

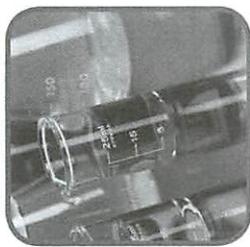
# Chemistry 1302A/B

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## Course Workbook

# Discovering Chemical Energetics



2019/2020 EDITION

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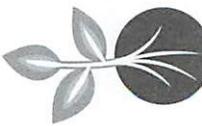
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# Chemistry 1302A/B

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# Chapter 1

## Gases



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Concern for man himself and his fate must always form the chief interest of all technical endeavours...in order that the creations of our minds shall be a blessing and not a curse to mankind. Never forget this in the midst of your diagrams and your equations.

### 1.1 Gases

#### OBJECTIVES

After studying this topic, you should be able to:

- Describe the three states of matter at a molecular level.
- Write the mathematical expressions for Boyle's and Charles's law, and apply these laws to problems involving pressure, volume, and temperature.
- Use the ideal gas equation to derive gas pressure, volume, or temperature given the quantities for the remaining terms.

#### INTRODUCTION

In this topic, the basic properties of gases are discussed and the *ideal gas law*, one of the most important relationships in chemistry, is developed.

#### Units

The following SI units of measurement will be used in this topic:

- Pressure = Force per Area =  $N \text{ m}^{-2} = \text{Pa}$  (pascal)
- 1 bar =  $10^5 \text{ Pa} = 100 \text{ kPa}$
- 1 atmosphere (atm) =  $101.33 \text{ kPa}$

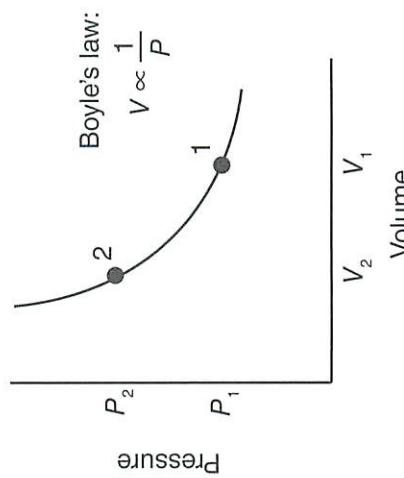
#### THE THREE STATES OF MATTER

The three states of matter studied in chemistry are solid, liquid, and gas.

Albert Einstein (1879–1955)

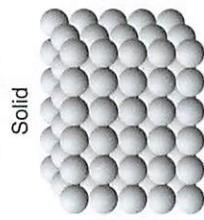
#### Topics Covered:

- 1.1 Gases
- 1.2 The Ideal Gas Law



**Solids**

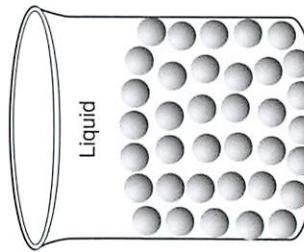
At some temperature, every substance (with the possible exception of helium) will form a solid. In the solid state, atoms, molecules, or ions are locked into a fixed position relative to others in the substance. The forces that hold this “lattice” together can be extremely strong, as is the case with ionic solids, or extremely weak, as is the case with some atomic solids like the inert gases.



The strength of these interactions determines the melting point of the solid in a predictable and obvious way. The stronger the interaction, the higher the melting point. Although atoms or molecules in a solid are not moving relative to each other, they always possess vibrational energy, even at absolute zero, and this vibrational energy increases with temperature. At some point, the magnitude of these vibrational modes overcomes the attractive forces, and the atoms or molecules will lose their fixed positions and become a liquid.

**Liquids**

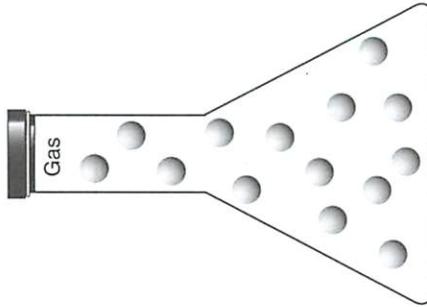
In liquids, the attraction between the atoms or molecules still keeps them touching, although the species are free to move about within a sea of their partners. In the liquid state, a substance will take the shape of the container that holds it.



In the liquid state of a substance, each atom or molecule takes up a little more space than in the solid state due to the increased motion. Therefore, the solid state of a substance is normally denser than its corresponding liquid, and the solid form will sink in its own liquid when the two are at the same temperature. One of the few exceptions to this rule is water. Ice is less dense than water at the same temperature, and, of course, ice floats. This seemingly insignificant observation has profound consequences. If it were not the case, seas, rivers, and lakes would freeze from the bottom up, not the top down, and fish and plant life could not survive in a frozen-solid environment. Indeed, life may not have evolved in the way it has if ice were more dense than water.

