dilution does not affect pH as much.

KHP is a NIST "standard buffer" (Chapter 13). The pH of its solution is fixed, but it is not buffered.

2. Unprotonated Salt. Unprotonated phosphate is a fairly strong Brønsted base in solution and ionizes as follows:

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad K_b = \frac{K_w}{K_{a3}} \qquad (7.100)$$

The constant K_{a3} is very small, and so the equilibrium lies significantly to the right. Because $K_{a3} \ll K_{a2}$, hydrolysis of HPO_4^{2-} is suppressed by the OH^- from the first step, and the pH of PO_4^{3-} can be calculated just as for a salt of a monoprotic weak acid. However, because K_{a3} is so small, K_b is relatively large, and the amount of OH^- is not negligible compared with the initial concentration of PO_4^{3-}, and the quadratic equation must be solved, that is, PO_4^{3-} is quite a strong base.

Example 7.20

Calculate the pH of 0.100 M Na_3PO_4.

Solution

$$\begin{array}{ccccc} PO_4^{3-} & + H_2O & \rightleftharpoons & HPO_4^{2-} & + OH^- \\ 0.100 - x & & & x & x \end{array}$$

$$\frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = K_b = \frac{K_w}{K_{a3}} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.020$$

$$\frac{(x)(x)}{0.100 - x} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.020$$

The concentration is only five times K_b, so the quadratic equation is used:

$$x^2 + 0.020x - 2.0 \times 10^{-3} = 0$$

$$x = \frac{-0.020 \pm \sqrt{(0.020)^2 - 4(-2.0 \times 10^{-3})}}{2}$$

$$x = [OH^-] = 0.036\ M$$

$$pH = 12.56$$

The dissociation (hydrolysis) is 36% complete, and phosphate is quite a strong base. See the text **website** for a program that performs the quadratic equation calculation. ■

Example 7.21

Calculate the pH of 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0 *M* solutions each of H_3PO_4, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. Neglect activity corrections.

Solution

We must calculate ten separate pH values for each of the four compounds, which we will do in batches of 10 at a time using the powerful program, Solver. This problem allows us to explore the powers of Microsoft Excel Solver^{TM}, which can solve for more than one parameter (or more than one equation) at a time. At the time of this writing, Excel 2010 is the current version of Excel and Solver has many more capabilities in this version compared to previous versions, including the ability to save a scenario with up to 32 adjustable parameters and solve for up to 200 parameters at a time (although we do not recommend the latter); frequently it actually requires more time to solve say 50 one-parameter (e.g., in terms of H^+) equations four times than to solve 200 one-parameter equations at a time. In comparison, Goal Seek can only solve one parameter in a single equation, and does not allow for incorporating constraints in the parameter we want to solve (e.g., if we are solving for pH, it may be helpful for us to tell the computing algorithm that our solution lies within 0 and 14).

Solver is not automatically installed when you first install Office 2010 in your computer. After opening Excel, go to File/Options/Add-Ins, click on Go and select the Solver Add-In and click OK to install it. The next time you open Excel, if you go to the Data tab, you should see the icon for Solver in the right-hand corner of the menu bar.

Refer to the file Example 7.21.xlsx downloadable from the text **website**. But presently, just start with an empty spreadsheet.Very similar to what we had done in Example 7.19, in cells B1:B4 we have put down the numerical values of K_{a1}, K_{a2}, K_{a3}, and K_w and named them KAA, KAB, KAC, and KW, respectively. First, we are going to do phosphoric acid (H_3PO_4) and we write this down as a heading in row 5. Beginning in row 6 and starting at cell A6, we now create 10 columns and title them CP, pH, H^+, CNA, OH, Q3, Alpha1, Alpha2, Alpha3, and Equation. In A7:A16, we serially type in the concentrations our problem states, i.e., 0.001 to 1.0 as enumerated in the problem. In pH column (cell B7) let us enter a placeholder number, e.g., 1 for now. In the H^+ column (cell C7) we define is relationship with pH ($= 10^{-B7}$). Then in the CNA column cell D7 we type in zero. (The sodium concentration is zero in all of the pure H_3PO_4 solutions.) In the OH^- column (cell E7) we enter the relationship between OH^- and H^+ (given in cell C7) by entering =KW/C7. In the Q3 column (cell F7) we put in (much the same as in Example 7.19):

$$= C7\text{^}3 + KAA^*C7\text{^}2 + KAA^*KAB^*C7 + KAA^*KAB^*KAC$$

Note that rather than defining and using H we are using the cell reference C7 because we will be solving a number of equations, each for the hydrogen ion concentration, in a separate row at one time. The hydrogen ion concentration in each row will be different (in C7:C16), rather than be a single value, and we cannot designate this by naming a single value called H as we did in Example 7.19. Alpha1: Alpha3 in cells G7:I16 are also put in exactly as in Example 7.19 but using C7 rather than H. Our charge balance equation is the same as Equation 7.85, except $[Na^+]$ is added on the left side, for the sodium containing solutions and when expressed in terms of the equilibrium constants, is the same

as Equation 7.86, again with [Na^+] added on the left. Finally, there is the equation in J7 to be put in; we square the charge balance expression (see why below). Although CNA is zero for H_3PO_4, we have retained this term in the charge balance expression so that we can use the same expression for all four of our cases, and multiply the whole by 10^{10}:

$$= (1E10)^*(C7 + D7\text{-}E7\text{-}A7^*(G7 + 2^*H7 + 3^*I7))\text{^}2$$

We now highlight cells B7:J7 and copy and paste (Ctrl-C, Ctrl-V) beginning in cell B8; thus B8:J8 are filled. We could copy the same serially all the way down to B17:J16, but it is more expedient to highlight the two rows (B7:J8) and drag the cursor at the bottom corner of J8 down to J16 and thus fill up the remaining rows. (Note that if we had performed the drag-and-fill operation with only row 7 filled, in all the nonformula cells, by default Excel would have incremented the numerical value by 1 in each step in each of the succeeding rows, e.g., the initial assigned pH cell value would have been 2 in B8, 3 in B9, and so on, until 10 in B16; we do not necessarily want that. By having the same value in cell B8 as in B7, during drag-and-fill, Excel is being told that the increment is zero between the rows in that column and it follows that instruction.)

Next we are going to solve the set of 10 equations in J7:J16 by solving for the correct values of pH in cells B7:B16 simultaneously. First, in cell J18 we sum up the value of all of the equation expression values by typing there:

$$= SUM(J7:J16)$$

Now we are ready to invoke Solver. Go to the Data tab and then click on the Solver icon 

on the top right-hand corner of the menu bar. Solver will open as a drop-down menu box. In the top "Set Objective" box you should already have J18 appearing and highlighted, because you opened Solver with your cursor on this cell. If not, type in J18 here. In order to solve our equations, we want J18 (the charge balance expression) to be zero. If each equation expression is zero, the sum of them must also be zero. In the digital domain, within the numerical resolution we are able to achieve, the best solution will rarely, if ever, be exactly zero but will be able to reach a very small number (especially when you remember that we have already multiplied the expression by 10^{10}). Because we solve a number of equations at one time by taking the sum of the expressions, you will understand why we use the square of the expressions rather than the expressions. From the point of view of solving an equation, one side of which is zero, obviously it does not matter if we try to solve $x = 0$ or $x^2 = 0$. However, if we have two equations $x = 0$ and $y = 0$ and try to solve them individually by trying to get $x + y = 0$, we may never reach the correct solution because for any nonzero value of x and y where $x = -y$ that condition will be made. However, for any real value of x and y, a solution that achieves $x^2 + y^2 = 0$ necessarily achieves the solutions $x = 0$ and $y = 0$.

Next in Solver, there is a choice to set our objective "To" maximize (max), minimize (min), or to a value that we have the option to specify. We can pick either the "min" button (preferred) or "to value 0," both will have the same impact. Because we have squared our expressions, the value in J18 can never be less than zero, so attempting to minimize it will have the same effect as trying to get it to be zero.

Next we click the box "By Changing Variable Cells." We need to either type in what we want to solve (B7:B16) or to use our cursor to select these cells. This box should now read $B$7:$B$16. The box "Make Unconstrained Variables Non-negative" should already be ticked. Our variable is pH and it should indeed be non-negative for most practical problems. The default method in the "Select a Solving Method" box is "GRG nonlinear" (others are "Simplex LP" and "Evolutionary") and we will use this in all our work; GRG stands for *Generalized Reduced Gradient*). You can read about the differences between these solving approaches in Excel.

In "Subject to the Constraints" box, we want to add that our pH values will be below 14. We click the "Add" button, a new box opens up. In the box "Cell Reference" we type in or select B7:B16. The condition box gives us a choice of <=, =, >=, an integer (int) among others. We are already in the default <= operator; this is what we need. So we proceed on to the next box, "Constraint," and type in 14. Then hit ENTER or click on OK. We are returned to the main Solver box. The "Options" button can open a number of adjustable options that you should explore but presently just proceed on. Move the Solver dialog Box to one corner of the screen, so that you can see the contents of J18, which you are trying to minimize. Presently it is likely a very large number. Now click on the button that says "Solve." A new box "Solver Results" will appear. Move it so that you can look at the contents of J18. You will see that it is smaller than before but it is still very large. We may need to invoke "Solver" several times so tick the box that says "Return to Solver Parameters Dialog" and click "OK." As the Solver main menu appears, click on "Solve" again. This time Solver results will likely have made a major difference in the value in J18. But we will keep doing this until there is no change. In fact, in only one more round, J18 will have gone to a value of the order of 10^{-15}, which will not change on further Solver invocations. This time when the Solver dialog box appears, click on "Close," rather than "Solve." Your solved pH values are in columns B7:B16 and range from 3.03 to 1.00.

Let us now do the same thing for NaH_2PO_4. We will write a title in row 21 as **MONOSODIUM PHOSPHATE**. Copy the entire calculation set including headings (A6:J18) beginning in cell A22. The only thing we need to change is the CNA column, noting that the CNA value for monosodium phosphate is always equal to CP, in cell D23 we write =A23 and then drag and fill that cell value though D32. Of course, your equation values will immediately change to very high values. We click on the new sum in cell J34 and invoke Solver. It will open with the previous conditions (e.g., J18 as the target cell, etc.); this you will have to change to the current needs. We set the target cell to J34, and specify that B23:B32 are the variable cells and select the entry in the constraints box and hit "Change." When the Change Constraints box appears, change B7:B16 to B23:B32 and click OK and Solve (make sure you have highlighted Cell J34 in the target cell). Again, in about four rounds you will see that the result is very small and does not change any more. The pH values will change from 5.08 at CP = 0.001 to 4.54 at CP = 1.0 *M*, you will also see how after about a concentration of 0.1 *M*, the pH hardly changes any more.

We similarly do this for Na_2HPO_4 and Na_3PO_4, the only changes we need to make is that for the Na_2HPO_4 case, we note that in the CNA cells, for the Na_2HPO_4 case, the value of the CNA cell is equal to 2* the value of the corresponding CP cell. Similarly in the Na_3PO_4 case the value of the CNA cell will be equal to 3* the value of the corresponding CP cell. When you finish solving these, notice the pattern. The pH for the Na_2HPO_4 case will converge to a value of 9.72 at high CP concentrations while the pH for the Na_3PO_4 case will continually increase with concentration. ■

Example 7.22

EDTA is a polyprotic acid with four protons (H_4Y); it can be further protonated to form a hexaprotic acid (H_6Y^{2+}). Calculate the hydrogen ion concentration of a 0.0100 *M* solution of Na_2EDTA (Na_2H_2Y).

Solution

The two equilibria involving H_2Y^{2-} are

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{3-} \qquad K_{a3} = 6.9 \times 10^{-7}$$

and

$$H_2Y^{2-} + H_2O \rightleftharpoons H_3Y^- + OH^- \qquad K_b = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-3}}$$

Compared to the previously considered case of the partially neutralized salt of a diprotic acid, H_2Y^{2-} is the equivalent of HA^-, and H_3Y^- is the equivalent of H_2A. The equilibrium constants involved are K_{a2} and K_{a3} (the former for the conjugate acid H_3Y^- of the hydrolyzed salt). Thus,

$$[H^+] = \sqrt{K_{a2}K_{a3}} = \sqrt{(2.2 \times 10^{-3})\,(6.9 \times 10^{-7})}$$
$$= 3.9 \times 10^{-5}\ M$$

7.13 Physiological Buffers—They Keep You Alive

The pH of the blood in a healthy individual remains remarkably constant in a range of 7.35 to 7.45. This is because the blood contains a number of buffers that protect against pH change due to the presence of acidic or basic metabolites. From a physiological viewpoint, a change of ±0.3 pH units is extreme. Acid metabolites are ordinarily produced in greater quantities than basic metabolites, and carbon dioxide is the principal one. The buffering capacity of blood for handling CO_2 is estimated to be distributed among various buffer systems as follows: hemoglobin and oxyhemoglobin, 62%; $H_2PO_4^-/HPO_4^{2-}$, 22%; plasma proteins, 11%; HCO_3^-, 5%. Proteins contain carboxylic and amino groups, which are weak acids and bases, respectively. They are, therefore, effective buffering agents. The combined buffering capacity of blood to neutralize acids is designated by clinicians as the "alkali reserve," and this is frequently determined in the clinical laboratory. Certain diseases cause disturbances in the acid balance of the body. For example, diabetes may give rise to "acidosis," which can be fatal.

An important diagnostic analysis is the CO_2/HCO_3^- balance in blood. This ratio is related to the pH of the blood by the Henderson–Hasselbalch equation (7.45):

$$\text{pH} = 6.10 + \log \frac{[HCO_3^-]}{[H_2CO_3]} \tag{7.101}$$

where H_2CO_3 can be considered equal to the concentration of dissolved CO_2 in the blood; 6.10 is pK_{a1} of carbonic acid in blood at body temperature (37°C). Normally, the HCO_3^- concentration in blood is about 26.0 mmol/L, while the concentration of carbon dioxide is 1.3 mmol/L. Accordingly, for the blood,

$$\text{pH} = 6.10 + \log \frac{26\ \text{mmol/L}}{1.3\ \text{mmol/L}} = 7.40$$

The HCO_3^- concentration may be determined by titrimetry (Experiment 10), or the total carbon dioxide content (HCO_3^- + dissolved CO_2) can be determined by acidification and measurement of the evolved gas.[7] If both analyses are performed, the ratio of HCO_3^-/CO_2 can be calculated, and hence conclusions can be drawn concerning acidosis or alkalosis in the patient. Alternatively, if the pH is measured

The CO_2/HCO_3^- balance can be assessed from measuring two of the parameters in Equation (7.101).

[7] The volume of CO_2 is measured, but from the temperature and atmospheric pressure, the number of millimoles of CO_2 and hence its concentration in mmol/L in the solution it originated from can be calculated. At standard temperature and pressure (0°C and 1 atm pressure), 22.4 L contain one mole gas.

(at 37°C), either HCO_3^- or total CO_2 need be measured for a complete knowledge of the carbonic acid balance because the ratio of $[HCO_3^-]/[H_2CO_3]$ can be calculated from Equation 7.101.

The partial pressure, p_{CO_2} of CO_2, may also be measured (e.g., using a CO_2 electrode), in which case $[H_2CO_3] \approx 0.30 p_{CO_2}$. Then, only pH or $[HCO_3^-]$ need be determined.

Note that these equilibria and Equation 7.101 hold although there are other buffer systems in the blood. The pH is the result of all the buffers and the $[HCO_3^-]/[H_2CO_3]$ ratio is set by this pH.

The HCO_3^-/H_2CO_3 buffer system is the most important one in buffering blood in the lung (alveolar blood). As oxygen from inhaled air combines with hemoglobin, the oxygenated hemoglobin ionizes, releasing a proton. This excess acid is removed by reacting with HCO_3^-.

$$H^+ + HCO_3^- \rightarrow H_2CO_3$$

But note that the $[HCO_3^-]/[H_2CO_3]$ ratio at pH 7.4 is $26/1.3 = 20{:}1$. This is not a very effective buffering ratio; and as significant amounts of HCO_3^- are converted to H_2CO_3, the pH would have to decrease to maintain the new ratio. But, fortunately, the H_2CO_3 produced is rapidly decomposed to CO_2 and H_2O by the enzyme *carbonic anhydrase*, and the CO_2 is exhaled by the lungs. Hence, the ratio of HCO_3^-/H_2CO_3 remains constant at 20:1.

Example 7.23

The total carbon dioxide content ($HCO_3^- + CO_2$) in a blood sample is determined by acidifying the sample and measuring the volume of CO_2 evolved with a Van Slyke manometric apparatus. The total concentration was determined to be 28.5 mmol/L. The blood pH at 37°C was determined to be 7.48. What are the concentrations of HCO_3^- and CO_2 in the blood?

Solution

$$\text{pH} = 6.10 + \log \frac{[HCO_3^-]}{[CO_2]}$$

$$7.48 = 6.10 + \log \frac{[HCO_3^-]}{[CO_2]}$$

$$\log \frac{[HCO_3^-]}{[CO_2]} = 1.38$$

$$\frac{[HCO_3^-]}{[CO_2]} = 10^{1.38} = 24$$

$$[HCO_3^-] = 24[CO_2]$$

But

$$[HCO_3^-] + [CO_2] = 28.5 \text{ mmol/L}$$

$$24[CO_2] + [CO_2] = 28.5$$

$$[CO_2] = 1.1_4 \text{ mmol/L}$$

$$[HCO_3^-] = 28.5 - 1.1 = 27.4 \text{ mmol/L}$$

7.14 Buffers for Biological and Clinical Measurements

Many biological reactions of interest occur in the pH range of 6 to 8. A number, particularly specific enzyme reactions that might be used for analyses (see Chapter 23), may occur in the pH range of 4 to 10 or even outside of this. The proper selection of buffers for the study of biological reactions or for use in clinical analyses can be critical in determining whether or not they influence the reaction. A buffer must have the correct pK_a, near physiological pH so the ratio of $[A^-]/[HA]$ in the Henderson–Hasselbalch equation is not too far from unity, and it must be physiologically compatible.

PHOSPHATE BUFFERS

One useful series of buffers are phosphate buffers. Biological systems usually contain some phosphate already, and phosphate buffers will not interfere in many cases. By choosing appropriate mixtures of $H_3PO_4/H_2PO_4^-$, $H_2PO_4^-/HPO_4^{2-}$, or HPO_4^{2-}/PO_4^{3-}, solutions over a wide pH range can be prepared. See G. D. Christian and W. C. Purdy, *J. Electroanal. Chem.*, **3** (1962) 363 for the compositions of a series of phosphate buffers at a constant ionic strength of 0.2. Ionic strength is a measure of the total salt content of a solution (see Chapter 6), and it frequently influences reactions, particularly in kinetic studies. Hence, these buffers could be used in cases where the ionic strength must be constant. However, the buffering capacity decreases markedly as the pH approaches the values for the single salts listed, and the single salts are not buffers at all. The best buffering capacity, obtained at the half neutralization points, is within ±1pH unit of the respective pK_a values, that is, 1.96 ± 1, 7.12 ± 1, and 12.32 ± 1.

Example 7.24

What weights of NaH_2PO_4 and Na_2HPO_4 would be required to prepare 1 L of a buffer solution of pH 7.45 that has an ionic strength of 0.100?