### Gases

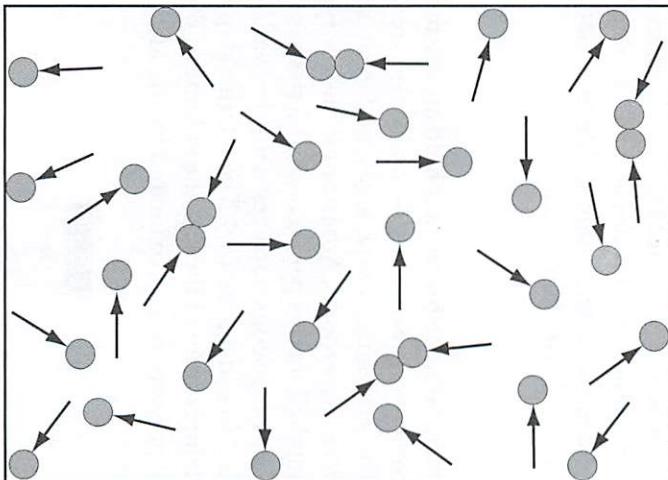
At a high enough temperature, the forces that hold atoms and molecules together are completely overcome, and the atoms or molecules are able to escape from their partner's grip. The substance is now a gas, and each atom or molecule has much more freedom to move around. Atomic motions for typical air gases are in the range of several hundred metres per second, and the gas will expand to fill its container. The collisions of gaseous particles with the walls of the container are the “pressure of the gas” (see image below). The relationship between the amount of gas (in moles), the temperature of the gas, the volume of the container in which it is captured, and the pressure is approximated by the ideal gas law.



### THE BEHAVIOUR OF GASES

In the development of chemical laws, theorems, and hypotheses, it is often necessary to make certain approximations and restrictive assumptions under which the theory applies. For the study of gases in this course, it is assumed that:

- the pressure is not too high, and
- the temperature is not close to the condensation temperature.



These assumptions are combined with the following approximations:

1. The atoms or molecules of the gas have no volume. At low pressure, the volume of the atoms or molecules will be very small compared to the total volume of the container, so their volume is indeed negligible.
2. There are no forces acting between the atoms or molecules of the gas. In other words, noncovalent interactions that normally would turn the gas into a liquid are taken to be negligible. This will be the case provided the gas is well above the vapourization/condensation temperature.

Our understanding of the behaviour of gases is based on the work of several scientists.

**Boyle's Law**

Boyle's law, first published in 1662, is named after Englishman Robert Boyle. Through experimentation, Boyle established the inverse relationship between the pressure of a gas and the volume it occupied, as described by:

$$P \times V = \text{constant}, \text{ or } V \propto \frac{1}{P}$$

where  $P$  is the pressure of the gas and  $V$  is its volume. In text form, the law reads:

*For a fixed amount of gas at a constant temperature, the gas volume is inversely proportional to the gas pressure.*

As long as the temperature is kept constant and the moles of the gas are fixed, the value of the constant will not change when pressure and volume are varied. Boyle's law is typically used to predict the result of introducing a change, in volume and pressure only, to the initial state of a fixed quantity of gas. So if  $P_1$  and  $V_1$  represent the initial state of the gas, and  $P_2$  and  $V_2$  the final state, then:

$$P_1 V_1 = P_2 V_2$$

Figure 1.1.1 shows the inverse relationship between gas pressure and volume.

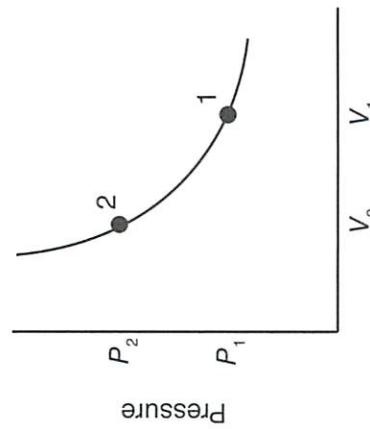


Figure 1.1.1 Inverse relationship between gas pressure and volume.

**Example 1.1.1. Applying Boyle's Law**

Determine the final volume occupied by an ideal gas when 1.00 L of the gas is compressed from a pressure of 100 kPa to 250 kPa at a constant temperature.

**Solution:** Since the pressure increases 2.5 times, the volume must decrease by a factor of 2.5.  $P_1 = 100 \text{ kPa}$ ,  $P_2 = 250 \text{ kPa}$ ,  $V_1 = 1.00 \text{ L}$ . Therefore,

$$V_2 = \frac{100 \text{ kPa} \times 1.00 \text{ L}}{250 \text{ kPa}} = 0.400 \text{ L}$$

**Example 1.1.2. Final Pressure after Expansion (In-Class Exercise)**

A container fitted with a piston initially at a volume of 1.50 L and a pressure of 125 kPa is allowed to expand at constant temperature to a final volume of 3.50 L. What is the final pressure of the gas inside the container?

**Charles's Law**

The next important stride in the study of gases came in the early 1800s in France. This was the golden age of hot air ballooning and scientists were anxious to improve the performance of their balloons. Two important French scientists, Jacques Charles and Joseph-Louis Gay-Lussac, made detailed measurements on how the volume of a gas was affected by its temperature.

In the same way that Robert Boyle kept all properties of the gas constant except for the pressure and volume, Jacques Charles kept all properties of the gas constant except for temperature and volume. The volume of the gas increased as the temperature increased, and this was found to be a linear relationship (see Figure 1.1.2). The mathematical expression for Charles's law is:

$$\frac{V}{T} = \text{constant, or } V \propto T$$

In other words, if the temperature (always expressed in K) of a sample of a fixed number of moles of gas is doubled, the volume should double. In text form, Charles's law reads:

*The volume of a fixed amount of gas at constant pressure is directly proportional to the Kelvin (absolute) temperature.*

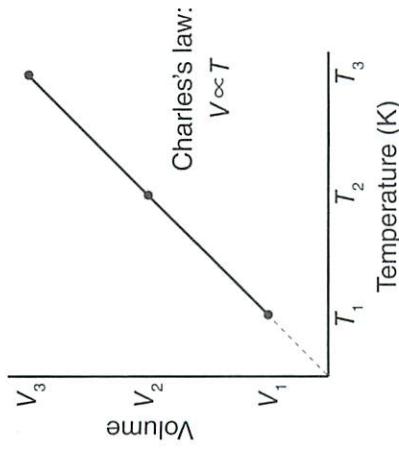


Figure 1.1.2 Linear relationship between gas volume and absolute temperature.