Solution

Let $x = [Na_2HPO_4]$ and $y = [NaH_2PO_4]$. There are two unknowns, and two equations are needed. (Remember there must be the same number of equations as unknowns to solve.) Our first equation is the ionic strength equation:

$$\mu = \tfrac{1}{2}\sum C_i Z_i^2$$

$$0.100 = \tfrac{1}{2}[Na^+](1)^2 + [HPO_4^{2-}](2)^2 + [H_2PO_4^-](1)^2$$

$$0.100 = \tfrac{1}{2}[(2x + y)(1)^2 + x(2)^2 + y(1)^2)]$$

$$0.100 = 3x + y \qquad (1)$$

Our second equation is the Henderson–Hasselbalch equation:

$$\text{pH} = pK_{a2} + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$7.45 = 7.12 + \log\frac{x}{y} \qquad (2)$$

$$\frac{x}{y} = 10^{0.33} = 2.1_4$$

$$x = 2.1_4 y \qquad (3)$$

Substitute in (1):

$$0.100 = 3(2.1_4)y + y$$

$$y = 0.013_5\ M = [NaH_2PO_4]$$

Substitute in (3):

$$x = (2.1_4)(0.013_5) = 0.028_9\ M = [Na_2HPO_4]$$

$$gNaH_2PO_4 = 0.013_5\ \text{mol/L} \times 120\ \text{g/mol} = 1.6_2\ \text{g/L}$$

$$gNa_2HPO_4 = 0.028_9\ \text{mol/L} \times 142\ \text{g/mol} = 4.1_0\ \text{g/L}$$

SOLVING EXAMPLE 7.24 USING EXCEL SOLVER

We can use Example 7.21.xlsx as a template and use only one row of the numbers. Since we know that the ionic strength is going to be 0.1, CP must be significantly less than 0.1. On an initial basis, we enter both 0.1 for CP and CNa. We enter pH (cell B7) as 7.45—this is not a variable in the present problem; this has been given to us. We insert another column before the equation, ionic strength, and in cell J7 express it as

$$= 0.5^*(C7 + D7 + E7 + A7^*(G7 + 4^*H7 + 9^*I7))$$

We need to vary CP and CNA to get the charge balance equation expression to be zero and ionic strength I to be 0.1. The latter is tantamount to saying that we want to solve the equation I − 0.1 = 0. In cell L7 we write this expression: = J7-0.1. Now in cell M7 we have the sum of the squares of the two equation expressions we want to solve, multiplied by 10^{10}. As constraints we merely put in that CP must be less than 0.1. Solver is invoked; we ask cell M7 to be minimized by changing CP (A7) and CNA (D7).

Solver comes up with the solution that CP = 0.0424 *M* and CNA = 0.0712 *M*. If I start by making 0.0424 *M* NaH_2PO_4, I will have left 0.0712-0.0424 = 0.0288 *M* Na, this will then go to making 0.0288 *M* Na_2HPO_4, leaving 0.0424-0.0288 = 0.0136 *M* NaH_2PO_4.

The solved problem is presented in the **website** as 7.24.xlsx.

The use of phosphate buffers is limited in certain applications. Besides the limited buffering capacity at certain pH values, phosphate will precipitate or complex many polyvalent cations, and it frequently will participate in or inhibit a reaction. It should not be used, for example, when calcium is present if its precipitation would affect the reaction of interest.

TRIS BUFFERS

Tris buffers are commonly used in clinical chemistry measurements.

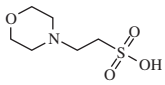
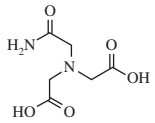
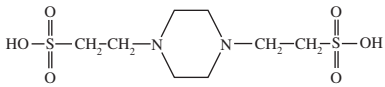
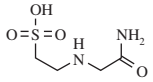
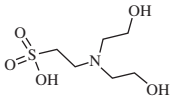
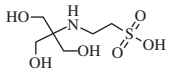
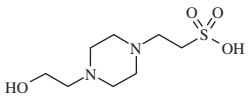
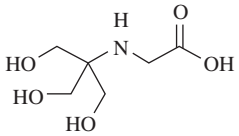
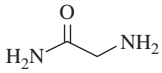
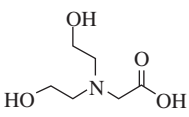
A buffer that is widely used in the clinical laboratory and in biochemical studies in the physiological pH range is that prepared from *tris*(hydroxymethyl)aminomethane [$(HOCH_2)_3CNH_2$ —**Tris**, or **THAM**] and its conjugate acid (the amino group is protonated). It is a primary standard and has good stability, has a high solubility in physiological fluids, is nonhygroscopic, does not absorb CO_2 appreciably, does not precipitate calcium salts, does not appear to inhibit many enzyme systems, and is compatible with biological fluids. It has a p*K* close to physiological pH ($pK_a = 8.08$ for the conjugate acid), but its buffering capacity below pH 7.5 does begin to diminish, a disadvantage. Other disadvantages are that the primary aliphatic amine has considerable potential reactivity and it is reactive with linen fiber junctions, as found in saturated calomel reference electrodes used in pH measurements (Chapter 13); a reference electrode with a ceramic, quartz, or sleeve junction should be used. These buffers are usually prepared by adding an acid such as hydrochloric acid to a solution of Tris to adjust the pH to the desired value.

GOOD BUFFERS

Norman E. Good and coworkers sought to prepare reasonably inexpensive stable optically transparent ($\lambda \geq 230$ nm) buffering components to buffer in the biologically important pH range of 6–8. They wanted these buffers to have good solubility in water but poor solubility in lipids (and hence will not permeate through cell membranes), exhibit minimum salt effects (see following Section 7.12) and temperature effects, and not interact with typical cations that are present in biological systems (at least not precipitate). Based on their experimental study came up with a list of suggested buffering compounds that also included Tris. A few are not easily commercially available, the rest are listed in Table 7.3.

Table 7.3

Good's Buffers[1]

Compound		pK_a at 20°C
Morpholinoethane sulfonic acid (MES)		**6.15**
N-(2-acetamido)iminodiacetic acid (ADA)		**6.6**
Piperazine-N,N′-bis(ethanesulfonic acid)		**6.8**
N-(2-Acetamido)-2-aminoethanesulfonic acid		**6.9**
N,N-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES)		**7.15**
N-[Tris(hydroxymethyl)methyl] 2-aminoethanesulfonic acid (TES)		**7.5**
4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES)		**7.55**
N-[Tris(hydroxymethyl)methyl]glycine (Tricine)		**8.15**
Glycinamide		**8.2**
N-[Bis(hydroxymethyl)methyl]glycine (Bicine)		**8.35**

[1]N. E. Good, G. D. Winget, W. Winter, T. N. Connolly, S. Izawa, and R. M. M. Singh, *Biochemistry* 5 (1966) 467.

For a discussion of Good's buffers, see Q. Yu, A. Kardegedara, Y. Xu, and D. B. Rorabacher, "Avoiding Interferences from Good's Buffers: A Contiguous Series of Noncomplexing Tertiary Amine Buffers Covering the Entire pH Range of pH 3–11," *Anal. Biochem.*, **253(1)** (1997) 50–56.

7.15 Diverse Ion Effect on Acids and Bases: ${}^cK_a$ and ${}^cK_b$ — Salts Change the pH

In Chapter 6, we discussed the thermodynamic equilibrium constant based on activities rather than on concentrations. Diverse salts affect the activities and therefore the extent of dissociation of weak electrolytes such as weak acids or bases. The activity coefficient of the undissociated acid or base is essentially unity if it is uncharged. Then, for the acid HA,

$$K_a = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}} \approx \frac{a_{H^+} \cdot a_{A^-}}{[HA]} \tag{7.102}$$

$$K_a = \frac{[H^+]f_{H^+} \cdot [A^-]f_{A^-}}{[HA]} = {}^cK_a f_{H^+} f_{A^-} \tag{7.103}$$

$${}^cK_a = \frac{K_a}{f_{H^+} f_{A^-}} \tag{7.104}$$

where K_a is the true equilibrium constant at zero ionic strength and ${}^cK_a$ is the "concentration constant" effective at a finite ionic strength.

Therefore, we would predict an increase in ${}^cK_a$ and in the dissociation with increased ionic strength, as the activity coefficients decrease. See Example 6.18, and Problem 22 in Chapter 6. A similar relationship holds for weak bases (see Problem 65 at the end of this chapter).

In the following discussions, by pH, we mean the pH measured with an electrode; this is $-\log a_{H^+}$ Since the ionic strength affects the dissociation of weak acids and bases, it will have an effect on the pH of a buffer. We can write the Henderson–Hasselbalch equation as:

$$\text{pH} = \text{p}K_a + \log \frac{a_{A^-}}{[HA]} = \text{p}K_a + \log \frac{[A^-]}{[HA]} + \log f_{A^-} \tag{7.105}$$

By adding some indifferent salt (e.g., NaCl) to a buffer, the concentration ratio $[A^-]/[HA]$ in a buffer will not change. In Equation 7.105, the only term on the right that is affected by salt addition or dilution is the $\log f_A$ term. If a buffer solution is diluted, its ionic strength will decrease, and f_{A-} and $\log f_{A-}$ will increase, and so will pH. See Footnote 4, earlier in this chapter.

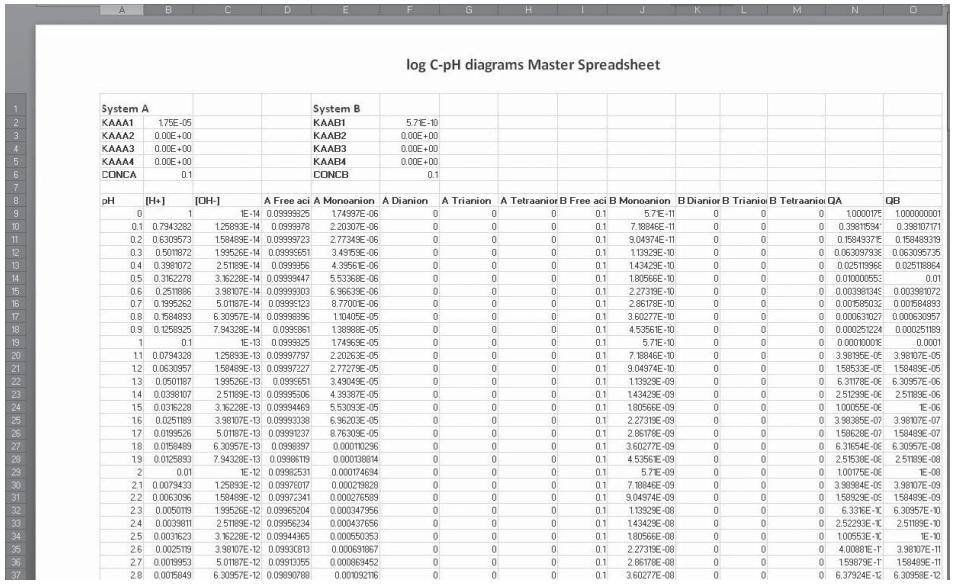
For a $HPO_4^{2-}/H_2PO_4^-$ buffer, the ratio of $a_{HPO_4^{2-}}/a_{H_2PO_4^-}$ will also decrease with increased ionic strength because the effect is greater on the multiply charged ion.

7.16 log C — pH Diagrams

Plots of concentrations of various acid–base species vs. pH are essentially log–log plots that help visualize the status of a system over a large range of concentrations and pH. Especially when combined with the corresponding lines for $[H^+]$ and $[OH^-]$, they provide a global overview that is helpful to understand the nature of a system, even a complex one. It allows for approximate pH estimates of simple and even some

reasonably complex systems. It may be argued, however, that exact pH computations of such systems may be even more straightforward by the charge balance method (see Examples 7.19 and 7.19b on the text **website**) relative to the effort needed to generate a log C-pH diagram. A more detailed exposition of this is therefore deferred to the text **website** but here we present a general description of how to create such a diagram and its usefulness. Regardless of whether exact solutions by the charge balance approach is superior, log C-pH diagrams provide a visual perspective that is unmatched by other approaches. In a way they are much fancier versions of ladder diagrams.

The first step to create such a diagram is to make a spreadsheet that has the necessary data for plotting. We could use the α-value spreadsheet that we generated previously, but let us create a spreadsheet expressly for this purpose and one that can be generically used to generate any log C-pH diagram incorporating one or more acid–base systems.The master spreadsheet is a valuable tool that is on the text **website** as logC-pH Master.xlsx and you should refer to that in our discussion here. Note again that for the present purposes, even if a base is involved, it is easier to treat it in terms of its conjugate acid. Referring to the spreadsheet logC-pH Master.xlsx, a partial screen shot of which appears as Figure 7.4, the first three columns (A:C) (download the spreadsheet from the **website** and open) has pH values (0-14, 0.1 pH units apart, A9:A149) and columns B and C have corresponding values of $[H^+]$ and $[OH^-]$ (calculated respectively as 10^{-pH} and $10^{-(14-pH)}$). The top of the spreadsheet has details for the constants and concentrations of up to two acid–base systems A and B. These are both set up as tetraprotic acid systems (with respective dissociation constants KAAA1, KAAA2, KAAA3, KAAA4, and KAAB1, KAAB2, etc.) and total concentrations of CONCA and CONCB, respectively. Note that mathematical considerations of a *n*-protic acid system *automatically* reduce to that for a $(n-1)$-protic acid system if K_n is entered as zero. Thus, if KAAA4 is entered as zero, system A will be treated as a triprotic acid, if KAAA4 and KAAA3 are both entered as zero, system A will be treated as a diprotic acid, etc. In fact, the spreadsheet will open with nonzero values for only KAAA1 and KAAB1, with all the others entered as zero, i.e., it will open with default values for two monoprotic acid–base systems (KAAA1 $= 1.75 \times 10^{-5}$, the same as that for HOAc, and KAAB1 $= 5.71 \times 10^{-10}$, the same as that for NH_4^+), both with default concentrations of 0.1 *M*. So as it opens, the spreadsheet corresponds to the situation for 0.1 *M* NH_4OAc.



log C-pH diagrams Master Spreadsheet

System A				System B											
KAAA1	1.75E-05			KAAB1	5.71E-10										
KAAA2	0.00E+00			KAAB2	0.00E+00										
KAAA3	0.00E+00			KAAB3	0.00E+00										
KAAA4	0.00E+00			KAAB4	0.00E+00										
CONCA	0.1			CONCB	0.1										
pH	[H+]	[OH-]	A Free aci	A Monoanion	A Dianion	A Trianion	A Tetraanior	B Free aci	B Monoanion	B Dianior	B Trianio	B Tetraanio	QA	QB	
0	1	1E-14	0.09999825	1.74997E-06	0	0	0	0.1	5.71E-11	0	0	0	1.000017	1.000000001	
0.1	0.7943282	1.25893E-14	0.0999978	2.20307E-06	0	0	0	0.1	7.18846E-11	0	0	0	0.39811594	0.398107171	
0.2	0.6309573	1.58489E-14	0.09999723	2.77349E-06	0	0	0	0.1	9.04974E-11	0	0	0	0.15843371	0.158489319	
0.3	0.5011872	1.99526E-14	0.09995651	3.49159E-06	0	0	0	0.1	1.13929E-10	0	0	0	0.063097938	0.063095735	
0.4	0.3981072	2.51189E-14	0.0999956	4.39561E-06	0	0	0	0.1	1.43429E-10	0	0	0	0.025119868	0.025118864	
0.5	0.3162278	3.16228E-14	0.09999447	5.53368E-06	0	0	0	0.1	1.80566E-10	0	0	0	0.010000553	0.01	
0.6	0.2511886	3.98107E-14	0.09999303	6.96639E-06	0	0	0	0.1	2.27319E-10	0	0	0	0.003981345	0.003981072	
0.7	0.1995262	5.01187E-14	0.09995123	8.77001E-06	0	0	0	0.1	2.86178E-10	0	0	0	0.001585032	0.001584893	
0.8	0.1584893	6.30957E-14	0.09998996	1.10405E-05	0	0	0	0.1	3.60277E-10	0	0	0	0.000631027	0.000630957	
0.9	0.1258925	7.94328E-14	0.0999861	1.38988E-05	0	0	0	0.1	4.53561E-10	0	0	0	0.000251224	0.000251189	
1	0.1	1E-13	0.0999825	1.74983E-05	0	0	0	0.1	5.71E-10	0	0	0	0.00010007	0.0001	
1.1	0.0794328	1.25893E-13	0.09997797	2.20263E-05	0	0	0	0.1	7.18846E-10	0	0	0	3.98195E-05	3.98107E-05	
1.2	0.0630957	1.58489E-13	0.09997227	2.77279E-05	0	0	0	0.1	9.04974E-10	0	0	0	1.58533E-05	1.58489E-05	
1.3	0.0501187	1.99526E-13	0.0995651	3.49049E-05	0	0	0	0.1	1.13929E-09	0	0	0	6.31178E-06	6.30957E-06	
1.4	0.0398107	2.51189E-13	0.09995306	4.39387E-05	0	0	0	0.1	1.43429E-09	0	0	0	2.51299E-06	2.51189E-06	
1.5	0.0316228	3.16228E-13	0.09994469	5.53093E-05	0	0	0	0.1	1.80566E-09	0	0	0	1.00055E-06	1E-06	
1.6	0.0251189	3.98107E-13	0.09993038	6.96203E-05	0	0	0	0.1	2.27319E-09	0	0	0	3.98385E-07	3.98107E-07	
1.7	0.0199526	5.01187E-13	0.09991237	8.76309E-05	0	0	0	0.1	2.86178E-09	0	0	0	1.58628E-07	1.58489E-07	
1.8	0.0158489	6.30957E-13	0.0998897	0.000110296	0	0	0	0.1	3.60277E-09	0	0	0	6.31654E-08	6.30957E-08	
1.9	0.0125893	7.94328E-13	0.09986119	0.000138814	0	0	0	0.1	4.53561E-09	0	0	0	2.51538E-08	2.51189E-08	
2	0.01	1E-12	0.09982531	0.000174694	0	0	0	0.1	5.71E-09	0	0	0	1.00175E-08	1E-08	
2.1	0.0079433	1.25893E-12	0.09976017	0.000219828	0	0	0	0.1	7.18846E-09	0	0	0	3.98984E-09	3.98107E-09	
2.2	0.0063096	1.58489E-12	0.09972341	0.000276589	0	0	0	0.1	9.04974E-09	0	0	0	1.58929E-09	1.58489E-09	
2.3	0.0050119	1.99526E-12	0.09965204	0.000347956	0	0	0	0.1	1.13929E-08	0	0	0	6.33186E-10	6.30957E-10	
2.4	0.0039811	2.51189E-12	0.09956234	0.000437656	0	0	0	0.1	1.43429E-08	0	0	0	2.52293E-10	2.51189E-10	
2.5	0.0031623	3.16228E-12	0.09944365	0.000550353	0	0	0	0.1	1.80566E-08	0	0	0	1.00553E-10	1E-10	
2.6	0.0025119	3.98107E-12	0.0993081	0.000691867	0	0	0	0.1	2.27319E-08	0	0	0	4.00881E-11	3.98107E-11	
2.7	0.0019953	5.01187E-12	0.09913055	0.000869452	0	0	0	0.1	2.86178E-08	0	0	0	1.59879E-11	1.58489E-11	
2.8	0.0015849	6.30957E-12	0.09890788	0.001092116	0	0	0	0.1	3.60277E-08	0	0	0	6.37924E-12	6.30958E-12	

Fig. 7.4. Screen shot of the top portion of Figure 7.5.xlsx.