Charles's law can be used to predict the effect of temperature change on the volume of a gas. For a fixed number of moles of gas at a fixed pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles's law can also be combined with Boyle's law to obtain the following relationship:

$$\frac{P \times V}{T} = \text{constant}$$

Thus, for a fixed number of moles of gas:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

#### Example 1.1.3. Temperature of a Gas after Heating and Pressure Increase

A gas at 0 °C, 1 bar, is heated at constant volume until  $P = 2$  bar. What is the final temperature of the gas?

**Solution:** Implicit in the question is that  $n$ , the amount of gas, is constant. First, convert the temperatures to K and then list the known quantities:

$$P_1 = 1 \text{ bar}; P_2 = 2 \text{ bar}; V_1 = V_2; T_1 = 273.15 \text{ K}; T_2 = ? \text{ K}$$

Next, substitute the known values into:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{1\text{bar} \times V_1}{273.15\text{K}} = \frac{2\text{bar} \times V_1}{T_2}$$

Therefore:  $T_2 = 546.3\text{ K}$ .

#### Example 1.1.4. Pressure of a Gas after Cooling and Compression (In-Class Exercise)

A 15.0 L sample of  $\text{N}_2(\text{g})$  at 120.0 kPa and 385 K is compressed to 9.50 L and then cooled to 250 K. What is the final pressure?

#### Example 1.1.5. Volume of a Gas after Pressure Increase and Heating (In-Class Exercise)

The absolute temperature of a gas inside a balloon doubles while the pressure quadruples. By what factor does the volume of the balloon change?

#### Avogadro's Law

In 1811, Italian scientist Amedeo Avogadro hypothesized that:

*Equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules.*

This means that if the number of molecules of gas increases, the volume of the gas must also increase in a linear fashion.

Mathematically, this is expressed by:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{V}{n} = \text{constant, or } V \propto n$$

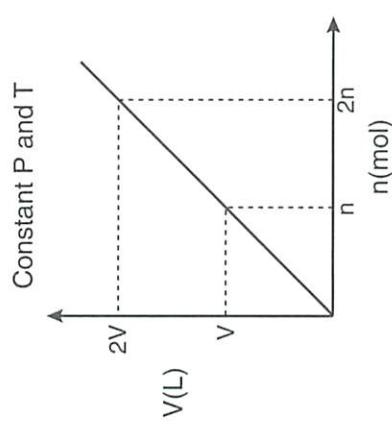


Figure 1.1.3 Linear relationship between gas volume and number of molecules of gas.

Avogadro's law can be used to determine the volume of a gas after the number of molecules (or moles) of gas have changed. The pressure and temperature of the gas must remain constant.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

#### **Development of the Ideal Gas Law**

The “laws” put forward by Boyle, Charles, and Avogadro all relate the volume of gas to some other property of the gas. These three laws may be combined to give one expression that describes “ideal” gas behaviour.

$$\text{Boyle: } V \propto \frac{1}{P}$$

$$\text{Charles: } V \propto T$$

$$\text{Avogadro: } V \propto n$$

Combining the laws, we get:  $V \propto \frac{nT}{P}$

This relationship may be converted to an equality by inserting a constant, which is known as  $R$ , the ideal gas constant.

$$\text{So, } V = R \times \frac{nT}{P}$$

$$\text{or: } PV = nRT$$

Note that the absolute value of the constant  $R$  is the same for all ideal gases but the value used when solving problems depends on the type of problem and the units needed in the solution (see Table 1.1.1).

TABLE 1.1.1 DIFFERENT VALUES OF  $R$  USED IN THE IDEAL GAS EQUATION

VALUE	APPLICATION	HOW DERIVED
$0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$	$V$ in litres, $P$ in atmospheres	$1 \text{ atm} = 101.33 \text{ kPa}$
$0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$	$V$ in litres, $P$ in bar	$1 \text{ atm} = 1.0133 \text{ bar}$
$8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$	$V$ in litres, $P$ in kilopascals	$1 \text{ atm} = 101.33 \text{ kPa}$
$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$	Determination of energy (J)	$1 \text{ L atm} = 101.33 \text{ J}$
$8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$	Molecular speed (mass in kg)	$1 \text{ J} = \text{kg m}^2 \text{ s}^{-2}$
$8.314 \times 10^3 \text{ g m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$	Molecular speed (mass in g)	$1 \text{ J} = 10^3 \text{ g m}^2 \text{ s}^{-2}$

**Example 1.1.6. Application of Ideal Gas Equation (In-Class Exercise)**

15.0 g of sulfur dioxide,  $\text{SO}_2(\text{g})$ , occupy a volume of 4.00 L at 105 °C. What is the pressure of the gas in kPa?