Leaving 10 columns (D:M) as room for the five A-species and B-species, we enter the formulas for the alpha value denominators in columns N and O (titled QA and QB) in row 9. The concentrations of the various A-species $C\alpha_0$ through $C\alpha_4$ are then formulated in columns D:H and those for the corresponding B-species are formulated in columns I:M. Selecting D9:O9 and double-clicking on the right bottom corner of O9 will now fill up the entire spreadsheet.

For the 0.1 *M* NH_4OAc system, before we plot, let us delete (Alt-E D, Shift cells left) the A anions that don't exist for this system (F8:H149) and remove the empty space. We relabel "A Free Acid" and "A Monoanion" as "HOAc" and "OAc^-," respectively, and "B Free Acid" and "B Monoanion" as "NH_4^+" and "NH_3," respectively. We now select columns A through G and plot by selecting **Insert-Charts-Scatter**. Pick the plot with smooth lines without points; we have too many points for individual data points to be shown. Click on Layout 3 to get the grid and the linear trend lines, then delete the trend lines (you may find it more expedient to precisely click on the lines if you expand the graph by dragging outward from the corners of the frame and clicking on the lines where the plot is least crowded). Now let us label the axes, click on the **Axis Title** for the X-axis, highlight "Axis Title" and type in "pH." Similarly change the Y-axis title to read "Concentration." We do not want the pH axis to read up to 16, which it presently does. Hover your cursor around the tick mark for "16" on the X-axis until you see the label "**Horizontal (Value) Axis**"; now right-click. You will have a pop-up menu with the bottom entry being "**Format Axis**." Click on "Format Axis." A new "Format Axis" menu will appear. In the second row for the maximum value of the X-axis, click on the **Fixed** button and enter 14 for the maximum value. While you can keep your multicolor plot as is, for the purposes of the book we would like to make it in shades of gray. So we click on **Style 1** on the menu bar in **Chart Styles**.

The plot that appears is the C vs pH plot. To see the concentration changes better over a larger range, we need to make it a log C vs pH plot. Rather than computing the log of the concentrations, it is easier to make the ordinate logarithmic. Move the cursor again slowly near where the Y-axis has tick marks with the numeric labels—when you see a label pop up that says "**Vertical (Value) Axis**," you are in the right place; right-click now. Click on **Format Axis**. A new "Format Axis" menu will appear. Tick the box that says logarithmic scale.To avoid the Y-axis labels running into the Axis title, we should make the labels all appear in scientific notation. Format the Y-axis again, click on **Number** on the **Format Axis** menu (second entry on the left pane) and pick **Scientific**. This problem is gone. Now we may want to use dashed lines for some of the traces to make the traces more clearly different; let us do this for the HOAc and the NH_3 traces. Looking at the right edge of the graph, from the bottom, the second line is the HOAc trace. Pick this trace by right-clicking on it and in the pop-up menu, select **Format Data Series**. When this menu appears, click on **Line Style**, click on the pull-down arrow on the **Dash type** submenu and pick the short dashes (fourth entry from top). Repeat this process for the NH_3 trace—this is the second line from the bottom on the left edge of the graph.

You will now have the figure depicted as Figure 7.5, the log C-pH diagram for the system. This shows the distribution of all the species in the system at any pH. The diagonal line with -1 slope is the $[H^+]$ line and the diagonal line with $+1$ slope is the $[OH^-]$ line. Except at extremes of pH, these concentrations are much lower than the $HOAC/OAc^-$ or NH_4^+/NH_3 species.

Can we determine from Figure 7.5 what the pH of a 0.1 *M* NH_4OAc solution is? For starters, it is always good to assume that the dominant species is what you are putting in. If we are putting in NH_4OAc, let us assume that NH_4^+ and OAc^- are the dominant species and if so they must be equal. Indeed, over the entire range of pH 5.5–8.5 both of these are almost the same $\sim$ 0.1 *M*. While this can tell us that NH_4OAc will have good buffer intensity across this entire pH range, it does not tell us accurately

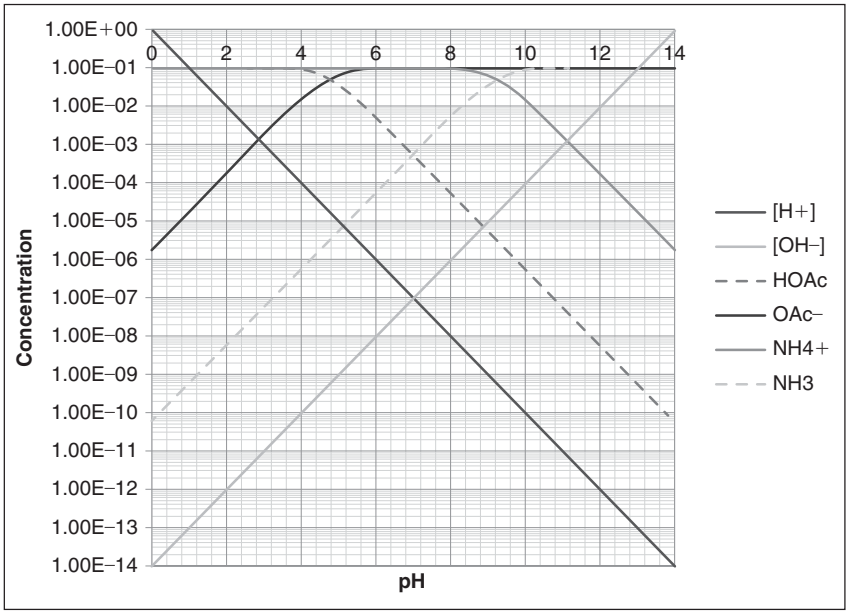


Fig. 7.5. log C-pH diagram for 0.1 *M* NH_4OAc

what the pH of the solution is. $[NH_4^+] = [OAc^-]$ where the two traces intersect each other. If you greatly magnify the Y-axis scale in this region by formatting the axis to have a minimum and maximum value of 0.09 and 0.1, you will be able to see that the intersection is at pH 7. If you want to magnify the X-axis by limiting its span between 6 and 8, you will be able to see that the intersection occurs at pH 7.0.

As an exercise, make a log C-pH diagram for 0.1 *M* $(NH_4)_2HPO_4$. You will enter the three relevant dissociation constants of H_3PO_4 in cells B2:B4, and noting that the concentration of the NH_4^+/NH_3 system will be 0.2 *M*, change the value in cell F6 (CONCB) to read 0.2. Once again assume that the initial species put in (NH_4^+ and HPO_4^{2-}) are the dominant species. If so, the charge balance equation will be

$$[NH_4^+] = 2\,[HPO_4^{2-}]$$

If you have generated the log C-pH diagram correctly, you will be able to verify that at a pH of ~ 8.4, the $[NH_4^+]$ trace has twice the value of the $[HPO_4^{2-}]$ trace and also that at this pH the concentration of all other charged species are much lower and the equality above, which neglect all other charged species, is defensible. The text **website** has the relevant spreadsheet and a log C-pH diagram for the system. See also the applet in Section 7.11 that provides both distribution and log plots for mono- to tetraprotic acids (the log plots show the different acid species, but not $[H^+]$ and $[OH^-]$).

7.17 Exact pH Calculators

A powerful program for calculating pH values of simple to complex mixtures of strong and weak acids and bases is described at: www.phcalculation.se. The program is accessed from the text **website** and detailed instructions are given therein. (See Reference 15 for QR code access to see a description of the program.) The Newton–Raphson approach is used. Calculations can be made using concentrations (ConcpH) or activities (ActpH). Activity coefficients are automatically calculated from the input concentrations and ion size parameters for the Debye–Hückel equation (see Chapter 6). Author of this text worked with Sig Johansson in Sweden to refine this versatile program for activity calculations. Equilibrium concentrations of all species

are calculated. ActpH also calculates activity coefficients of the species and the ionic strength. The two workable programs are on your text **website**.

The program requires input of pK values for ConcpH and concentrations of the reacting species, both acids and bases. For ActpH, additionally, ion size parameters are required, obtained from the Kielland table, Reference 9 in Chapter 6 (and given on the pHcalculation website). ActpH is what a pH meter measures, i.e., $-\log a_{H^+}$ (see Chapter 13).

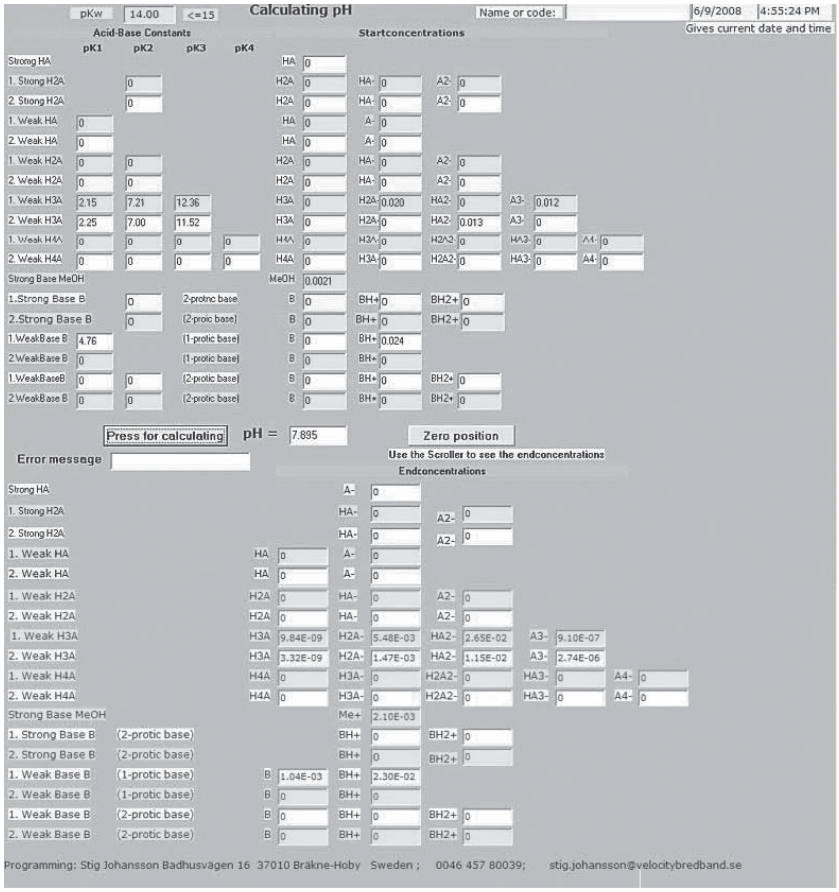
The pH calculator website gives the following example of a complex mixture:

Calculate pH for a mixture of 0.012M $(NH_4)_2LiPO_4$, 0.020 *M* NaH_2PO_4, 0.013 *M* K_2HAsO_4, and 0.0021 *M* NaOH.

H_3PO_4 : $pK_1 = 2.15$ $pK_2 = 7.21$ $pK_3 = 12.36$ $H_3A = 0$ $H_2A^- = 0.020$ $HA^{2-} = 0$ $A^{3-} = 0.012$ H_3AsO_4 : $pK_1 = 2.25$ $pK_2 = 7.00$ $pK_3 = 11.52$ $H_3A = 0$ $H_2A^- = 0$ $HA^{2-} = 0.013$ $A^{3-} = 0$ MeOH = 0.0021

NH_4^+ : $K_b = 4.76$ B = 0 $BH^+ = 0.024$

Inputting the data gives (if you go to the text's website, Stig Johannson folder, 4. Products, you can more readily view and compare this and the next example - the illustrations here give you a quick overview and show the power of the calculator):



The calculated pH is 7.985. The equilibrium concentrations of all species are given.

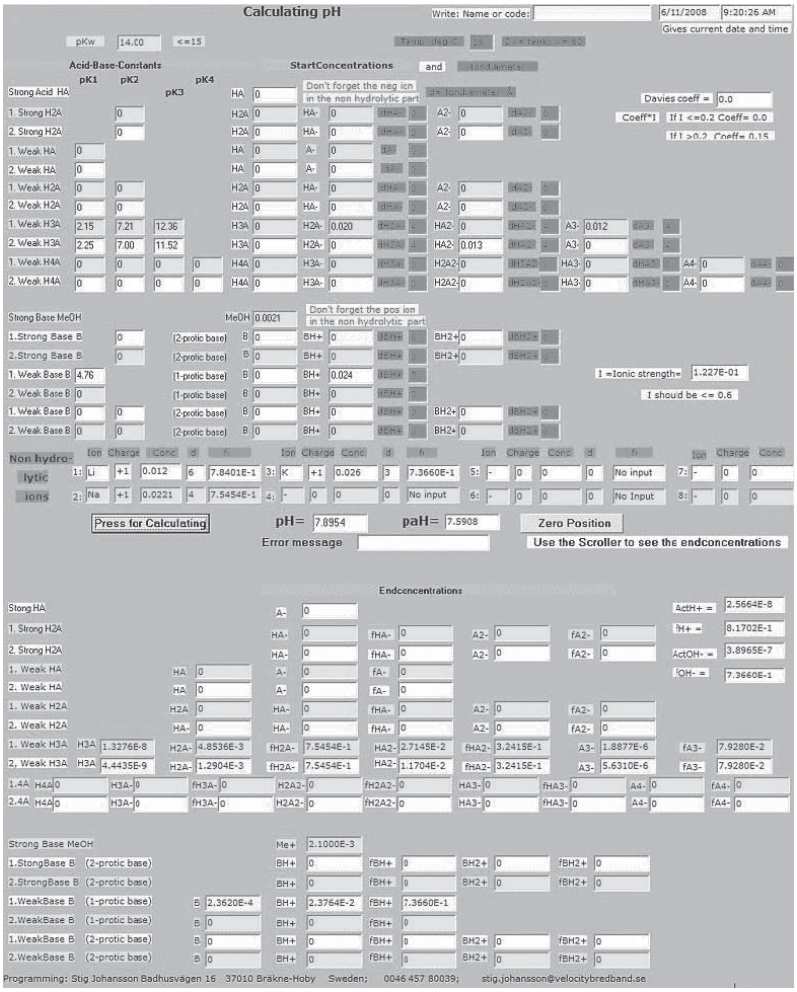
To calculate ActpH for the same mixture, the following addition must be done.

The values of ion diameters:

For all acid ions $d = 4$, $NH_4^+ d = 3$, $Li^+ d = 6$, $Na^+ d = 4$, $K^+ d = 3$

The concentrations for the nonhydrolytic ions: $Li^+ = 0.026$, $Na^+ = 0.0221$ and $K^+ = 0.026$

Inputting the parameters gives:



This program calculates both ConcpH and ActpH. The latter is 7.5908, compared with 7.8354 for ConcpH. The calculations should be rounded to 0.01 pH since absolute pH cannot be measured with greater accuracy, although discriminations or changes at the 0.001 pH level may be of interest. Note that the activity coefficients of all the equilibrium species are given, along with the concentrations, and so the activities are known.

This program can be used to calculate the pH of virtually any mixture of acids and bases, if the pK values (and ion size parameters for Act pH) are known. Use this example as a practice. Then try making up a mixture and calculate the pH.

A second useful program is CurTiPot by Ivano Gutz, Universidad de São Paulo, Brazil: http://www2.iq.usp.br/docente/gutz/Curtipot_.html. (See Reference 16 for QR code access.)

It is a powerful and very versatile program that performs the same pH and paH calculations, but also titration curves, alpha plots, etc. It provides:

- pH calculation of any aqueous solution of acids, bases, and salts, including buffers, zwitterionic amino acids, from single component to complex mixtures (30 or more species in equilibrium)

- buffer capacity, ionic strength, fractional distribution, activities and apparent dissociation constants of all species at equilibrium.

It has a higher learning curve, but with practices, it provides a wealth of information. You might try doing the same calculations using both programs. You should get the same result.

We can also solve the pH of mixtures of acids and bases using Goal Seek. See the **video** illustrating this for a mixture of NaOH and H_2CO_3.

Professor's Favorite Problems

Contributed by Professor Michael De Grandpre, University of Montana

Example 7.25 pH of Seawater

Did you know that ocean pH is decreasing (see the figures on the next page)? A portion of the CO_2 from fossil fuel combustion is absorbed by the oceans, forming carbonic acid. This process, named "ocean acidification," has decreased the average pH in the surface oceans by 0.1 units over the past ~100 years. Chemical oceanographers have long realized the importance of tracking and studying CO_2 in the oceans and in the 1980s began developing improved analytical tools to do this, including new methods for measuring pH. Glass pH electrodes, the workhorse for most pH applications, are not accurate enough to document these small pH changes over time. Oceanographers revitalized an old but rarely used method, the spectrophotometric measurement of pH using indicators. As you may have guessed, the function for deriving the pH is simply the Henderson–Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a' + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

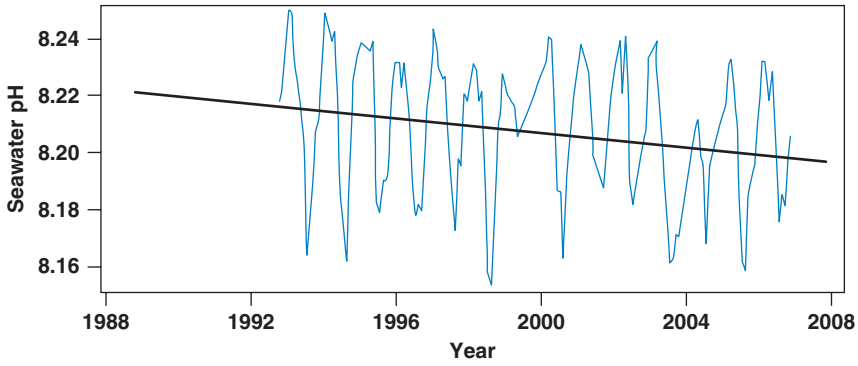
where pH is defined on the total hydrogen ion scale (for a definition and description see References 17 and 19.) . The $\mathrm{p}K_a'$ is the apparent dissociation constant, and $[\mathrm{A}^-]$ and [HA] are the unprotonated and protonated forms of the pH indicator. The improvement came in the determination of $\mathrm{p}K_a'$ on a pH scale consistent with the CO_2 equilibria in seawater (see References 19 and 20). The indicator concentrations $[\mathrm{A}^-]$ and [HA] are quantified on a spectrophotometer by recording 100% transmittance with pure seawater (the blank) and adding a small amount of indicator to the seawater sample at a fixed temperature. Using Beer's law you might expect the ratio $[\mathrm{A}^-]/[\mathrm{HA}]$ to be:

$$\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{\mathrm{A}_2\varepsilon_{1\mathrm{HA}}}{\mathrm{A}_1\varepsilon_{2\mathrm{A}}} \tag{7.106}$$

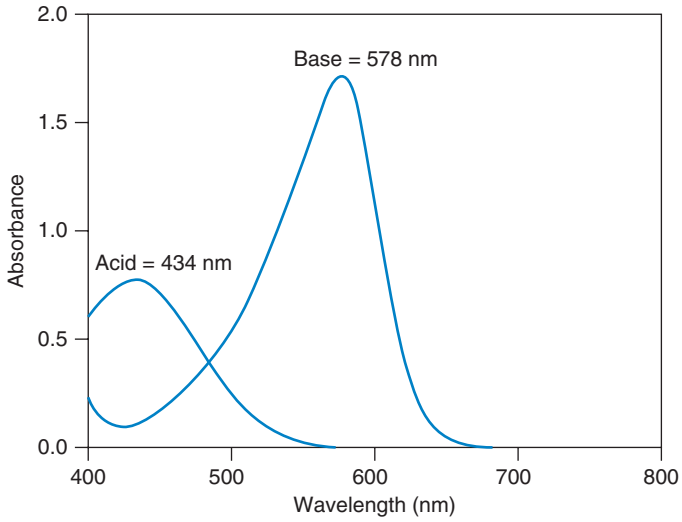
where A_i and ε are the indicator absorbances and molar absorptivities, respectively, at the absorbance maxima for the protonated (1) and unprotonated (2) forms (see the second figure on the next page). However, for the sulfonephthalein indicators used for this application, the spectra of the two forms overlap, and the following equation must be used (References 20 and 21):

$$\mathrm{pH} = \mathrm{p}K_a' + \log\left[\frac{(\mathrm{A}_2/\mathrm{A}_1) - \mathrm{e}_1}{\mathrm{e}_2 - \mathrm{e}_3(\mathrm{A}_2/\mathrm{A}_1)}\right] \tag{7.107}$$

where $e_1 = \varepsilon_{2HA}/\varepsilon_{1HA}$, $e_2 = \varepsilon_{2A}/\varepsilon_{1HA}$, and $e_3 = \varepsilon_{1A}/\varepsilon_{1HA}$. Equation 7.107 gives very reproducible measurements of seawater pH at a given temperature and salinity.[8].