## Section 1.1 Practice Problems

1. A sample of air in a balloon initially at a volume of 2.00 L and a pressure of 100 kPa is allowed to expand at a constant temperature to 3.00 L. What is the final pressure inside the balloon?
2. A 1.00 L sample of  $\text{CO}_2(\text{g})$  at 200 K is heated to 400 K and allowed to expand at a constant pressure. What is the final volume?
3. A sample of butane ( $\text{C}_4\text{H}_{10}$ ) at 100 kPa and 298 K is heated to 398 K at a constant volume. What is the pressure after heating?
4. If equal masses of the gases Xe, Ar, and Ne are placed in separate flasks of equal volume at the same temperature, which one of the following statements is correct?
  - a. The pressure in the Ne flask is the greatest.
  - b. The pressure in the Ar flask is the greatest.
  - c. The pressure in the Xe flask is the greatest.
  - d. All flasks contain the same number of atoms.
  - e. The pressure in all of the three flasks is the same.
5. If equal masses of  $\text{O}_2$  and  $\text{N}_2$  are placed in identical containers at the same temperature, which one of the following statements is correct?
  - a. Both containers contain the same number of molecules.
  - b. There will be more molecules in the  $\text{O}_2$  flask than the  $\text{N}_2$  flask.
  - c. The pressure in the  $\text{N}_2$  flask will be greater than the pressure in the  $\text{O}_2$  flask.
  - d. None of the other statements is correct.
  - e. This question can't be answered unless the masses of  $\text{O}_2$  and  $\text{N}_2$  in the flasks are known.
6. A 20.0 L sample of air at 104.0 kPa and 400 K is cooled to 300 K and the volume of the container is reduced to 15.0 L. What is the final pressure of the system?

7. The air inside a rubber balloon at 80 °C has a pressure of 140 kPa. After cooling, the balloon's volume is reduced by 10%, and its inside pressure decreases to 125 kPa. What is the final temperature, in °C, inside the cooled balloon?
8. The density of liquid water at its boiling point of 100.0 °C is 0.96 g mL<sup>-1</sup>. Calculate the factor by which liquid water at 100.0 °C expands (i.e., the ratio  $V_{\text{steam}}^{\text{liquid}}/V_{\text{liquid}}$ ) when it turns into steam at 100.0 °C and 101 kPa pressure. Hint: Think of what happens to *one mole* of water on evaporation.
9. What pressure would 10.0 g of molecular nitrogen, N<sub>2</sub>, exert at 120.0 °C if it occupies a volume of 2.50 L?
10. 8.80 g of CO<sub>2</sub>(g) occupies a volume of 12.0 L at 54.5 kPa pressure. What is its temperature?
11. Xenon (Xe) filled lamps are used in the automobile industry. What mass, in g, of Xe gas is contained in a 65.0 mL lightbulb at 553 kPa pressure at 25 °C?
12. If 100 g of sulfur is burned to produce SO<sub>2</sub>(g), what pressure (in kPa) would the product exert in a volume of 200 L at 40.0 °C?
13. Commercially, nitrogen is sold as a compressed gas contained in cylinders. If a cylinder of volume 116 L is filled with N<sub>2</sub> to a pressure of  $1.38 \times 10^4$  kPa at 25.0 °C, what mass of N<sub>2</sub> does the cylinder contain? Assume ideal gas behaviour.
14. Regarding the above, if the tap were opened and the gas allowed to escape, how many litres of N<sub>2</sub> gas at 100 kPa pressure and 25.0 °C would come out of the cylinder?
15. A 10.0 L container is initially filled with propane (C<sub>3</sub>H<sub>8</sub>) at a pressure of 50.0 kPa and a temperature of 28.0 °C. One mole of Ar gas is then added and the mixture is heated to 90.0 °C. What is the final pressure, in kPa, in the container?
16. An evacuated 560 mL light bulb was found to weigh 14.56 g. When filled with the vapour of a volatile compound at 100.0 °C and 98.7 kPa, the bulb weighed 17.09 g. Analysis of the compound showed it to contain 84.4% carbon and 15.6% hydrogen by mass. Determine the molar mass and the molecular formula of the compound.

17. Which of the following statements is/are correct for two moles of an ideal gas?

- a. A plot of  $P$  versus  $T$  at constant  $V$  will give a straight line.
- b. A plot of  $V$  versus  $T$  at constant  $P$  will give a straight line with slope =  $R/P$ .
- c. A plot of  $PV/T$  versus  $P$  will give a straight line with a zero slope.
- d. A plot of  $PV$  versus  $T$  will give a straight line with a zero slope.
- e. A plot of  $PV/RT$  versus  $P$  will give a straight line with a slope = 2.



## 1.2 The Ideal Gas Law

### OBJECTIVES

After studying this topic, you should be able to:

- Use the ideal gas law to determine densities and molar masses.
- Describe and apply Dalton's law and the relationship between partial pressure and mole fraction.
- Perform stoichiometric calculations using gas volumes and/or pressures.
- Describe and apply Graham's law and the relationship between molecular mass, effusion rate, and enhancement factor.

### INTRODUCTION

In the previous topic, Boyle's law, Charles's law, and Avogadro's law were reviewed, and their contribution to the development of the ideal gas law ( $PV = nRT$ ) was explained. In this topic, the ideal gas law is discussed in detail, and more complex scenarios are presented. The kinetic theory of gases is also introduced.

### THE MOLAR VOLUME OF A GAS

For solids and liquids, the mass and volume of one mole of a substance depends on the substance being considered. For example, one mole of sulfuric acid ( $H_2SO_4$ ) weighs 98 g and occupies 54 mL, while one mole of benzene ( $C_6H_6$ ) weighs 78 g and occupies 89 mL.

Although different gases have different molar masses, Avogadro's law states that one mole of any ideal gas always occupies the same volume at a given temperature and pressure, regardless of the gas in question. This also means that equal volumes of different gases at the same temperature and pressure contain the same number of moles.

According to the ideal gas law, the volume of one mole of an ideal gas at 0 °C and 1 atm is:

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})}{(1 \text{ atm})} = 22.4 \text{ L}$$

0 °C (273.15 K) and 1 atm (101.33 kPa) are called *normal temperature and pressure* (NTP), and are common reference conditions used when defining the properties of gases. The volume 22.4 L is known as the *normal volume of an ideal gas* at NTP. Previously, these conditions were usually called *standard temperature and pressure*, which is the name still used in many texts.

#### VARIATIONS OF THE IDEAL GAS LAW

The ideal gas law can be used to determine the molar mass of a gas at fixed volume, temperature, and pressure. The density ( $d$ ) of any substance is defined as the mass occupied per unit volume:

$$d = \frac{m}{V}$$

In turn, the mass of any substance is related to its molar mass ( $MM$ ) and the number of moles ( $n$ ):

$$m = MM \times n$$

The ideal gas equation,  $PV = nRT$ , can then be used to derive a general relationship between gas density and its molar mass:

$$d = \frac{(MM)P}{RT} \quad \text{or} \quad MM = \frac{dRT}{P} \quad (1.2.1)$$

Equation 1.2.1 shows that, at constant temperature, gas density is directly proportional to its pressure. In addition, at constant pressure and temperature, density is related to the molar mass of a gas.

**Example 1.2.1. Density and Molar Mass of a Gas**

A 5.00 L flask holds 18.55 g of a gas at 115 °C and 1.00 atm. What is (a) the density of the gas under these conditions, and (b) its molar mass?

**Solution:**

- $d = \frac{m}{V} = \frac{18.55\text{ g}}{5.00\text{ L}} = 3.71\text{ g L}^{-1}$
- Equation 1.2.1 can be used to find the molar mass:  $MM = \frac{dRT}{P}$

$R = 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}$  when  $V$  is in L and  $P$  is in atm. Convert the temperature from °C to K. Then:

$$MM = \frac{(3.71\text{ g L}^{-1})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(388.15\text{ K})}{(1.00\text{ atm})} = 118.23\text{ g mol}^{-1}$$

**Example 1.2.2. Molar Mass and Molecular Formula of a Gas (In-Class Exercise)**

A gas with the formula  $\text{SO}_x$  has a density of 2.968 g L<sup>-1</sup> at 35 °C and 95.0 kPa.

Determine the following:

- The molar mass of the gas.
- The value of  $x$ .

**DALTON'S LAW OF PARTIAL PRESSURES**

In the case of a mixture of several ideal gases, the total volume of the mixture, the total pressure, and total number of moles behave as a single gas with respect to the ideal gas law:

$$PV = nRT \quad \text{or} \quad P_{\text{total}} \times V_{\text{total}} = n_{\text{total}} \times R \times T$$

Each of the constituents in a gas mixture is said to exhibit a *partial pressure* that contributes to the total pressure. The relationship between the partial pressures and total pressure of a gas mixture was first proposed by Englishman John Dalton in 1801. Dalton's law of partial pressures states:

*The total pressure exerted by a mixture of gases is the sum of all the partial pressures of these gases.*

Dalton's law is illustrated in Figure 1.2.1 for three gases. For a mixture of three gases (A, B, and C), the total pressure would be:

$$P_T = P_A + P_B + P_C$$

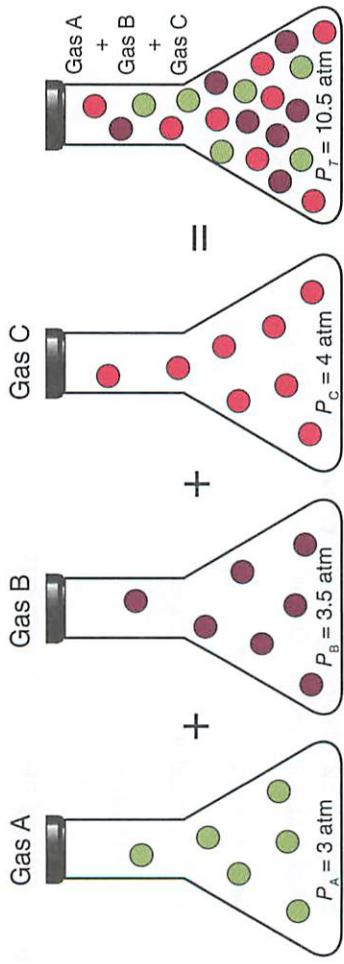


Figure 1.2.1 Dalton's law of partial pressures.

### Mole Fractions and Partial Pressure

If  $n_i$  is the number of moles of an individual constituent in a gas mixture and  $n_T$  is the total number of moles in the mixture, the *mole fraction*,  $X_i$ , is:

$$X_i = \frac{n_i}{n_T}$$

At a constant temperature and volume, the pressure is directly proportional to the moles. This means:

$$\frac{P_i}{P_T} = \frac{n_i}{n_T} = X_i$$

which can be arranged to give:  $P_i = X_i P_T$

Dalton's Law says that the sum of the partial pressures,  $P_A$ ,  $P_B$ , and  $P_C$  of a mixture of ideal gases A, B, and C equals the total pressure,  $P_T$ . If the pressures of each gas are expressed in terms of the mole fractions, then:  $P_A = X_A P_T$ ,  $P_B = X_B P_T$ , and  $P_C = X_C P_T$ . Note that the sum of all the mole fractions is always 1. In other words,  $X_A + X_B + X_C = 1$ .

The ideal gas law can be applied to each individual constituent of a gas mixture, as well as the gas mixture as a whole. For each constituent, the ideal gas law can be written as:

$$P_i V = n_i RT$$

**Example 1.2.3. Partial Pressure and Mole Fraction of a Gas (In-Class Exercise)**

Flask A and Flask B are connected by a stopcock. Flask A has a volume of 400 mL and initially contains O<sub>2</sub>(g) at a pressure of 90.0 kPa. Flask B has a volume of 700 mL and initially contains N<sub>2</sub>(g) at a pressure of 70.0 kPa. The stopcock is opened and the gases mix. The temperature is held constant.