(Source: N. R. Bates/From M.D. Degrandpre. Data for plot, courtesy of Nicholas B. Bates. Reproduced with permission.)



(Source: M. D. Degranpre/From M. D. Degrandpre. Reproduced with permission.)

Example 7.26

At the Bermuda Atlantic Time-Series station (BATS), a sample taken from the ocean surface is analyzed using the indicator meta-cresol purple (mCP). The analytical wavelengths are 434 nm and 578 nm, corresponding to the absorbance maxima of the protonated and unprotonated forms, respectively. At these wavelengths e_1, e_2, and e_3 and are equal to 0.00691, 2.222, and 0.1331, respectively. The mCP $pK'_a = 1245.69/T + 3.8275 + (2.11 \times 10^{-3})(35 - S)$ where T is temperature in Kelvin and S

[8]In very recent work, to avoid any effect of the indicator addition on the sea water pH, measurements are made by adding different amounts of indicator and extrapolating the measured pH to zero indicator added. A single injection of the indicator into a flowing sea water stream, using basic flow-injection techniques can generate the necessary data.

is salinity (parts per thousand) (Reference 20). A small amount of mCP is added to the seawater sample and the absorbances, measured using a UV–VIS spectrophotometer are found to be $A_1 = 0.3892$ and $A_2 = 0.8528$. What is the pH of the seawater sample? The measurement temperature is 22.3°C and salinity = 35.16 ppt. Small effects due to perturbation of the seawater pH from the weak acid indicator and e_i temperature dependence are neglected.

Solution

The absorbance is the result of the overlapping spectra of the two species. If measured at two wavelengths, typically at the absorbance maxima of the two forms, the absorbances are the sum of the individual species absorbances:

$$A_2 = \varepsilon_{2HA} b[HA] + \varepsilon_{2A} b[A^-] \tag{1}$$

$$A_1 = \varepsilon_{1HA} b[HA] + \varepsilon_{1A} b[A^-] \tag{2}$$

Solving (1) for [HA] and substituting into (2) gives:

$$[A^-] = \frac{A_2\varepsilon_{1HA} - A_1\varepsilon_{2HA}}{\varepsilon_{1HA}\varepsilon_{2A} b - \varepsilon_{2HA}\varepsilon_{1A} b}$$

Similarly, solving (2) for $[A^-]$ and substituting into (1) gives:

$$[HA] = \frac{A_1\varepsilon_{2A} - A_2\varepsilon_{1A}}{\varepsilon_{1HA}\varepsilon_{2A} b - \varepsilon_{2HA}\varepsilon_{1A} b}$$

Substituting $[A^-]$ and [HA] into the Henderson–Hasselbalch equation gives Equation 7.107 above.

$$pH = pK_a' + \log\left[\frac{(A_2/A_1) - e_1}{e_2 - e_3(A_2/A_1)}\right]$$

Where $e_1 = \varepsilon_{2HA}/\varepsilon_{1HA}$, $e_2 = \varepsilon_{2A}/\varepsilon_{1HA}$, and $e_3 = \varepsilon_{1A}/\varepsilon_{1HA}$. When there is no overlap $e_1 = e_3 = 0$ and the equation simplifies to Equation 7.106 in the example (this can be directly derived by using Equations 7.106 and 7.107 where $\varepsilon_{2HA} = \varepsilon_{1A} = 0$):

$$pH = pK_a' + \log\left[\frac{A_2\varepsilon_{1HA}}{A_1\varepsilon_{2A}}\right]$$

Substituting the values of T (Kelvin) and S in the pK_a' equation, and of e_1, e_2, e_3, A_1, and A_2 in the pH equation, gives pK_a' to be 8.0430 at this temperature and salinity. The seawater pH from the BATS site is calculated to be 8.0967. ■

Questions

1. Explain the difference between a strong electrolyte and a weak electrolyte. Is an "insoluble" salt a weak or a strong electrolyte?
2. What is the Brønsted acid–base theory? What is the Lewis acid–base theory?
3. What is a conjugate acid? Conjugate base?
4. Write the ionization reaction of aniline, $C_6H_5NH_2$, in glacial acetic acid, and identify the conjugate acid of aniline. Write the ionization reaction of phenol, C_6H_5OH, in ethylene diamine, $NH_2CH_2CH_2NH_2$, and identify the conjugate base of phenol.
5. What are Good Buffers?

Problems

STRONG ACIDS AND BASES

6. Calculate the pH and pOH of the following strong acid solutions: (a) 0.020 *M* $HClO_4$, (b) 1.3×10^{-4} *M* HNO_3, (c) 1.2 *M* HCl, (d) 1.2×10^{-9} *M* HCl, (e) 2.4×10^{-7} *M* HNO_3.

7. Calculate the pH and pOH of the following strong base solutions: (a) 0.050 *M* NaOH, (b) 0.14 *M* $Ba(OH)_2$, (c) 2.4 *M* NaOH, (d) 3.0×10^{-7} *M* KOH, (e) 3.7×10^{-3} *M* KOH.

8. Calculate the hydroxide ion concentration of the following solutions: (a) 2.6×10^{-5} *M* HCl, (b) 0.20 *M* HNO_3, (c) 2.7×10^{-9} *M* $HClO_4$, (d) 1.9 *M* $HClO_4$.

9. Calculate the hydrogen ion concentration of the solutions with the following pH values: (a) 3.47, (b) 0.20, (c) 8.60, (d) −0.60, (e) 14.35, (f) −1.25.

10. Calculate the pH and pOH of a solution obtained by mixing equal volumes of 0.10 *M* H_2SO_4 and 0.30 *M* NaOH.

11. Calculate the pH of a solution obtained by mixing equal volumes of a strong acid solution of pH 3.00 and a strong base solution of pH 12.00.

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Noel Motta, University of Puerto Rico, Rio Piedras

12. V_a mL of a strong acid solution of pH 2.00 is mixed with V_b mL of a strong base solution of pH 11.00. Express V_a in terms of V_b if the mixture is neutral. The solution temperature is 24°C.

TEMPERATURE EFFECT

13. Calculate the hydrogen ion concentration and pH of a neutral solution at 50°C ($K_w = 5.5 \times 10^{-14}$ at 50°C).

14. Calculate the pOH of a blood sample whose pH is 7.40 at 37°C.

WEAK ACIDS AND BASES

15. The pH of an acetic acid solution is 3.26. What is the concentration of acetic acid and what is the percent acid ionized?

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Wen Yen Lee, The University of Texas at El Paso

16. K_a for acetic acid (CH_3COOH) is 1.75×10^{-5}. K_w is 1.00×10^{-14}. (a) Find K_b for acetate ion (CH_3COO^-). (b) When 0.1 *M* of sodium acetate (CH_3COONa) dissolves in water at 24°C, what is the pH of the solution? Assume the ions behave ideally.

17. The pH of a 0.20 *M* solution of a primary amine, RNH_2, is 8.42. What is the pK_b of the amine?

18. A monoprotic organic acid with a K_a of 6.7×10^{-4} is 3.5% ionized when 100 g of it is dissolved in 1 L. What is the formula weight of the acid?

19. Calculate the pH of a 0.25 *M* solution of propanoic acid.

20. Calculate the pH of a 0.10 *M* solution of aniline, a weak base.

21. Calculate the pH of a 0.1 *M* solution of iodic acid, HIO_3.

22. The first proton of sulfuric acid is completely ionized, but the second proton is only partially dissociated, with an acidity constant K_{a2} of 1.2×10^{-2}. Calculate the hydrogen ion concentration in a 0.0100 *M* H_2SO_4 solution.

23. Calculate the hydrogen ion concentration in a 0.100 *M* solution of trichloroacetic acid.

24. An amine, RNH_2, has a pK_b of 4.20. What is the pH of a 0.20 *M* solution of the base?

25. What is the concentration of a solution of acetic acid if it is 3.0% ionized?

26. By how much should a 0.100 *M* solution of a weak acid HA be diluted in order to double its percent ionization? Assume $C > 100K_a$.

SALTS OF WEAK ACIDS AND BASES

27. If 25 mL of 0.20 *M* NaOH is added to 20 mL of 0.25 *M* boric acid, what is the pH of the resulting solution?

28. Calculate the pH of a 0.010 *M* solution of NaCN.

29. Calculate the pH of a 0.050 *M* solution of sodium benzoate.

30. Calculate the pH of a 0.25 *M* solution of pyridinium hydrochloride (pyridine · HCl, $C_6H_5NH^+Cl$).

31. Calculate the pH of the solution obtained by adding 12.0 mL of 0.25 *M* H_2SO_4 to 6.0 mL of 1.0 *M* NH_3.

32. Calculate the pH of the solution obtained by adding 20 mL of 0.10 *M* HOAc to 20 mL of 0.10 *M* NaOH.

33. Calculate the pH of the solution prepared by adding 0.10 mol each of hydroxylamine and hydrochloric acid to 500 mL water.

34. Calculate the pH of a 0.0010 *M* solution of sodium salicylate, $C_6H_4(OH)COONa$.

35. Calculate the pH of a 1.0×10^{-4} *M* solution of NaCN.

POLYPROTIC ACIDS AND THEIR SALTS

36. What is the pH of 0.0100 *M* solution of phthalic acid?

37. What is the pH of a 0.0100 *M* solution of potassium phthalate?

38. What is the pH of a 0.0100 *M* solution of potassium acid phthalate (KHP)?

39. Calculate the pH of a 0.600 *M* solution of Na_2S.

40. Calculate the pH of a 0.500 *M* solution of Na_3PO_4.

41. Calculate the pH of a 0.250 *M* solution of $NaHCO_3$.

42. Calculate the pH of a 0.600 *M* solution of NaHS.

43. Calculate the pH of a 0.050 *M* solution of the trisodium salt of EDTA (ethylenediaminetetraacetic acid), Na_3HY.

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Bin Wang, Marshall University

44. What is the dominant species in solution:

(a) in a diprotic acid (H_2X) system if (i) pH > pK_{a2}; (ii) pK_{a1} < pH < pK_{a2}; and (c) pH < pK_{a1}?

(b) in a triprotic acid system (H_3A) (i) if pH = $\frac{1}{2}(pK_2 + pK_3)$, (ii) pH > pK_a?

BUFFERS

45. Calculate the pH of a solution that is 0.050 *M* in formic acid and 0.10 *M* in sodium formate.

46. Calculate the pH of a solution prepared by mixing 5.0 mL of 0.10 *M* NH_3 with 10.0 mL of 0.020 *M* HCl.

47. An acetic acid–sodium acetate buffer of pH 5.00 is 0.100 *M* in NaOAc. Calculate the pH after the addition of 10 mL of 0.1 *M* NaOH to 100 mL of the buffer.

48. A buffer solution is prepared by adding 20 mL of 0.10 *M* sodium hydroxide solution to 50 mL of 0.10 *M* acetic acid solution. What is the pH of the buffer?

49. A buffer solution is prepared by adding 25 mL of 0.050 *M* sulfuric acid solution to 50 mL of 0.10 *M* ammonia solution. What is the pH of the buffer?

50. Aspirin (acetylsalicylic acid) is absorbed from the stomach in the free (nonionized) acid form. If a patient takes an antacid that adjusts the pH of the stomach contents to 2.95 and then takes two 5-grain aspirin tablets (total 0.65 g), how many grams of aspirin are available for immediate absorption from the stomach, assuming immediate dissolution? Also assume that aspirin does not change the pH of the stomach contents. The pK_a of aspirin is 3.50, and its formula weight is 180.2.

51. *Tris*(hydroxymethyl)aminomethane [$(HOCH_2)_3CNH_2$—Tris, or THAM] is a weak base frequently used to prepare buffers in biochemistry. Its K_b is 1.2×10^{-6} and pK_b is 5.92. The corresponding pK_a is 8.08, which is near the pH of the physiological buffers, and so it exhibits good buffering capacity at physiological pH. What weight of THAM must be taken with 100 mL of 0.50 *M* HCl to prepare 1 L of a pH 7.40 buffer?

52. Calculate the hydrogen ion concentration for Problem 23 if the solution contains also 0.100 *M* sodium trichloroacetate.

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Bin Wang, Marshall University

53. Use the Henderson–Hasselbalch equation to find the value of $[C_6H_5COOH]/[C_6H_5COO^-]$ in a solution at (a) pH 3.00, and (b) pH 5.00. For C_6H_5COOH, pK_a is 4.20.

BUFFERS FROM POLYPROTIC ACIDS

54. What is the pH of a solution that is 0.20 *M* in phthalic acid (H_2P) and 0.10 *M* in potassium acid phthalate (KHP)?

55. What is the pH of a solution that is 0.25 *M* each in potassium acid phthalate (KHP) and potassium phthalate (K_2P)?

56. The total phosphate concentration in a blood sample is determined by spectrophotometry to be 3.0×10^{-3} *M*. If the pH of the blood sample is 7.45, what are the concentrations of $H_2PO_4^-$ and HPO_4^{2} in the blood?

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Bin Wang, Marshall University

57. A student weighed out 0.6529 g of anhydrous monohydrogen sodium phosphate (Na_2HPO_4) and 0.2477 g of dihydrogen sodium phosphate ($NaH_2PO_4H_2O$), then dissolved them into 100 mL of distilled water. What is the pH?

BUFFER INTENSITY

58. A buffer solution contains 0.10 *M* NaH_2PO_4 and 0.070 *M* Na_2HPO_4. What is its buffer intensity in moles/liter per pH? By how much would the pH change if 10 µL(0.010 mL) of 1.0 *M* HCl or 1.0 *M* NaOH were added to 10 mL of the buffer?

59. You wish to prepare a pH 4.76 acetic acid–sodium acetate buffer with a buffer intensity of 1.0 *M* per pH. What concentrations of acetic acid and sodium acetate are needed?

CONSTANT-IONIC-STRENGTH BUFFERS

60. What weight of Na_2HPO_4 and KH_2PO_4 would be required to prepare 200 mL of a buffer solution of pH 7.40 that has an ionic strength of 0.20? (See Chapter 6 for a definition of ionic strength.)

61. What volume of 85% (wt/wt) H_3PO_4 (sp. gr. 1.69) and what weight of KH_2PO_4 are required to prepare 200 mL of a buffer of pH 3.00 that has an ionic strength of 0.20?

α CALCULATIONS

62. Calculate the equilibrium concentrations of the different species in a 0.0100 *M* solution of sulfurous acid, H_2SO_3, at pH 4.00 ($[H^+] = 1.0 \times 10^{-4}$ *M*).

63. Derive Equations 7.75, 7.76, and 7.77 for α_1, α_2, and α_3 of phosphoric acid.

DIVERSE SALT EFFECT

64. Calculate the hydrogen ion concentration for a 0.0200 *M* solution of HCN in 0.100 *M* NaCl (diverse ion effect).

65. Derive the equivalent of Equation 7.104 for the diverse salt effect on an uncharged weak base B.

LOGARITHMIC CONCENTRATION DIAGRAMS

You can use the HOAc spreadsheet exercise on the text **website** as a guide for Problem 66 (Spreadsheet Problems). Prepare a spreadsheet for Problem 69 using α-values—see the text **website** for HOAc log plots using α-values.

66. Construct the log–log diagram for a 10^{-3} M solution of acetic acid.

67. From the diagram in Problem 66, estimate the pH of a 10^{-3} M solution of acetic acid. What is the concentration of acetate ion in this solution?

68. For Problem 66, derive the expression for log[OAc^-] in acid solution and calculate the acetate concentration at pH 2.00 for a 10^{-3} M acetic acid solution. Compare with the value estimated from the log–log diagram.

69. Construct the log–log diagram for a 10^{-3} M solution of malic acid by preparing a spreadsheet using α values.

70. From the diagram in Problem 69, estimate the pH and concentrations of each species present in (a) 10^{-3} M malic acid and (b) 10^{-3} M sodium malate solution.

71. For Problem 69, derive the expressions for the HA^- curves in the acid and alkaline regions.

72. Derive expressions for (a) log[H_3PO_4] between pH = pK_{a1} and pK_{a2}, (b) log[$H_2PO_4^-$] between pH = pK_{a2} and pK_{a3}, (c) log[HPO_4^{2-}] at between pH = pK_{a2} and pK_{a1}, and (d) log [PO_4^{3-}] at between pH = pK_{a3} and pK_{a2}. Check with representative points on the curves.

73. Construct a log–log diagram for 0.001 M H_3PO_4 using α values. Start with the spreadsheet for Figure 7.2 (given in the text **website**). Compare the chart with Figure 7.16.3 on the text **website** (Addendum to Section 7.16). Vary the H_3PO_4 concentration and see how the curves change.

74. The Stig Johansson pH calculator has been shown to give pH calculations of NIST standard buffers that are within a few thousandths of a pH unit of the NIST values. The NIST buffers are given in Table 13.2 in Chapter 13. Use the calculator in Reference 15 to calculate the ActpH of the NIST phosphate buffer consisting of 0.025 M KH_2PO_4 and 0.025 M Na_2HPO_4 (footnote *e*) at 50°C, and compare with the NIST value of 6.833. Use pK_w = 13.26, pK_1 = 2.25, pK_2 = 7.18, and pK_3 = 12.36 for 50°C. Don't forget to enter the temperature.