Determine the following:

- The partial pressure of each gas after mixing.
- The total pressure.
- The mole fraction of each gas in the final mixture.

From Avogadro's law, we know that at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles.

**Example 1.2.4. Partial Pressures of Atmospheric Gases (In-Class Exercise)**

By volume, air contains 78% nitrogen (N<sub>2</sub>), 21% oxygen (O<sub>2</sub>), and the remaining 1% is composed of rare gases (argon), carbon dioxide, and variable amounts of water vapour, etc. Determine the partial pressure of each of the two main constituents (N<sub>2</sub> and O<sub>2</sub>) at an altitude where the atmospheric pressure is 0.80 atm.

**Vapour-Liquid Equilibrium and Vapour Pressure**

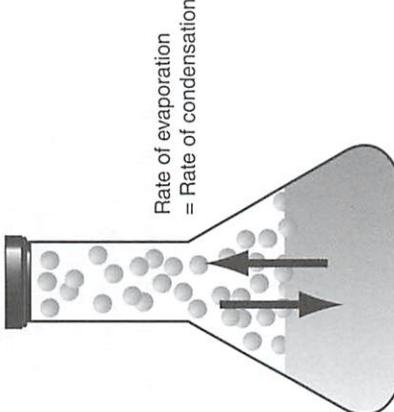
Suppose a flask was partially filled with water and, before being stoppered, the air in the flask was replaced with nitrogen gas. Some of the liquid water will evaporate until an equilibrium state is reached. At equilibrium, the rates of evaporation and condensation will be the same, and the pressure of the  $\text{H}_2\text{O(g)}$  will remain constant.



At this point, the total pressure of the gas in the flask would be equal to the  $\text{N}_2$  pressure plus the pressure added by the gaseous  $\text{H}_2\text{O}$  molecules:

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{water}}$$

The partial pressure of the water vapour ( $P_{\text{water}}$ ) is referred to as the *vapour pressure* of water. The vapour pressure of water depends *only* on the temperature of water; it does not depend on the volume of the container or the presence of another gas. At higher temperatures, vapour pressure increases as more energy is provided to the liquid molecules, allowing them to escape into the gas phase. Solvents that are more volatile (i.e., have lower boiling points) have higher vapour pressures. The boiling point is defined as the temperature at which the vapour pressure of a liquid is equal to atmospheric pressure.



**Example 1.2.5. Vapour Pressure and the Mass of a Gas Collected over Water (In-Class Exercise)**

A sample of O<sub>2</sub> gas collected at 37 °C over water with the same temperature has a volume of 15.0 L and a total pressure of 102.0 kPa. What is the mass, in grams, of the O<sub>2</sub> in the sample? The vapour pressure of water at 37 °C is 6.3 kPa.

**Average Molar Mass of a Mixture**

The average molar mass,  $\overline{MM}$ , of a mixture of different gases (e.g., gas A, gas B, gas C, etc.) is the weighted average of the molar masses of the different components. Mathematically, this can be represented as:

$$\overline{MM} = (X_A \times MM_A) + (X_B \times MM_B) + (X_C \times MM_C)$$

Since  $\overline{MM}$  is based on a weighted average, its value is usually closest to the molar mass of the component in the greater quantity.

**Example 1.2.6. Average Molar Mass of a Mixture of Gases (In-Class Exercise)**

A sample contains 0.123 moles O<sub>2</sub>(g), 0.568 moles N<sub>2</sub>(g), and 1.68 moles Cl<sub>2</sub>(g). What is the average molar mass of this mixture?

**Example 1.2.7. Average Molar Mass and Density of a Mixture of Gases (In-Class Exercise)**

A gaseous mixture of ethane, C<sub>2</sub>H<sub>6</sub>(g), and propane, C<sub>3</sub>H<sub>8</sub>(g), exerts a total pressure of 85.0 kPa at 20 °C. If the pressure of ethane is 40.0 kPa, what is the density of the mixture?

### GAS REACTION STOICHIOMETRY

The ideal gas law,  $PV = nRT$ , shows that at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles. Likewise, at constant temperature and volume, the pressure of a gas is directly proportional to the number of moles. Therefore, in the stoichiometry of gas reactions, the stoichiometric coefficients of gaseous reactants and products (i.e., the number of moles) are directly related to the volume and pressure. When the pressure and temperature are constant, mole ratios are the same as volume ratios. Likewise, at constant volume and temperature, mole ratios are the same as pressure ratios.

The typical gas stoichiometry scenarios encountered in chemistry are:

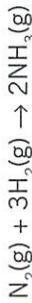
1. Mole-volume
2. Mass-volume
3. Volume-volume
4. Pressure-pressure

The meaning of these scenarios will become clear in the following examples.

#### Example 1.2.8. Stoichiometric Relationship between Moles and Volume

In the Haber-Bosch process, hydrogen gas and nitrogen gas react over an iron substrate to produce ammonia, which is used in the production of fertilizer. Given this process, how many litres of  $\text{NH}_3$  can be produced at  $27.0\text{ }^\circ\text{C}$  and  $1.0\text{ atm}$  if  $20.0$  moles of  $\text{N}_2$  are reacted with excess hydrogen?

**Solution:** Start with the balanced equation:



According to the balanced equation,  $1$  mole of  $\text{N}_2$  and  $3$  moles of  $\text{H}_2$  will give  $2$  moles of  $\text{NH}_3$ . Similarly, if  $20$  moles of  $\text{N}_2$  are consumed,  $40$  moles of  $\text{NH}_3$  can be produced. Use the ideal gas law to find the volume of  $\text{NH}_3$ .

$$V = \frac{nRT}{P} = \frac{(40.0\text{ mol})(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(300.15\text{ K})}{(1.0\text{ atm})} = 990\text{ L}$$

**Example 1.2.9. Stoichiometric Relationship between Mass and Volume**

In this example, the mass of one component is known and the volume of another component must be determined at a stated temperature and pressure.

Referring again to the Haber-Bosch process, how many litres of  $\text{H}_2$  will be required at a temperature of 300.15 K and 3.0 atm pressure to consume 56.0 grams of  $\text{N}_2$ ?

**Solution:**



56.0 grams of  $\text{N}_2$  corresponds to 2.00 moles of  $\text{N}_2$  ( $M = 28.0 \text{ g mol}^{-1}$ ). To consume 2 moles of  $\text{N}_2$ , 6.00 moles of  $\text{H}_2$  are needed. Using the given temperature and pressure, find the volume occupied by 6.00 moles of  $\text{H}_2$ :

$$V = \frac{nRT}{P} = \frac{(6.00 \text{ mol})(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(300.15 \text{ K})}{(3.0 \text{ atm})} = 50 \text{ L}$$

**Example 1.2.10. Stoichiometric Relationship Based on Volume Change (In-Class Exercise)**

Referring again to the Haber-Bosch process, how many litres of  $\text{NH}_3$  can be produced if 10 litres of  $\text{N}_2$  are consumed? The volumes are measured at the same temperature and pressure.



**Example 1.2.11. Stoichiometric Relationship Based on Pressure Change (In-Class Exercise)**

A sealed vessel contains propane gas and oxygen gas with partial pressures of 60 kPa and 200 kPa, respectively. The mixture is reacted according to the following unbalanced equation:

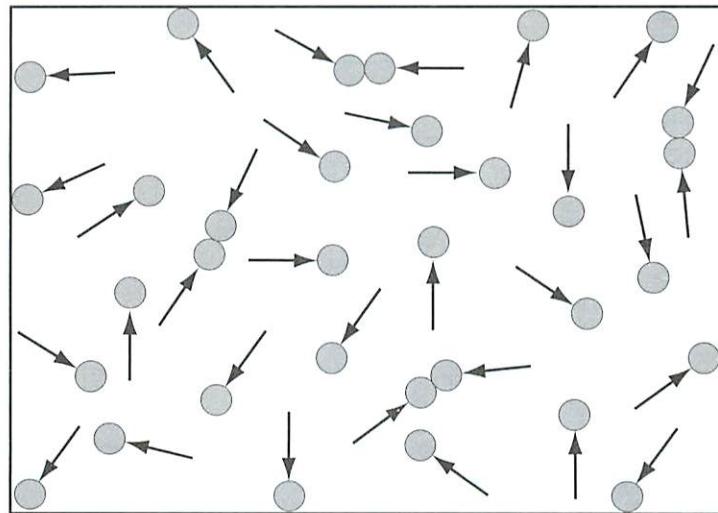


and then cooled to the initial temperature.

- a. What is the partial pressure of the  $\text{CO}_2$  produced?
- b. What is the partial pressure of the excess reagent after the reaction?
- c. What is the total pressure of the gaseous mixture?
- d. What is the mole fraction of  $\text{H}_2\text{O}$  in the gaseous mixture?

### THE KINETIC MOLECULAR THEORY OF GASES

The ideal gas law describes the observable behaviour of gases, but does not provide any insight into what happens to a gas at the molecular level, and does not explain how the behaviour of gas molecules results in the relationships embedded in  $PV = nRT$ .



In the 19th century, detailed analysis of gaseous atoms and molecules by physicists Rudolf Clausius, James Clerk Maxwell, and Ludwig Boltzman led to the development of the *kinetic molecular theory* of gases. The kinetic molecular theory of gases is based on the following assumptions:

1. The size of molecules is negligible when compared to the space between them and the volume of their container.
2. Molecules moving through space are considered to be *point particles*. As such, they do not have any vibrational or rotational energy, just translational (kinetic) energy.

3. The collisions that occur between molecules, and between molecules and their container, are considered elastic. That is, the total momentum and energy of colliding molecules are conserved during the collisions, and the molecules move in straight lines at constant velocities. Moreover, gas pressure is the result of molecules colliding with the container walls (see image on previous page).
4. There are no attractive or repulsive forces between the molecules.

5. The average kinetic energy of the molecules is proportional to the temperature ( $T$ ) in Kelvin. When the temperature is increased, the kinetic energy increases.  
The kinetic energy of the gas molecules is given by:

$$\overline{E}_K = \frac{1}{2}m\bar{u}^2 \quad (1.2.2)$$

where  $m$  is the mass of one molecule and  $\bar{u}$  is the speed.

The bars above  $E_K$  and  $\bar{u}$  in Equation 1.2.2 indicate average values. Average values for speed must be used because not all the molecules are moving at the same speed at any given time. The term  $\bar{u}^2$  is called the *mean-square speed* and is found by taking an average of the squares of the speeds of the molecules. For example:

$$\text{Gas A: } \bar{u} = 250 \text{ m s}^{-1}$$

$$\text{Gas B: } \bar{u} = 300 \text{ m s}^{-1}$$

$$\text{Gas C: } \bar{u} = 325 \text{ m s}^{-1}$$

$$\bar{u}^2 = \frac{(250 \text{ m s}^{-1})^2 + (300 \text{ m s}^{-1})^2 + (325 \text{ m s}^{-1})^2}{3}$$

$$= 8.604 \times 10^4 \text{ m}^2 \text{ s}^{-2}$$

How can this information be used to derive a theory that explains the behaviour of gases? Consider the factors that determine the pressure of a gas in a container. The mass,  $m$ , of each molecule and speed,  $\bar{u}$ , of the molecules are two factors. The frequency of collisions—that is, the number of collisions per second—is a third factor.