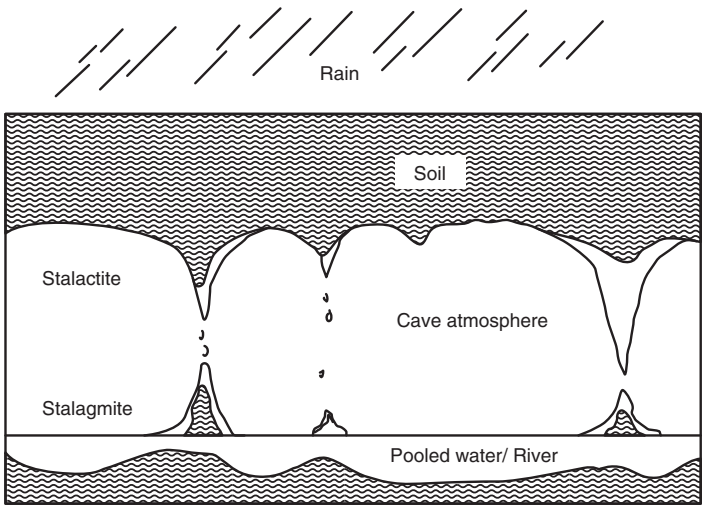
75. Use the Stig Johansson pH calculator to calculate the pH in Problem 41.

76. Use the Stig Johansson pH calculator to calculate the pH in Problem 43.

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor George S. Wilson, University of Kansas

77. Many geochemical processes are governed by simple chemical equilibria. One example is the formation of stalactites and stalagmites in a limestone cave, and is a good illustration of Henry's law. This is illustrated in the diagram below:



Rainwater percolates through soil. Due to microbial activity in the soil, the gaseous CO_2 concentration in the soil interstitial space (expressed as the partial pressure of CO_2, pCO_2,

in atmospheres), is 3.2×10^{-2} atm, significantly higher than that in the ambient atmosphere (3.9×10^{-4} atm; CO_2 concentration in the ambient atmosphere is presently increasing by 2×10^{-6} atm each year, see http://CO2now.org for the current atmospheric CO_2 concentration). Water percolating through the soil reaches an equilibrium (called Henry's law equilibrium) with the soil interstitial pCO_2 as given by Henry's law:

$$[H_2CO_3] = K_H pCO_2$$

where H_2CO_3 is the aqueous carbonic acid concentration and K_H is the Henry's law constant for CO_2, 4.6×10^{-2} *M*/atm at the soil temperature of 15°C. The CO_2-saturated water effluent from the soil layer then percolates through fractures and cracks in a limestone layer, whereupon it is saturated with $CaCO_3$. This $CaCO_3$ saturated water drips from the ceiling of the cave.

Because of the diurnal temperature variation outside the cave, the cave "breathes": the CO_2 concentration in the cave atmosphere is essentially the same as in ambient air (3.9×10^{-4}atm). Show that when the water dripping from the ceiling re-equilibrates with the pCO_2 concentration in the cave atmosphere, some of the calcium in the drip water will re-precipitate as $CaCO_3$, thus forming stalactites and stalagmites. Assume cave temperature to be 15°C as well. At this temperature the successive dissociation constants of H_2CO_3 are: $K_{a1} = 3.8 \times 10^{-7}$ and $K_{a2} = 3.7 \times 10^{-11}$, K_w is 4.6×10^{-15} and K_{sp} of $CaCO_3$ is 4.7×10^{-9}.

See the text **website** (as well as the Solutions Manual) for a detailed solution of this complex problem. Corresponding Goal Seek calculations are also given on the **website**.

PROFESSOR'S FAVORITE CHALLENGE:

Contributed by Professor Noel Motta, University of Puerto Rico, Rio Piedras

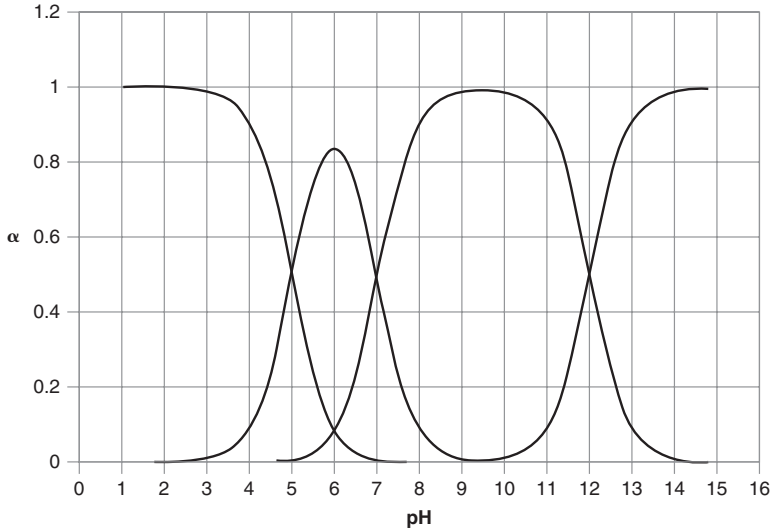
78. The following 5 mathematical expressions can be used to approximately calculate H^+ concentrations in different contexts: (a) $\sqrt{K_a C_a}$ (b) $\frac{10^{-14}}{\sqrt{K_b C_b}}$ (c) $\sqrt{\frac{K_w K_a}{K_b}}$ (d) $\sqrt{\frac{C_a K_1 K_2}{K_1 + C_a}}$ (e) $\sqrt{\frac{C_a K_2 K_3}{K_2 + C_a}}$

For each of the following salts in 0.10 *M* aqueous solutions, match the most appropriate expression to calculate $[H^+]$: (i) K_2HPO_4, (ii) NH_4CN, (iii) CH_3NH_3Cl, (iv) Na_2CO_3, (v) $NaHSO_3$, (vi) $CH_3COONH(CH_3)_3$, (vii) Na_2H_2Y (where: H_4Y = EDTA, $H_4C_{10}H_{12}N_2O_8$).

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Noel Motta, University of Puerto Rico

79. A given polyprotic acid H_nX has the following fractional composition (alpha-values) vs. pH:



What is *n*?

If 15.0 mL of 0.10 *M* H_nX is titrated with 0.10 *M* NaOH, the titration curve should *clearly* show: (a) only an equivalence point at $V = 15.0$ mL; (b) an equivalence point at $V = 15.0$ mL, and another at $V = 30.0$ mL; (c) only an equivalence point at $V = 30.0$ mL; (d) an equivalence point at $V = 15.0$ mL, and another at $V = 45.0$ mL; (e) an equivalence point at $V = 15.0$ mL, another at $V = 30.0$ mL, and another at $V = 45.0$ mL.

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WEB pH CALCULATORS

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16. www2.iq.usp.br/docente/gutz/Curtipot.html. A free program that calculates the pH and paH of mixtures of acids and bases, and also titration curves and distribution curves, alpha plots, and more. The Curtipot program is available on the text's **website**.

(Source: Stig Johansson/ www.phcalculation.se/Courtesy of Late Stig Johannson.)

SEAWATER pH SCALES

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21. Chloride in serum is determined by titration with $Hg(NO_3)_2$; $2Cl^- + Hg^{2+} \rightleftharpoons HgCl_2$. The $Hg(NO_3)_2$ is standardized by titrating 2.00 mL of a 0.0108 *M* NaCl solution, requiring 1.12 mL to reach the diphenylcarbazone end point. A 0.500-mL serum sample is treated with 3.50 mL water, 0.50 mL 10% sodium tungstate solution, and 0.50 mL of 0.33 *M* H_2SO_4 solution to precipitate proteins. After the proteins are precipitated, the sample is filtered through a dry filter into a dry flask. A 2.00-mL aliquot of the filtrate is titrated with the $Hg(NO_3)_2$ solution, requiring 1.23 mL. Calculate the mg/L chloride in the serum. (Note: mercury is rarely used today due to its toxicity. The problem is illustrative.)

PROFESSOR'S FAVORITE PROBLEM

Contributed by Professor Bin Wang, Marshall University

22. A 0.1021 g sample containing ZnO was titrated using a standard EDTA solution with Erichrome Black T as indicator. It took 25.52 mL of 0.0100 *M* EDTA to reach the end point. What is the percentage of ZnO in the sample?

SPREADSHEET PROBLEMS

See the textbook **website**, Chapter 9, for suggested setups.

23. Prepare a spreadsheet for Figure 9.2, log K_f' vs. pH for the EDTA chelates of calcium, lead, and mercury. This will require calculating α_4 for EDTA and the K_f values for the chelates of calcium, lead, and mercury. Calculate at 0.5 pH intervals. Compare your plot with Figure 9.2.

24. Prepare a spreadsheet for the titration of 100.00 mL of 0.1000 *M* Hg^{2+} with 0.1000 *M* Na_2EDTA at pH 10 (similar to pCa vs. mL EDTA—Figure 9.3). Start out at pHg = 1 and go up to pHg = 17 with a resolution of 0.1. See Figure 9.3.xlsx. (See the text **website** for the solution.)

25. Prepare a spreadsheet to plot the seven fractional values (from α_M to α_{ML6}) present in a $Ni^{2+} - NH_3$ system as a function of $[NH_3]$. Plot the results from 0.001 to 1.0 *M* NH_3, with a resolution of 0.001 *M*, use logarithmic scaling for the *X*-axis (ammonia concentration).

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Chapter Ten
GRAVIMETRIC ANALYSIS AND PRECIPITATION EQUILIBRIA

"Some loads are light, some heavy. Some people prefer the light to the heavy . . ."
—Mao Tse-tung

Learning Objectives

WHAT ARE SOME OF THE KEY THINGS WE WILL LEARN FROM THIS CHAPTER?

- Steps of a gravimetric analysis: precipitation, digestion, filtration, washing, drying, weighing, calculation, p. 343
- Gravimetric calculations (key equations: 10.1, 10.3, 10.5), pp. 349, 350
- The solubility product, the common ion effect, p. 355
- The diverse ion effect (key equation: 10.10), p. 361

Gravimetry is among the most accurate analytical techniques (but it is tedious!). T. W. Richards used it to determine atomic weights. He received the Nobel Prize in 1914 for his work. See *Z. Anorg. Chem.*, **8** (1895), 413, 419, and 421 for some of his careful studies on contamination. See also http://nobelprizes.com.

Theodore W. Richards

Gravimetric analysis is one of the most accurate and precise methods of macroquantitative analysis. In this process the analyte is selectively converted to an insoluble form. The separated precipitate is dried or ignited, possibly to another form, and is accurately weighed. From the weight of the precipitate and a knowledge of its chemical composition, we can calculate the weight of analyte in the desired form.

Gravimetric analysis is capable of exceedingly precise analysis. In fact, gravimetric analysis was used to determine the atomic masses of many elements to six figure accuracy. Theodore W. Richards at Harvard University developed highly precise and accurate gravimetric analysis of silver and chlorine. He used these methods to determine the atomic weights of 25 elements by preparing pure samples of the chlorides of the elements, decomposing known weights of the compounds, and determining the chloride content by gravimetric methods. For this work, he was the first American to receive the Nobel Prize. He was the ultimate analytical chemist!

Gravimetry does not require a series of standards for calculation of an unknown since calculations are based only on atomic or molecular weights. Only a precise analytical balance is needed for measurements. Gravimetric analysis, due to its high degree of accuracy, can also be used to calibrate other instruments in lieu of reference standards. While it is tedious and time consuming, it may find use where very precise results are needed, for example, in determining the iron content of an ore, whose price is determined by the iron content. It is used to determine the chloride content of cement. In environmental chemistry, sulfate is precipitated with barium ion, and in the petroleum field, hydrogen sulfide in desulfurization waste water is precipitated with silver ion.

This chapter describes the specific steps of gravimetric analysis, including preparing the solution in proper form for precipitation, the precipitation process and how to obtain the precipitate in pure and filterable form, the filtration and washing of the precipitate to prevent losses and impurities, and heating the precipitate to convert it to a weighable form. It gives calculation procedures for computing the quantity of analyte from the weight of precipitate, following the principles introduced in Chapter 5. It also provides some common examples of gravimetric analysis. Finally, it discusses the solubility product and associated precipitation equilibria.

10.1 How to Perform a Successful Gravimetric Analysis

A successful gravimetric analysis consists of a number of important operations designed to obtain a pure and filterable precipitate suitable for weighing. You may wish to precipitate silver chloride from a solution of chloride by adding silver nitrate. There is more to the procedure than simply pouring in silver nitrate solution and then filtering.

Accurate gravimetric analysis requires careful manipulation in forming and treating the precipitate.

WHAT STEPS ARE NEEDED?

The steps required in a gravimetric analysis, after the sample has been dissolved, can be summarized as follows:

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

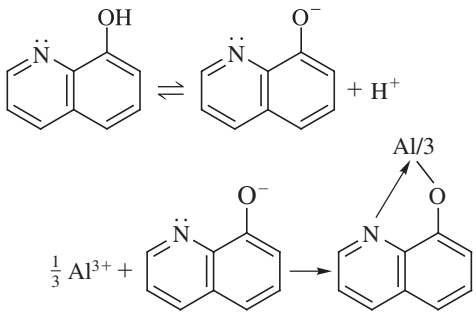
These operations and the reasons for them are described below.

FIRST PREPARE THE SOLUTION

The first step in performing gravimetric analysis is to prepare the solution. Some form of preliminary separation may be necessary to eliminate interfering materials. Also, we must adjust the solution conditions to maintain low solubility of the precipitate and to obtain it in a form suitable for filtration. Proper adjustment of the solution conditions prior to precipitation may also mask potential interferences. Factors that must be considered include the volume of the solution during precipitation, the concentration range of the test substance, the presence and concentrations of other constituents, the temperature, and the pH.

Although preliminary separations may be required, in other instances the precipitation step in gravimetric analysis is sufficiently selective that other separations are not required. The pH is important because it often influences both the solubility of the analytical precipitate and the possibility of interferences from other substances. For example, calcium oxalate is insoluble in basic medium, but at low pH the oxalate ion combines with the hydrogen ions to form a weak acid and begins to dissolve. 8-Hydroxyquinoline (oxine—also known as 8-quinolinol) can be used to precipitate a large number of elements, but by controlling pH, we can precipitate elements selectively. Aluminum ion can be precipitated at pH 4, but the concentration of the anion form of oxine is too low at this pH to precipitate magnesium ion; magnesium oxinate has a much greater solubility product, the solubility product concept is discussed later in the chapter.

Usually, the precipitation reaction is selective for the analyte.



8-Hydroxyquinoline can be used in combination with pH adjustments for selective precipitation of different metals. Al^{3+} can be selectively precipitated over Mg^{2+} at pH 4.

A higher pH is required to shift the ionization step to the right in order to precipitate magnesium. If the pH is too high, however, magnesium hydroxide will precipitate, causing interference.

The effects of the other factors mentioned above will become apparent as we discuss the precipitation step.

THEN DO THE PRECIPITATION—BUT UNDER THE RIGHT CONDITIONS

After preparing the solution, the next step is to do the precipitation. Again, certain conditions are important. The precipitate should first be *sufficiently insoluble* that the amount lost due to solubility will be negligible. It should consist of *large crystals* that can be easily filtered. All precipitates tend to carry some of the other constituents of the solution with them. This contamination should be negligible. Keeping the crystals large can minimize this contamination.

We can achieve an appreciation of the proper conditions for precipitation by first looking at the **precipitation process**. When a solution of a precipitating agent is added to a test solution to form a precipitate, such as in the addition of $AgNO_3$ to a chloride solution to precipitate AgCl, the actual precipitation occurs in a series of steps. The precipitation process involves heterogeneous equilibria and, as such, is not instantaneous (see Chapter 6). The equilibrium condition is described by the solubility product, discussed at the end of the chapter. First, **supersaturation** occurs, that is, the solution phase contains more of the dissolved salt than it can carry at equilibrium. This is a metastable condition, and the driving force will be for the system to approach equilibrium (saturation). This is started by **nucleation**. For nucleation to occur, a minimum number of particles must come together to produce microscopic nuclei of the solid phase. The higher the degree of supersaturation, the greater the rate of nucleation. The formation of a greater number of nuclei per unit time will ultimately produce more total crystals of smaller size. The total crystal surface area will be larger, and there will be more danger that impurities will be adsorbed (see below).

During the precipitation process, supersaturation occurs (this should be minimized!), followed by nucleation and precipitation.

Although nucleation should theoretically occur spontaneously, it is usually induced, for example, on dust particles, scratches on the vessel surface, or added seed crystals of the precipitate (not in quantitative analysis).

Following nucleation, the initial nucleus will grow by depositing other precipitate particles to form a crystal of a certain geometric shape. Again, the greater the supersaturation, the more rapid the crystal growth rate. An increased growth rate increases the chances of imperfections in the crystal and trapping of impurities.

Von Weimarn discovered that the particle size of precipitates is inversely proportional to the relative supersaturation of the solution during the precipitation process:

$$\text{Relative supersaturation} = \frac{Q - S}{S}$$

where Q is the concentration of the mixed reagents *before* precipitation occurs, S is the **solubility** of the precipitate at equilibrium, and $Q - S$ is the **degree of supersaturation**. This ratio, $(Q - S)/S$, relative supersaturation, is also called the **von Weimarn ratio**.

As previously mentioned, when a solution is supersaturated, it is in a state of metastable equilibrium, and this favors rapid nucleation to form a large number of small particles. That is,

High relative supersaturation → many small crystals (high surface area)

Low relative supersaturation → fewer, larger crystals (low surface area)

Obviously, then, we want to keep Q low and S high during precipitation. Several steps are commonly taken to maintain *favorable conditions for precipitation*:

1. Precipitate from *dilute solution*. This keeps Q low.
2. Add dilute precipitating reagents *slowly*, with effective *stirring*. This also keeps Q low. Stirring prevents local excesses of the reagent.
3. Precipitate from *hot solution*. This increases S. The solubility should not be too great or the precipitation will not be quantitative (with less than 1 part per thousand remaining). The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.
4. Precipitate at as *low* a *pH* as is possible to maintain quantitative precipitation. As we have seen, many precipitates are more soluble in acid medium, and this slows the rate of precipitation. They are more soluble because the anion of the precipitate (which comes from a weak acid) combines with protons in the solution.

Here is how to minimize supersaturation and obtain larger crystals.

Most of these operations can also decrease the degree of contamination. The concentration of impurities is kept lower and their solubility is increased, and the slower rate of precipitation decreases their chance of being trapped. The larger crystals have a smaller specific surface area (i.e., a smaller surface area relative to the mass) and so have less chance of adsorbing impurities. Note that the most insoluble precipitates do not make the best candidates for pure and readily filterable precipitates. An example is hydrous iron oxide (or iron hydroxide), which forms a gelatinous precipitate of large surface area.

Very insoluble precipitates are not the best candidates for gravimetric analysis! They supersaturate too easily.

When the precipitation is performed, a slight excess of precipitating reagent is added to decrease the solubility by mass action (common ion effect) and to assure complete precipitation. A large excess of precipitating agent should be avoided because this increases chances of adsorption on the surface of the precipitate, in addition to being wasteful. If the approximate amount of analyte is known, a 10% excess of reagent is generally added. Completeness of precipitation is checked by waiting until the precipitate has settled and then adding a few drops of precipitating reagent to the clear solution above it. If no new precipitate forms, precipitation is complete.

Don't add too much excess precipitating agent. This will increase adsorption.

Check for completeness of precipitation!

DIGEST THE PRECIPITATE TO MAKE LARGER AND MORE PURE CRYSTALS

We know that very small crystals with a large specific surface area have a higher surface energy and a higher apparent solubility than large crystals. This is an initial rate phenomenon and does not represent the equilibrium condition, and it is one consequence of heterogeneous equilibria. When a precipitate is allowed to stand in the presence of the **mother liquor** (the solution from which it was precipitated), the large crystals grow at the expense of the small ones. This process is called **digestion**, or **Ostwald ripening**, and is illustrated in Figure 10.1. Small particles have greater surface energy associated with a greater surface area and display somewhat greater solubility than larger particles. The small particles tend to dissolve and reprecipitate on the surfaces of the larger crystals. In addition, individual particles **agglomerate** to effectively share a common counterion layer (see below), and the agglomerated particles finally *cement* together by forming connecting bridges. This noticeably decreases surface area.

Ostwald ripening improves the purity and crystallinity of the precipitate.

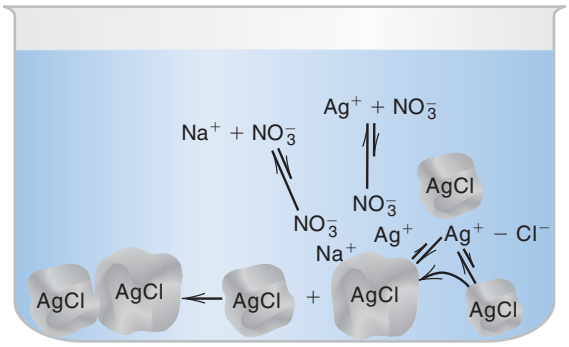


Fig. 10.1. Ostwald ripening.

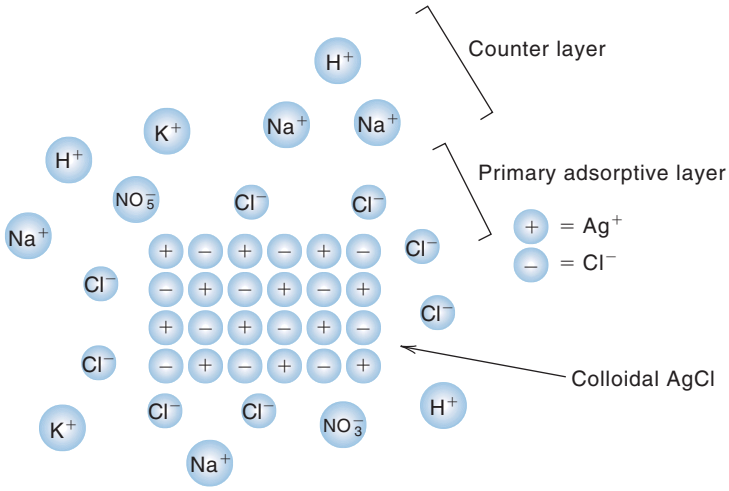


Fig. 10.2. Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.

Also, imperfections of the crystals tend to disappear, and adsorbed or trapped impurities tend to go into solution. Digestion is usually done at elevated temperatures to speed the process, although in some cases it is done at room temperature. It improves both the filterability of the precipitate and its purity.

Many precipitates do not give a favorable von Weimarn ratio, especially very insoluble ones. Hence, it is impossible to yield a crystalline precipitate (small number of large particles), and the precipitate is first **colloidal** (large number of small particles).

Colloidal particles are very small (1 to 100 nm) and have a very large surface-to-mass ratio, which promotes surface adsorption. They are formed by virtue of the precipitation mechanism. As a precipitate forms, the ions are arranged in a fixed pattern. In AgCl, for example, there will be alternating Ag^+ and Cl^- ions on the surface (see Figure 10.2). While there are localized + and − charges on the surface, the net surface charge is zero. However, the surface does tend to adsorb the ion of the precipitate particle that is in excess in the solution, for example, Ag^+ if precipitating Cl^- with an excess of Ag^+; this imparts a charge. (With crystalline precipitates, the degree of such adsorption will generally be small in comparison with particles that tend to form colloids.) The adsorption creates a **primary layer** that is strongly adsorbed and is an integral part of the crystal. It will attract ions of the opposite charge in a **counterlayer** or secondary layer so the particle will have an overall neutral charge. There will be solvent molecules interspersed between the layers. Normally, the counterlayer completely neutralizes the primary layer and is close to it, so the particles will collect together to form larger particles; that is, they will **coagulate**. However, if the secondary layer is loosely bound, the primary surface charge will tend to repel like particles, maintaining a colloidal state.

Peptization is the reverse of coagulation (the precipitate reverts to a colloidal state and is lost). It is avoided by washing with an electrolyte that can be volatized by heating.

When coagulated particles are filtered, they retain the adsorbed primary and secondary ion layers along with solvent. Washing the particles with water increases the extent of solvent (water) molecules between the layers, causing the secondary layer to be loosely bound, and the particles revert to the colloidal state. This process is called **peptization** and is discussed in more detail below where we describe washing the precipitate. Adding an electrolyte will result in a closer secondary layer and will promote coagulation. Heating tends to decrease adsorption and the effective charge in the adsorbed layers, thereby aiding coagulation. Stirring will also help.

While all colloidal systems cause difficulties in analytical determinations, some are worse than others. Depending on the affinity of the dispsersed material for water, colloidal systems can be classified into **hydrophilic** (water loving) and **hydrophobic** (do not like water). While the former ones tend to produce stable dispersions in water, the latter ones tend to aggregate.

AgCl forms a hydrophobic colloid (a sol), which readily coagulates. $Fe_2O_3 \cdot xH_2O$ forms a hydrophilic colloid (a gel) with large surface area.

Coagulation of a hydrophobic colloid is fairly easy and results in a curdy precipitate. An example is silver chloride. Coagulation of a hydrophilic colloid, such as hydrous ferric oxide, is more difficult, and it produces a gelatinous precipitate that is difficult to filter because it tends to clog the pores of the filter. In addition, gelatinous precipitates adsorb impurities readily because of their very large surface area. Sometimes a *reprecipitation* of the filtered precipitate is required. During the reprecipitation, the concentration of impurities in solution (from the original sample matrix) has been reduced to a low level, and adsorption will be very small.

Despite the colloidal nature of silver chloride, the gravimetric determination of chloride is one of the most accurate determinations compared to other techniques such as titrimetry. In fact, it was used for atomic weight determination by T. W. Richards, who used nephelometry (light scattering) to correct for colloidal silver chloride.

IMPURITIES IN PRECIPITATES

Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to become contaminated. This process is called **coprecipitation**. The process may be equilibrium based or kinetically controlled. There are a number of ways in which a foreign material may be coprecipitated.

Occlusion is the trapping of impurities inside the precipitate.

1. Occlusion and Inclusion. In the process of **occlusion**, material that is not part of the crystal structure is trapped within a crystal. For example, water may be trapped in pockets when $AgNO_3$ crystals are formed, and this can be removed to a degree by dissolution and recrystallization. If such mechanical trapping occurs during a precipitation process, the water will contain dissolved impurities. **Inclusion** occurs when ions, generally of similar size and charge, are trapped within the crystal lattice (isomorphous inclusion, as with K^+ in NH_4MgPO_4 precipitation). These are not equilibrium processes.

Occluded or included impurities are difficult to remove. Digestion may help some but is not completely effective. The impurities cannot be removed by washing. Purification by dissolving and reprecipitating is helpful.

Surface adsorption of impurities is the most common source of error in gravimetry. It is reduced by proper precipitation technique, digestion, and washing.

2. Surface Adsorption. As we have already mentioned, the surface of the precipitate will have a primary adsorbed layer of the lattice ions in excess. This results in **surface adsorption**, the most common form of contamination. For example, after barium sulfate is completely precipitated, the lattice ion in excess will be barium, and this will form the primary layer. The counterion will be a foreign anion, say, nitrate two for each barium. The net effect then is an adsorbed layer of barium nitrate, an equilibrium-based process. These adsorbed layers can often be removed by washing, or they can be replaced by ions that are readily volatilized. Gelatinous precipitates are especially troublesome, though. Digestion reduces the surface area and, therefore, the adsorbed amount.

3. Isomorphous Replacement. Two compounds are said to be **isomorphous** if they have the same type of formula and crystallize in similar geometric forms. When their lattice dimensions are about the same, one ion can replace another in a crystal, resulting in a **mixed crystal**. This process is called **isomorphous replacement** or isomorphous substitution. For example, in the precipitation of Mg^{2+} as magnesium

ammonium phosphate, K^+ has nearly the same ionic size as NH_4^+ and can replace it to form magnesium potassium phosphate. Isomorphous replacement, when it occurs, causes major interference, and little can be done about it. Precipitates in which it occurs are seldom used analytically. Chloride cannot be selectively determined by precipitation as AgCl, for example, in the presence of other halides and vice versa. Mixed crystal formation is a form of equilibrium precipitate formation, although it may be influenced by the rate of precipitation. Such a mixed precipitate is akin to a solid solution. The mixed crystal may be spatially homogeneous if the crystal is in equilibrium with the final solution composition (homogeneous coprecipitation) or heterogenous if it is in instaneous equilibrium with the solution as it forms (heterogenous coprecipitation), as the solution composition changes during precipitation.

4. Postprecipitation. Sometimes, when the precipitate is allowed to stand in contact with the mother liquor, a second substance will slowly form a precipitate with the precipitating reagent. This is called **postprecipitation**. For example, when calcium oxalate is precipitated in the presence of magnesium ions, magnesium oxalate does not immediately precipitate because it tends to form supersaturated solutions. But it will precipitate if the solution is allowed to stand too long before being filtered. Similarly, copper sulfide will precipitate in acid solution in the presence of zinc ions without zinc sulfide being precipitated, but eventually zinc sulfide will precipitate. Postprecipitation is a slow equilibrium process.

WASHING AND FILTERING THE PRECIPITATES—TAKE CARE OR YOU MAY LOSE SOME

Coprecipitated impurities, especially those on the surface, can be removed by washing the precipitate after filtering. The precipitate will be wet with the mother liquor, which is also removed by washing. Many precipitates cannot be washed with pure water, because **peptization** occurs. This is the reverse of coagulation, as previously mentioned.

The process of coagulation discussed above is at least partially reversible. As we have seen, coagulated particles have a neutral layer of adsorbed primary ions and counterions. We also saw that the presence of another electrolyte will cause the counterions to be forced into closer contact with the primary layer, thus promoting coagulation. These foreign ions are carried along in the coagulation. Washing with water will dilute and remove foreign ions, and the counterion will occupy a larger volume, with more solvent molecules between it and the primary layer. The result is that the repulsive forces between particles become strong again, and the particles partially revert to the colloidal state and pass through the filter. This can be prevented by adding an electrolyte to the wash liquid, for example, HNO_3 or NH_4NO_3 for AgCl precipitate (but not KNO_3 since it is nonvolatile—see below).

The electrolyte must be one that is volatile at the temperature to be used for drying or ignition, and it must not dissolve the precipitate. For example, dilute nitric acid is used as the wash solution for silver chloride. The nitric acid replaces the adsorbed layer of $Ag^+|\,anion^-$, and it is volatilized when dried at 110°C. Ammonium nitrate is used as the wash electrolyte for hydrous ferric oxide. It is decomposed to NH_3, HNO_3, N_2, and oxides of nitrogen when the precipitate is dried by ignition at a high temperature.

Test for completeness of washing.

When you wash a precipitate, you should conduct a test to determine when the washing is complete. This is usually done by testing the filtrate for the presence of an ion of the precipitating reagent. After several washings with small volumes of the wash liquid, a few drops of the filtrate are collected in a test tube for the testing. For example, if chloride ion is determined by precipitating with silver nitrate reagent, the filtrate is tested for silver ion by adding sodium chloride or dilute HCl. We describe the technique of filtering in Chapter 2.

DRYING OR IGNITING THE PRECIPITATE

If the collected precipitate is in a form suitable for weighing, it must be heated to remove water and to remove the adsorbed electrolyte from the wash liquid. This drying can usually be done by heating at 110 to 120°C for 1 to 2 h. **Ignition** at a much higher temperature is usually required if a precipitate must be converted to a more suitable form for weighing. For example, magnesium ammonium phosphate, $MgNH_4PO_4$, is decomposed to the pyrophosphate, $Mg_2P_2O_7$, by heating at 900°C. Hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$, is ignited to the anhydrous ferric oxide. Many metals that are precipitated by organic reagents (e.g., 8-hydroxyquinoline) or by sulfide can be ignited to their oxides. The technique of igniting a precipitate is also described in Chapter 2.

Drying removes the solvent and wash electrolytes.

10.2 Gravimetric Calculations—How Much Analyte Is There?

The precipitate we weigh is usually in a different form than the analyte whose weight we wish to report. The principles of converting the weight of one substance to that of another are given in Chapter 5 (Section 5.8), using stoichiometric mole relationships. We introduced the **gravimetric factor** (GF), which represents the weight of analyte per unit weight of precipitate. It is obtained from the ratio of the formula weight of the analyte to that of the precipitate, multiplied by the moles of analyte per mole of precipitate obtained from each mole of analyte, that is,

$$\begin{aligned} \text{GF} &= \frac{\text{fw analyte (g/mol)}}{\text{fw precipitate (g/mol)}} \times \frac{a}{b}(\text{mol analyte/mol precipitate}) \\ &= \text{g analyte/g precipitate} \end{aligned} \tag{10.1}$$

Grams precipitate × GF gives grams analyte.

So, if Cl_2 in a sample is converted to chloride and precipitated as AgCl, the weight of Cl_2 that gives 1 g of AgCl is

$$\begin{aligned} \text{g } Cl_2 &= \text{g AgCl} \times \frac{\text{fw } Cl_2 \text{ (g } Cl_2\text{/mol } Cl_2)}{\text{fw AgCl (g AgCl/mol AgCl)}} \times \frac{1}{2} \text{ (mol } Cl_2\text{/mol AgCl)} \\ &= \text{g AgCl} \times \text{GF (g } Cl_2\text{/g AgCl)} \\ &= \text{g AgCl} \times 0.2473_7 \text{ (g } Cl_2\text{/g AgCl)} \end{aligned}$$

Example 10.1

Calculate the grams of analyte per gram of precipitate for the following conversions:

Analyte	*Precipitate*
P	Ag_3PO_4
K_2HPO_4	Ag_3PO_4
Bi_2S_3	$BaSO_4$

Solution

$$\text{g P/g } Ag_3PO_4 = \frac{\text{at wt P (g/mol)}}{\text{fw } Ag_3PO_4 \text{ (g/mol)}} = \frac{1}{1} \text{ (mol P/mol } Ag_3PO_4)$$

$$\text{GF} = \frac{30.97 \text{ (g P/mol)}}{418.58 \text{ (g } Ag_3PO_4\text{/mol)}} \times \frac{1}{1} = 0.07399 \text{ g P/g } Ag_3PO_4$$

$$\text{g } K_2HPO_4/\text{g } Ag_3PO_4 = \frac{\text{fw } K_2HPO_4 \text{ (g/mol)}}{\text{fw } Ag_3PO_4 \text{ (g/mol)}} \times \frac{1}{1} \text{ (mol } K_2HPO_4/\text{mol } Ag_3PO_4)$$

$$\text{GF} = \frac{174.18 \text{ (g } K_2HPO_4/\text{mol)}}{418.58 \text{ (g } Ag_3PO_4/\text{mol)}} \times \frac{1}{1} = 0.41612 \text{ g } K_2HPO_4/\text{g } Ag_3PO_4$$

$$\text{g } Bi_2S_3/\text{g } BaSO_4 = \frac{\text{fw } Bi_2S_3 \text{ (g/mol)}}{\text{fw } BaSO_4 \text{ (g/mol)}} \times \frac{1}{3} \text{ (mol } Bi_2S_3/\text{mol } BaSO_4)$$

$$\text{GF} = \frac{514.15 \text{ (g } Bi_2S_3/\text{mol)}}{233.40 \text{ (g } BaSO_4/\text{mol)}} \times \frac{1}{3} = 0.73429 \text{ g } Bi_2S_3/\text{g } BaSO_4$$

In gravimetric analysis, we are generally interested in the percent composition by weight of the analyte in the sample, that is,

$$\%\text{ substance sought} = \frac{\text{weight of substance sought (g)}}{\text{weight of sample (g)}} \times 100\% \tag{10.2}$$

We obtain the weight of substance sought from the weight of the precipitate and the corresponding weight/mole relationship (Equation 10.1):

$$\begin{aligned}\text{Weight of substance sought (g)} &= \text{weight of precipitate (g)} \\ &\quad \times \frac{\text{fw substance sought (g/mol)}}{\text{fw precipitate (g/mol)}} \\ &\quad \times \frac{a}{b} \text{ (mol substance sought/mol precipitate)} \\ &= \text{weight of precipitate (g)} \\ &\quad \times \text{GF (g sought/g precipitate)}\end{aligned} \tag{10.3}$$

Calculations are usually made on a percentage basis:

$$\%\text{ A} = \frac{g_A}{g_{sample}} \times 100\% \tag{10.4}$$

where g_A represents the grams of analyte (the desired test substance) and g_{sample} represents the grams of sample taken for analysis.

Check units!

We can write a general formula for calculating the percentage composition of the substance sought:

$$\%\text{ sought} = \frac{\text{weight of precipitate (g)} \times \text{GF (g sought/g precipitate)}}{\text{weight of sample (g)}} \times 100\% \tag{10.5}$$

Example 10.2

Orthophosphate (PO_4^{3-}) is determined by weighing as ammonium phosphomolybdate, $(NH_4)PO_4 \cdot 12MoO_3$. Calculate the percent P in the sample and the percent P_2O_5 if 1.1682 g precipitate (ppt) were obtained from a 0.2711-g sample. Perform the % P calculation using the gravimetric factor and just using dimensional analysis.

Solution

$$\%\ \mathrm{P} = \frac{1.1682\ \mathrm{g\ ppt} \times \dfrac{\mathrm{P}}{(\mathrm{NH_4})_3\mathrm{PO_4} \cdot\ 12\mathrm{MoO_3}}\ (\mathrm{g\ P/g\ ppt})}{0.2711\ \mathrm{g\ sample}} \times 100\%$$

$$= \frac{1.1682\ \mathrm{g} \times (30.97/1876.5)}{0.2711\ \mathrm{g}} \times 100\% = 7.111\%$$

$$\%\ \mathrm{P_2O_5} = \frac{1.1682\ \mathrm{g\ ppt} \times \dfrac{\mathrm{P_2O_5}}{2(\mathrm{NH_4})_3\mathrm{PO_4} \cdot\ 12\mathrm{MoO_3}}(\mathrm{g\ P_2O_5/g\ ppt})}{0.2711\ \mathrm{g\ sample}} \times 100\%$$

$$= \frac{1.1682\ \mathrm{g} \times [141.95/(2 \times 1876.5)]}{0.2711\ \mathrm{g}} \times 100\%$$

$$= 16.30\%$$

Let's do the same calculation using dimensional analysis for the % P setup.

$$\%\ \mathrm{P} = \frac{1.982\ \mathrm{g}\ \cancel{(\mathrm{NH_4})_2\mathrm{PO_4} \cdot\ 12\mathrm{MoO_3}} \times (30.97/1867.5)\mathrm{g\ P/g}\ \cancel{(\mathrm{NH_4})_2\mathrm{PO_4} \cdot\ 12\mathrm{MoO_3}}}{0.2771\ \mathrm{g\ sample}}$$

$$\times\ 100\%$$

$$= (7.111\ \mathrm{g\ P/g\ sample}) \times 100\% = 7.111\%\ \mathrm{P}$$

Note that the $(\mathrm{NH_4})_2\mathrm{PO_4} \cdot 12\mathrm{MoO_3}$ species cancel one another (dimensional analysis), leaving only g P in the numerator.

When we compare this approach with the gravimetric factor calculation, we see that the setups are really identical. However, this approach better shows which units cancel and which remain. ■

Example 10.3

An ore is analyzed for the manganese content by converting the manganese to $\mathrm{Mn_3O_4}$ and weighing it. If a 1.52-g sample yields $\mathrm{Mn_3O_4}$ weighing 0.126 g, what would be the percent $\mathrm{Mn_2O_3}$ in the sample? The percent Mn?

Solution

$$\%\ \mathrm{Mn_2O_3} = \frac{0.126\ \mathrm{g\ Mn_3O_4} \times \dfrac{3\mathrm{Mn_2O_3}}{2\mathrm{Mn_3O_4}}(\mathrm{g\ Mn_2O_3/g\ Mn_3O_4})}{1.52\ \mathrm{g\ sample}} \times 100\%$$

$$= \frac{0.126\ \mathrm{g} \times [3(157.9)/2(228.8)]}{1.52\ \mathrm{g}} \times 100\% = 8.58\%$$

$$\%\ \mathrm{Mn} = \frac{0.126\ \mathrm{g\ Mn_3O_4} \times \dfrac{3\mathrm{Mn}}{\mathrm{Mn_3O_4}}(\mathrm{g\ Mn/g\ Mn_3O_4})}{1.52\ \mathrm{g\ sample}} \times 100\%$$

$$= \frac{0.126\ \mathrm{g} \times [3(54.94)/228.8]}{1.52\ \mathrm{g}} \times 100\% = 5.97\%$$

■

The following two examples illustrate some special additional capabilities of gravimetric computations.

Example 10.4

What weight of pyrite ore (impure FeS_2) must be taken for analysis so that the $BaSO_4$ precipitate weight obtained will be equal to one-half that of the percent S in the sample?

Solution

If we have A% of S, then we will obtain $\frac{1}{2}$ A g of $BaSO_4$. Therefore,

$$\text{A\% S} = \frac{\frac{1}{2}\text{A(g BaSO}_4) \times \frac{\text{S}}{\text{BaSO}_4}(\text{g S/g BaSO}_4)}{\text{g sample}} \times 100\%$$

or

$$1\%\ \text{S} = \frac{\frac{1}{2} \times \frac{32.064}{233.40}}{\text{g sample}} \times 100\%$$

$$\text{g sample} = 6.869\ \text{g}$$

■

PRECIPITATE MIXTURES—WE NEED TWO WEIGHTS

Example 10.5

A mixture containing only $FeCl_3$ and $AlCl_3$ weighs 5.95 g. The chlorides are converted to the hydrous oxides and ignited to Fe_2O_3 and Al_2O_3. The oxide mixture weighs 2.62 g. Calculate the percent Fe and Al in the original mixture.

Solution

There are two unknowns, so two simultaneous equations must be set up and solved. Let x = g Fe and y = g Al. Then, for the first equation,

$$\text{g FeCl}_3 + \text{g AlCl}_3 = 5.95\ \text{g} \tag{1}$$

$$x\left(\frac{\text{FeCl}_3}{\text{Fe}}\right) + y\left(\frac{\text{AlCl}_3}{\text{Al}}\right) = 5.95\ \text{g} \tag{2}$$

$$x\left(\frac{162.21}{55.85}\right) + y\left(\frac{133.34}{26.98}\right) = 5.95\ \text{g} \tag{3}$$

$$2.90x + 4.94y = 5.95\ \text{g} \tag{4}$$

$$\text{g Fe}_2\text{O}_3 + \text{g Al}_2\text{O}_3 = 2.62\ \text{g} \tag{5}$$

$$x\left(\frac{\text{Fe}_2\text{O}_3}{2\text{Fe}}\right) + y\left(\frac{\text{Al}_2\text{O}_3}{2\text{Al}}\right) = 2.62\ \text{g} \tag{6}$$

$$x\left(\frac{159.69}{2 \times 55.85}\right) + y\left(\frac{101.96}{2 \times 26.98}\right) = 2.62\ \text{g} \tag{7}$$

$$1.43x + 1.89y = 2.62\ \text{g} \tag{8}$$

See the **website** supplement to look up Example 10.5 Solving Simultaneous Equations that solves two-variable simultaneous equations.

Solving (4) and (8) simultaneously for x and y:

$$x = 1.07 \text{ g}$$

$$y = 0.58 \text{ g}$$

$$\% \text{ Fe} = \frac{1.07 \text{ g}}{5.95 \text{ g}} \times 100\% = 18.0\%$$

$$\% \text{ Al} = \frac{0.58 \text{ g}}{5.95 \text{ g}} \times 100\% = 9.8\%$$

10.3 Examples of Gravimetric Analysis

Some of the most precise and accurate analyses are based on gravimetry. There are many examples, and you should be familiar with some of the more common ones. These are summarized in Table 10.1, which lists the substance sought, the precipitate formed, the form in which it is weighed, and the common elements that will interfere and must be absent. We do not present more details because gravimetry is not currently used often (unless the much longer time and increased labor requirements can be justified by the necessity of high precision and accuracy). You should consult more advanced texts and comprehensive analytical reference books for details on these and other determinations.

10.4 Organic Precipitates

All the precipitating agents we have talked about so far, except for oxine, cupferrate, and dimethylglyoxime (Table 10.1), have been inorganic in nature. There are also a large number of organic compounds that are very useful precipitating agents for

Table 10.1

Some Commonly Employed Gravimetric Analyses

Substance Analyzed	Precipitate Formed	Precipitate Weighed	Interferences
Fe	$Fe(OH)_3$	Fe_2O_3	Many. Al, Ti, Cr, etc.
	Fe cupferrate	Fe_2O_3	Tetravalent metals
Al	$Al(OH)_3$	Al_2O_3	Many. Fe, Ti, Cr, etc.
	$Al(ox)_3$[a]	$Al(ox)_3$	Many. Mg does not interfere in acidic solution
Ca	CaC_2O_4	$CaCO_3$ or CaO	All metals except alkalis and Mg
Mg	$MgNH_4PO_4$	$Mg_2P_2O_7$	All metals except alkalis
Zn	$ZnNH_4PO_4$	$Zn_2P_2O_7$	All metals except Mg
Ba	$BaCrO_4$	$BaCrO_4$	Pb
SO_4^{2-}	$BaSO_4$	$BaSO_4$	NO_3^-, PO_4^{3-}, ClO_3^-
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, CN^-, S^{2-}, $S_2O_3^{2-}$
Ag	AgCl	AgCl	Hg(I)
PO_4^{3-}	$MgNH_4PO_4$	$Mg_2P_2O_7$	MoO_4^{2-}, $C_2O_4^{2-}$, K^+
Ni	$Ni(dmg)_2$[b]	$Ni(dmg)_2$	Pd

[a] ox = Oxine (8-hydroxyquinoline) monoanion.
[b] dmg = Dimethylglyoxime monoanion.

metals. Some of these are very selective, and others are very broad in the number of elements they will precipitate.

Organic precipitating agents have the advantages of giving precipitates with very low solubility in water and a favorable gravimetric factor. Most of them are **chelating agents** that form slightly soluble, uncharged **chelates** with the metal ions. A chelating agent is a type of complexing agent that has two or more groups capable of complexing with a metal ion. The complex formed is called a chelate. See Chapter 9 for a more thorough discussion of chelates.

Chelates are described in Chapter 9.

Since chelating agents are weak acids, the number of elements precipitated, and thus the selectivity, can usually be regulated by adjustment of the pH. The reactions can be generalized as (the underline indicates what is precipitated):

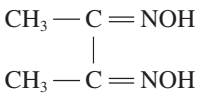
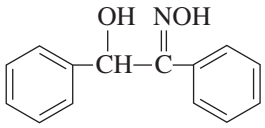
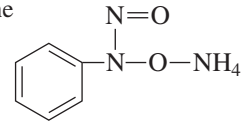
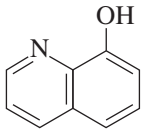
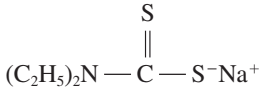
$$M^{n+} + nHX \rightleftharpoons \underline{MX_n} + nH^+$$

Metal chelate precipitates (which give selectivity) are sometimes ignited to metal oxides for improved stoichiometry.

There may be more than one ionizable proton on the organic reagent. The weaker the metal chelate, the higher the pH needed to achieve precipitation. Some of the commonly used organic precipitants are listed in Table 10.2. Some of these precipitates are not stoichiometric, and more accurate results are obtained by igniting them to form the metal oxides. Some, such as sodium diethyldithiocarbamate, can be used to perform group separations, as is done with hydrogen sulfide. You should consult specialized

Table 10.2

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime		Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α -Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, MoO_2^{+}, WO_2^{2+}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + nNH_4R \rightarrow \underline{MR_n} + nNH_4^{+}$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate		Many metals from acid solution ($M^{n+} + nNaR \rightarrow \underline{MRn} + nNa^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + NaR \rightarrow \underline{MR} + Na^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-. Acidic solution ($A^{n-} + nRCl \rightarrow R_nA + nCl^-$)

reference texts at the end of the chapter for applications of these and other organic precipitating reagents. The multivolume treatise by Hollingshead on the uses of oxine and its derivatives is very helpful for applications of this versatile reagent. (See Reference 4 at the end of the chapter.)

10.5 Precipitation Equilibria: The Solubility Product

When substances have limited solubility and their solubility is exceeded, the ions of the dissolved portion exist in equilibrium with the solid material. So-called insoluble compounds generally exhibit this property.

When a compound is referred to as insoluble, it is actually not completely insoluble but is **slightly soluble**. For example, if solid AgCl is added to water, a small portion of it will dissolve:

"Insoluble" substances still have slight solubility.

$$\underline{\text{AgCl}} \rightleftharpoons (\text{AgCl})_{aq} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \tag{10.6}$$

The precipitate will have a definite solubility (i.e., a definite amount that will dissolve) in g/L, or mol/L, at a given temperature (a saturated solution). A small amount of undissociated compound usually exists in equilibrium in the aqueous phase (e.g., on the order of 0.1%, although usually less for the precipitations employed for analysis, and depending on K_{sp}), and its concentration is constant. It is difficult to measure the undissociated species, and we are interested in the ionized form as a measure of a compound's solubility and chemical availability. Hence, we can generally neglect the presence of any undissociated species.

We can write an overall equilibrium constant for the above stepwise equilibrium, called the **solubility product** K_{sp}. $(\text{AgCl})_{aq}$ cancels when the two stepwise equilibrium constants are multiplied together.

The solid does not appear in K_{sp}.

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] \tag{10.7}$$

The "concentration" of any solid such as AgCl is constant and is combined in the equilibrium constant to give K_{sp}. The above relationship holds regardless of the presence of any undissociated intermediate; that is, the concentrations of free ions are rigorously defined by Equation 10.7, and we will take these as a measure of a compound's solubility. From a knowledge of the value of the solubility product at a specified temperature, we can calculate the equilibrium solubility of the compounds. (The solubility product is determined in the reverse order, by measuring the solubility.)

The amount of a slightly soluble salt that dissolves does *not* depend on the amount of the solid in equilibrium with the solution, so long as some solid is present. Instead, the amount that dissolves depends on the *volume* of the solvent. A nonsymmetric salt (one in which the cation and anion are not in the same ratio) such as Ag_2CrO_4 would have a K_{sp} as follows:

The concentration of solute in a saturated solution is the same whether the solution fills a beaker or a swimming pool, so long as there is solid in equilibrium with it. But much more solid will dissolve in the swimming pool! The concentration in a saturated solution is also independent of how much undissolved solid is present.

$$\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\ \text{Ag}^+ + \text{CrO}_4^{2-} \tag{10.8}$$

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \tag{10.9}$$

Such electrolytes do not dissolve or dissociate in steps because they are really strong electrolytes. That portion that dissolves ionizes completely. *Therefore, we do not have stepwise* K_{sp} *values*. As with any equilibrium constant, the K_{sp} product holds under all equilibrium conditions at the specified temperature. Since we are dealing with heterogeneous equilibria, the equilibrium state is achieved more slowly than with homogeneous solution equilibria.

THE SATURATED SOLUTION

Example 10.6

The K_{sp} of AgCl at 25°C is 1.0×10^{-10}. Calculate the concentrations of Ag^+ and Cl^- in a saturated solution of AgCl, and the molar solubility of AgCl.

Solution

When AgCl ionizes, equal amounts of Ag^+ and Cl^- are formed; $AgCl \rightleftharpoons Ag^+ + Cl^-$ and $K_{sp} = [Ag^+][Cl^-]$. Let s represent the molar solubility of AgCl. Since each mole of AgCl that dissolves gives one mole of either Ag^+ or Cl^-, then

$$[Ag^+] = [Cl^-] = s$$

$$s^2 = 1.0 \times 10^{-10}$$

$$s = 1.0 \times 10^{-5}\ M$$

The solubility of AgCl is $1.0 \times 10^{-5}\ M$. ■

DECREASING THE SOLUBILITY—THE COMMON ION EFFECT

If there is an excess of one ion over the other, the concentration of the other is suppressed (**common ion effect**), and the solubility of the precipitate is decreased. We can still calculate the concentration from the solubility product.

Example 10.7

Adding a common ion decreases the solubility.

Ten milliliters of 0.20 M $AgNO_3$ is added to 10 mL of 0.10 M NaCl. Calculate the concentration of Cl^- remaining in solution at equilibrium, and the solubility of the AgCl.

Solution

The final volume is 20 mL. The millimoles Ag^+ added equals $0.20 \times 10 = 2.0$ mmol. The millimoles Cl^- taken equals $0.10 \times 10 = 1.0$ mmol. Therefore, the millimoles excess Ag^+ equals $(2.0 - 1.0) = 1.0$ mmol. From Example 10.6, we see that the Ag^+ concentration contributed from the precipitate is small, that is, on the order of 10^{-5} mmol/mL in the absence of a common ion. This will be even smaller in the presence of excess Ag^+ since the solubility is suppressed. Therefore, we can neglect the amount of Ag^+ contributed from the precipitate compared to the excess Ag^+. Hence, the final concentration of Ag^+ is 1.0 mmol/20 mL = 0.050 M, and

$$(0.050)[Cl^-] = 1.0 \times 10^{-10}$$

$$[Cl^-] = 2.0 \times 10^{-9} M$$

The Cl^- concentration again equals the solubility of the AgCl, and so the solubility is $2.0 \times 10^{-9}\ M$. ■

Because the K_{sp} product always holds, *precipitation will not take place unless the product of* $[Ag^+]$ *and* $[Cl^-]$ *exceeds the* K_{sp}. If the product is just equal to K_{sp}, all the Ag^+ and Cl^- remains in solution.

The solubility product must be exceeded for precipitation to occur.

SOLUBILITY DEPENDS ON THE STOICHIOMETRY

Table 10.3 lists some solubility products along with the corresponding calculated molar solubilities for some slightly soluble salts. The molar solubility is not necessarily directly proportional to the K_{sp} value since it depends on the stoichiometry of the salt. The K_{sp} of AgI is 5×10^{15} larger than that of $Al(OH)_3$, but its molar solubility is only twice that of $Al(OH)_3$. That is, a 1:1 salt has a lower solubility than a nonsymmetric salt for a given K_{sp}. Note that HgS has a solubility product of only 4×10^{-53}, with a molar solubility of 6×10^{-27} M! This corresponds to less than one ion each of Hg^{2+} and S^{2-} in a liter in equilibrium with the precipitate, and it would take some 280 L for two ions to exist together (can you calculate this using Avogadro's number?). So it is like two ions finding each other in a good size bathtub! (Actually, they find the precipitate.) A more complete list of solubility products appears in Appendix C.

Example 10.8

What must be the concentration of added Ag^+ to just start precipitation of AgCl in a 1.0×10^{-3} M solution of NaCl?

Solution

$$[Ag^+](1.0 \times 10^{-3}) = 1.0 \times 10^{-10}$$

$$[Ag^+] = 1.0 \times 10^{-7}\ M$$

The concentration of Ag^+ must, therefore, just exceed 10^{-7} M to begin precipitation. Caveat: As we have observed before, in reality supersaturation is needed before precipitation begins. In practice it is unlikely that precipitation will begin when Ag^+ just exceeds 10^{-7} M ■

Table 10.3

Solubility Product Constants of Selected Slightly Soluble Salts

Salt	K_{sp}	Solubility, s (mol/L)
$PbSO_4$	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
$Al(OH)_3$	2×10^{-32}	5×10^{-9}
$Fe(OH)_3$	4×10^{-38}	2×10^{-10}
Ag_2S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

Example 10.9

What is the solubility of PbI_2, in g/L, if the solubility product is 7.1×10^{-9}?

Solution

The equilibrium is $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$, and $K_{sp} = [Pb^{2+}][I^-]^2 = 7.1 \times 10^{-9}$. Let s represent the molar solubility of PbI_2. Then

$$[Pb^{2+}] = s \quad \text{and} \quad [I^-] = 2s$$

$$(s)(2s)^2 = 7.1 \times 10^{-9}$$

$$s = \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3}\ M$$

Therefore, the solubility, in g/L, is

$$1.2 \times 10^{-3}\ \text{mol/L} \times 461.0\ \text{g/mol} = 0.55\ \text{g/L}$$

Note that the concentration of I^- was *not* doubled before squaring; $2s$ represented its actual equilibrium concentration, not twice its concentration. We could have let s represent the concentration of I^-, instead of the molar solubility of PbI_2, in which case $[Pb^{2+}]$ and the solubility of PbI_2 would have been $\frac{1}{2}s$. The calculated s would have been twice as great, but the concentrations of each species would have been the same. You try this calculation!

Example 10.10

A smaller K_{sp} with a nonsymmetrical precipitate does not necessarily mean a smaller solubility compared to a symmetrical one.

Calculate the molar solubility of $PbSO_4$ and compare it with that of PbI_2.

Solution

$$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$$

$$[Pb^{2+}][SO_4^{2-}] = 1.6 \times 10^{-8}$$

$$(s)(s) = 1.6 \times 10^{-8}$$

$$s = 1.3 \times 10^{-4}\ M$$

Although the K_{sp} of PbI_2 (7.1×10^{-9}) is smaller than that of $PbSO_4$ (1.6×10^{-8}), the solubility of PbI_2 is greater (see Example 10.9), due to the nonsymmetrical nature of the precipitate.

For electrolytes of the same valence type, the order of solubility will be the same as the order of the corresponding solubility products. But when we compare salts of different valence type, the order may be different. Compound AB will have a smaller molar solubility than compound AC_2 when both have identical K_{sp} values.

We take advantage of the common ion effect to decrease the solubility of a precipitate in gravimetric analysis. For example, sulfate ion is determined by precipitating $BaSO_4$ with added barium chloride solution. Figure 10.3 illustrates the effect of excess barium ion on the solubility of $BaSO_4$.

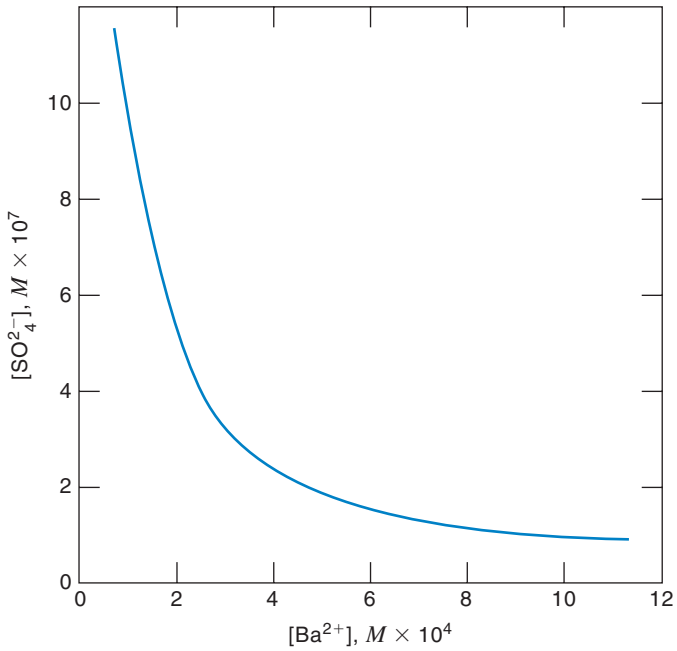


Fig. 10.3. Predicted effect of excess barium ion on solubility of $BaSO_4$. Sulfate concentration is amount in equilibrium and is equal to $BaSO_4$ solubility. In absence of excess barium ion, solubility is 10^{-5} M.

Example 10.11

What pH is required to just precipitate iron(III) hydroxide from a 0.10 M $FeCl_3$ solution?

$Fe(OH)_3$ actually precipitates in acid solution due to the small K_{sp}!

Solution

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$$

$$[Fe^{3+}][OH^-]^3 = 4 \times 10^{-38}$$

$$(0.1)[OH^-]^3 = 4 \times 10^{-38}$$

$$[OH^-] = \sqrt[3]{\frac{4 \times 10^{-38}}{0.1}} = 7 \times 10^{-13}\ \text{M}$$

$$\text{pOH} = -\log\ 7 \times 10^{-13} = 12.2$$

$$\text{pH} = 14.0 - 12.2\ =\ 1.8$$

Hence, we see that iron(III) hydroxide precipitates in acid solution, when the pH just exceeds 1.8! When you prepare a solution of $FeCl_3$ in water, it will slowly hydrolyze to form iron(III) hydroxide (hydrous ferric oxide), a rust-colored gelatinous precipitate. To stabilize the iron(III) solution, you must acidify the solution with, for example, hydrochloric acid.

Again, note that precipitation generally will not begin exactly at the calculated pH, as supersaturation is needed. ■

Example 10.12

Twenty-five milliliters of 0.100 *M* $AgNO_3$ is mixed with 35.0 mL of 0.0500 *M* K_2CrO_4 solution. (a) Calculate the concentrations of each ionic species at equilibrium. (b) Is the precipitation of silver quantitative (> 99.9%)?

Solution

(a) The reaction is

$$2Ag^+ + CrO_4^{2-} \rightleftharpoons \underline{Ag_2CrO_4}$$

We mix

$$25.0 \text{ mL} = 0.100 \text{ mmol/mL} = 2.50 \text{ mmol } AgNO_3$$

and

$$35.0 \text{ mL} \times 0.0500 \text{ mmol/mL} = 1.75 \text{ mmol } K_2CrO_4$$

Hence, 1.25 mmol of CrO_4^{2-} will react with 2.50 mmol Ag^+, leaving an excess of 0.50 mmol CrO_4^{2-}. The final volume is 60.0 mL. If we let s be the molar solubility of Ag_2CrO_4, then at equilibrium:

$$[CrO_4^{2-}] = 0.50 \text{ mmol}/60.0 \text{ mL} + s = 0.0083 + s \approx 0.0083 \, M$$

s will be very small due to the excess CrO_4^{2-} and may be neglected compared to 0.0083.

$$[Ag^+] = 2s$$

$$[K^+] = 3.50 \text{ mmol}/60.0 \text{ mL} = 0.0583 \, M$$

$$[NO_3^-] = 2.50 \text{ mmol}/60.0 \text{ mL} = 0.0417 \, M$$

$$[Ag^+]^2 \, [CrO_4^{2-}] = 1.1 \times 10^{-12}$$

$$(2s)^2 \, (8.3 \times 10^{-3}) = 1.1 \times 10^{-12}$$

$$s = \sqrt{\frac{1.1 \times 10^{-12}}{4 \times 8.3 \times 10^{-3}}} = 5.8 \times 10^{-6} \, M$$

$$[Ag^+] = 2(5.8 \times 10^{-6}) = 1.1_6 \times 10^{-5} \, M$$

(b) The percentage of silver precipitated is

$$\frac{2.50 \text{ mmol} - 60.0 \text{ mL} \times 1.1_6 \times 10^{-5} \text{ mmol/mL}}{2.50 \text{ mmol}} \times 100\% = 99.97\%$$

Or the percent remaining in solution is

$$\frac{60.0 \text{ mL} \times 1.1_6 \times 10^{-5} \text{ mmol/L}}{2.50 \text{ mmol}} \times 100\% = 0.028\%$$

Hence, the precipitation is quantitative.

10.6 Diverse Ion Effect on Solubility: K_{sp} and Activity Coefficients

In Chapter 6 we defined the thermodynamic equilibrium constant written in terms of activities to account for the effects of inert electrolytes on equilibria. The presence of diverse salts will generally increase the solubility of precipitates due to the shielding of the dissociated ion species. (Their activity is decreased.) Consider the solubility of AgCl. The thermodynamic solubility product K_{sp} is

$$K_{sp} = a_{Ag^+} \cdot a_{Cl^-} = [Ag^+]f_{Ag^+}[Cl^-]f_{Cl^-} \tag{10.10}$$

Since the *concentration* solubility product ${}^cK_{sp}$ is $[Ag^+][Cl^-]$, then

K_{sp} holds at all ionic strengths. ${}^cK_{sp}$ must be corrected for ionic strength.

$$K_{sp} = {}^cK_{sp}f_{Ag^+}f_{Cl^-} \tag{10.11}$$

or

$${}^cK_{sp} = \frac{K_{sp}}{f_{Ag^+}f_{Cl^-}} \tag{10.12}$$

The numerical value of K_{sp} holds at all activities. ${}^cK_{sp}$ equals K_{sp} at zero ionic strength, but at appreciable ionic strengths, a value must be calculated for each ionic strength using Equation 10.12. Note that this equation shows, as we predicted qualitatively, that decreased activity of the ions will result in an increased ${}^cK_{sp}$ and, therefore, an increase in molar solubility.

Example 10.13

Calculate the solubility of silver chloride in 0.10 M $NaNO_3$.

Solution

Diverse salts increase the solubility of precipitates and have more effect on precipitates with multiply charged ions.

The equilibrium constants listed in the Appendix C are for zero ionic strength; that is, they are really thermodynamic equilibrium constants.[1] Therefore, from Table C.3, $K_{sp} = 1.0 \times 10^{-10}$.

We need the activity coefficients of Ag^+ and Cl^-. The ionic strength is 0.10. From Reference 10 in Chapter 6, we find that $f_{Ag^+} = 0.75$ and $f_{Cl^-} = 0.76$. (You could also have used the values of α_{Ag^+} and α_{Cl^-} in the reference to calculate the activity coefficients using Equation 6.19.) From Equation 10.12

$$K_{sp} = \frac{1.0 \times 10^{-10}}{(0.75)(0.76)} = 1.8 \times 10^{-10} = [Ag^+][Cl^-] = s^2$$

$$s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} M$$

This is 30% greater than at zero ionic strength ($s = 1.0 \times 10^{-5} M$). ■

[1] Experimental K_{sp} values are often available at different ionic strengths and can be used to calculate molar solubilities at the listed ionic strengths without needing to calculate activity coefficients.

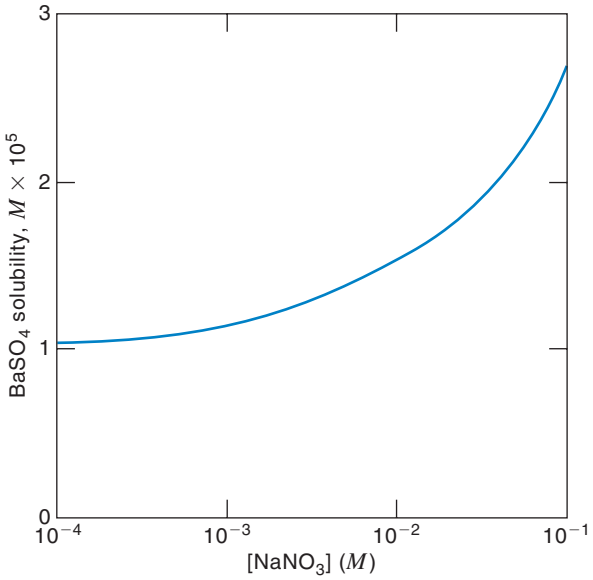


Fig. 10.4. Predicted effect of increased ionic strength on solubility of $BaSO_4$. Solubility at zero ionic strength is $1.0 \times 10^{-5} M$.

Figure 10.4 illustrates the increase in solubility of $BaSO_4$ in the presence of $NaNO_3$ due to the diverse ion effect.

The increase in solubility is greater with precipitates containing multiply charged ions. At very high ionic strengths, where activity coefficients may become greater than unity, the solubility is decreased. In gravimetric analysis, a sufficiently large excess of precipitating agent is added so that the solubility is reduced to such a small value that we do not need to worry about this effect.

Acids frequently affect the solubility of a precipitate. As the H^+ concentration increases, it competes more effectively with the metal ion of interest for the precipitating agent (which may be the anion of a weak acid). With less free reagent available, and a constant K_{sp}, the solubility of the salt must increase:

$$M^{n+} + nR^- \rightleftharpoons \underline{MR_n} \qquad \text{(desired reaction)}$$

$$R^- + H^+ \rightleftharpoons HR \qquad \text{(competing reaction)}$$

$$\underline{MR_n} + nH^+ \rightleftharpoons M^{n+} + nHR \qquad \text{(overall reaction)}$$

Similarly, a complexing agent that reacts with the metal ion of the precipitate will increase the solubility, for example, when ammonia reacts with silver chloride:

$$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2{}^+ + Cl^-$$

The quantitative treatment of these effects in solubility calculations will be covered in Chapter 11.

SPREADSHEET EXAMPLES

The iron content in a 2.287-g sample of iron ore is determined by precipitating as $Fe(OH)_3$, igniting to Fe_2O_3, and weighing. The result is a net weight of 0.8792 g. Prepare a spreadsheet to calculate the % Fe in the ore.

	A	B	C	D	E	F	G	H
1	Calculation of % Fe.							
2	g. sample:	2.287	g. Fe_2O_3:	0.8792				
3	% Fe:	**26.88797**						
4								
5	%Fe = {[g Fe_2O_3 × 2Fe/Fe_2O_3 (g Fe/g Fe_2O_3)]/g sample} × 100%							
6	=	{[0.8792 g Fe_2O_3 × 2(55.845/159.69)g Fe/g Fe_2O_3]/2.287 g sample} × 100%						
7	**B3 =**	(D2*2*(55.845/159.69)/B2)*100						
8								
9	The answer is 26.89% Fe.							

Questions

1. Describe the unit operations commonly employed in gravimetric analysis, and briefly indicate the purpose of each.
2. What is the von Weimarn ratio? Define the terms in it.
3. What information concerning optimum conditions of precipitation does the von Weimarn ratio give us?
4. What is digestion of a precipitate, and why is it necessary?
5. Outline the optimum conditions for precipitation that will obtain a pure and filterable precipitate.
6. What is coprecipitation? List the different types of coprecipitation, and indicate how they may be minimized or treated.
7. Why must a filtered precipitate be washed?
8. Why must a wash liquid generally contain an electrolyte? What are the requirements for this electrolyte?
9. What advantages do organic precipitating agents have?

Problems

GRAVIMETRIC FACTOR

10. Calculate the weight of sodium present in 50.0 g Na_2SO_4.
11. If the salt in Problem 10 is analyzed by precipitating and weighing $BaSO_4$, what weight of precipitate would be obtained?
12. Calculate the gravimetric factors for:

Substance Sought	Substance Weighed
As_2O_3	Ag_3AsO_4
$FeSO_4$	Fe_2O_3
K_2O	$KB(C_6H_5)_4$
SiO_2	$KAlSi_3O_8$

13. How many grams CuO would 1.00 g Paris green, $Cu_3(AsO_3)_2 \cdot 2As_2O_3 \cdot Cu(C_2H_3O_2)_2$, give? Of As_2O_3?

QUANTITATIVE CALCULATIONS

14. A 523.1-mg sample of impure KBr is treated with excess $AgNO_3$ and 814.5 mg AgBr is obtained. What is the purity of the KBr?
15. What weight of Fe_2O_3 precipitate would be obtained from a 0.4823-g sample of iron wire that is 99.89% pure?

16. The aluminum content of an alloy is determined gravimetrically by precipitating it with 8-hydroxyquinoline (oxine) to give $Al(C_9H_6ON)_3$. If a 1.021-g sample yielded 0.1862 g of precipitate. what is the percent aluminum in the alloy?

17. Iron in an ore is to be analyzed gravimetrically by weighing as Fe_2O_3. It is desired that the results be obtained to four significant figures. If the iron content ranges between 11 and 15%, what is the minimum size sample that must be taken to obtain 100.0 mg of precipitate?

18. The chloride in a 0.12-g sample of 95% pure $MgCl_2$ is to be precipitated as AgCl. Calculate the volume of 0.100 *M* $AgNO_3$ solution required to precipitate the chloride and give a 10% excess.

19. Ammonium ions can be analyzed by precipitating with H_2PtCl_6 as $(NH_4)_2PtCl_6$ and then igniting the precipitate to platinum metal, which is weighed [$(NH_4)_2PtCl_6 \xrightarrow{\text{heat}} Pt + 2NH_4Cl(g) + 2Cl_2(g)$]. Calculate the percent ammonia in a 1.00-g sample that yields 0.100 g Pt by this method.

20. A sample is to be analyzed for its chloride content by precipitating and weighing silver chloride. What weight of sample would have to be taken so that the weight of precipitate is equal to the percent chloride in the sample?

21. Pyrite ore (impure FeS_2) is analyzed by converting the sulfur to sulfate and precipitating $BaSO_4$. What weight of ore should be taken for analysis so that the grams of precipitate will be equal to 0.1000 times the percent of FeS_2?

22. A mixture containing only BaO and CaO weighs 2.00 g. The oxides are converted to the corresponding mixed sulfates, which weigh 4.00 g. Calculate the percent Ba and Ca in the original mixture.

23. A mixture containing only $BaSO_4$ and $CaSO_4$ contains one-half as much Ba^{2+} as Ca^{2+} by weight. What is the percentage of $CaSO_4$ in the mixture?

24. A mixture containing only AgCl and AgBr weighs 2.000 g. It is quantitatively reduced to silver metal, which weighs 1.300 g. Calculate the weight of AgCl and AgBr in the original mixture.

SOLUBILITY PRODUCT CALCULATIONS

25. Write solubility product expressions for the following: (a) AgSCN, (b) $La(IO_3)_3$, (c) Hg_2Br_2, (d) $Ag[Ag(CN)_2]$; (e) $Zn_2Fe(CN)_6$, (f) Bi_2S_3.

26. Bismuth iodide, BiI_3, has a solubility of 7.76 mg/L. What is its K_{sp}?

27. What is the concentration of Ag^+ and CrO_4^{2-} in a saturated solution of Ag_2CrO_4?

28. Calculate the concentration of barium in the solution at equilibrium when 15.0 mL of 0.200 *M* K_2CrO_4 is added to 25.0 mL of 0.100 *M* $BaCl_2$.

29. What must be the concentration of PO_4^{3-} to just start precipitation of Ag_3PO_4 in a 0.10 *M* $AgNO_3$ solution?

30. What must be the concentration of Ag^+ to just start precipitating 0.10 *M* PO_4^{3-}? 0.10 *M* Cl^-?

31. At what pH will $Al(OH)_3$ begin to precipitate from 0.10 *M* $AlCl_3$?

32. What weight of Ag_3AsO_4 will dissolve in 250 mL water?

33. What is the solubility of Ag_2CrO_4 in 0.10 *M* K_2CrO_4?

34. Compounds AB and AC_2 each have solubility products equal to 4×10^{-18}. Which is more soluble, as expressed in moles per liter?

35. The solubility product of Bi_2S_3 is 1×10^{-97} and that of HgS is 4×10^{-53}. Which is the least soluble?

36. A student proposes to analyze barium gravimetrically by precipitating BaF_2 with NaF. Assuming a 200-mg sample of Ba^{2+} in 100 mL is to be precipitated and that the precipitation must be 99.9% complete for quantitative results, comment on the feasibility of the analysis.

DIVERSE ION EFFECT ON SOLUBILITY

37. Write the thermodynamic solubility product expressions for the following:

(a) $\underline{BaSO_4} \rightleftharpoons Ba^{2+} + SO_4^{2-}$

(b) $\underline{Ag_2CrO_4} \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

38. Calculate the solubility of $BaSO_4$ in 0.0125 *M* $BaCl_2$. Take into account the diverse ion effect.

39. You are to determine fluoride ion gravimetrically by precipitating CaF_2. $Ca(NO_3)_2$ is added to give an excess of 0.015 *M* calcium ion after precipitation. The solution also contains 0.25 *M* $NaNO_3$. How many grams fluoride will be in solution at equilibrium if the volume is 250 mL?

EXCEL EXERCISES

Compare your answers with those on the text **website**.

40. Prepare a spreadsheet to calculate the percent P_2O_5 in Example 10.2. Use it to calculate the % P_2O_5 for the sample given in the example. Do a second calculation for a 0.5267 g sample that gives a precipitate of 2.0267 g.

41. Prepare a spreadsheet to calculate the solubility of $BaSO_4$ as a function of concentration of excess Ba^{2+} concentration, as in Figure 10.3. Prepare a graph of solubility versus Ba^{2+} concentration, using the Chart function of Excel, and compare it with Figure 10.3.

42. Prepare a spreadsheet to calculate the solubility of $BaSO_4$ as a function of ionic strength, as in Figure 10.4. Prepare a graph of solubility versus ionic strength using the Chart function of Excel, and compare it with Figure 10.4.

43. Solve Example 10.9, using Solver to calculate the solubility, *s*, of PbI_2.

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