The frequency of collisions is related to the number of molecules,  $N$ , the volume of the container,  $V$ , and again, the speed of the molecules,  $\bar{u}$ . Between collisions, the molecules move in straight lines in three-dimensional (3D) space. Only the speed in one dimension is needed since the motion in the other two dimensions is identical. This leads to the basic equation of the kinetic theory of gases:

$$P = \frac{1}{3} \frac{N}{V} m \bar{u}^2$$

From the ideal gas law:

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

it follows that:

$$\frac{1}{3} \frac{N}{V} m \bar{u}^2 = \frac{nRT}{V} \quad (1.2.3)$$

Since  $m$  is the mass of one molecule:

$$MM = m \times N_A \text{ and } n = \frac{N}{N_A}$$

Substituting into Equation 1.2.3 and rearranging gives:

$$\bar{u}^2 = \frac{3RT}{MM} \quad (1.2.4)$$

Equation 1.2.4 shows that the mean-square speed of gas molecules is directly proportional to the temperature and inversely proportional to the molar mass. If a gas is heated, the molecules will move faster. If two gases are at the same temperature, the lighter gas molecules move faster, on average, than the heavier gas molecules. Thus, at any given moment, some gas molecules are moving faster and some are moving slower.

The distribution of the speeds of the molecules is governed by the *Maxwell-Boltzmann distribution*. Figure 1.2.2 shows the Maxwell-Boltzmann distribution of molecular speeds for an equal number of moles of four noble gases at 25 °C.

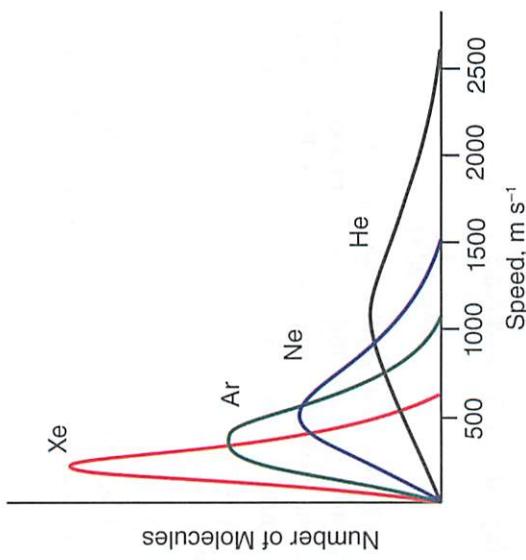


Figure 1.2.2 Maxwell-Boltzmann distribution of molecular speeds.

### Root-Mean-Square Speed of Gas Molecules

A more commonly used form of the mean-square speed term is the *root-mean-square* (rms) speed,  $u_{\text{rms}}$ , which is defined as:

$$u_{\text{rms}} = \sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{MM'}}$$

### Example 1.2.12. Root-Mean-Square Speed of Gas Molecules

Find the  $u_{\text{rms}}$  of methane ( $\text{CH}_4$ ) at 300 K.

$$\text{Solution: } u_{\text{rms}} = \sqrt{\frac{3RT}{MM'}}$$

$$3RT = (3)(8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(300 \text{ K})$$

$$= 7483 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}$$

$$MM \text{ of } \text{CH}_4 = 16.04 \text{ g mol}^{-1} = 0.01604 \text{ kg mol}^{-1}. \text{ Therefore:}$$

$$u_{\text{rms}} (\text{CH}_4) = \sqrt{\frac{7483 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}}{0.01604 \text{ kg mol}^{-1}}} = 683.0 \text{ m s}^{-1}$$

For two different gases, A and B, at the same temperature ( $T$  constant):

$$\frac{u_{\text{rms}}(\text{A})}{u_{\text{rms}}(\text{B})} = \sqrt{\frac{MM_{\text{B}}}{MM_{\text{A}}}}$$

Note that the  $u_{\text{rms}}$  for two gases is *inversely* proportional to the square root of the ratio of their molar masses.

The units for  $u_{\text{rms}}$  are metres per second ( $\text{m s}^{-1}$ ), so the molar mass of the gas has to be expressed in kilograms ( $\text{kg}$ ), and the value used for  $R$  must be:

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \text{ or}$$

$$R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

### **Effusion and Graham's Law**

Effusion is the flow of gas molecules at low pressures through tiny pores or pinholes in a container (see Figure 1.2.3). The rate of effusion of a gas is defined as the number of moles of the gas escaping the container per unit of time,

$$r_{\text{eff}} = \frac{n_{\text{eff}}}{t}$$

Scottish chemist Thomas Graham found that lighter molecules effuse more rapidly than heavier ones. In 1846, after extensive experimentation, he formulated what is now known as Graham's law:

*The rate of effusion of a gas is inversely proportional to the square root of its molar mass:*

$$r_{\text{eff}} \propto \frac{1}{\sqrt{MM}}$$

When two gases A and B with equal partial pressures effuse through a porous material or a small hole, Graham's law can be written as:

$$\frac{r_{\text{eff}}^{\text{A}}}{r_{\text{eff}}^{\text{B}}} = \sqrt{\frac{MM_{\text{B}}}{MM_{\text{A}}}} \quad (1.2.5)$$

Because lighter molecules effuse faster than heavier molecules, the gas that emerges from a container is *enriched* in the lighter component.

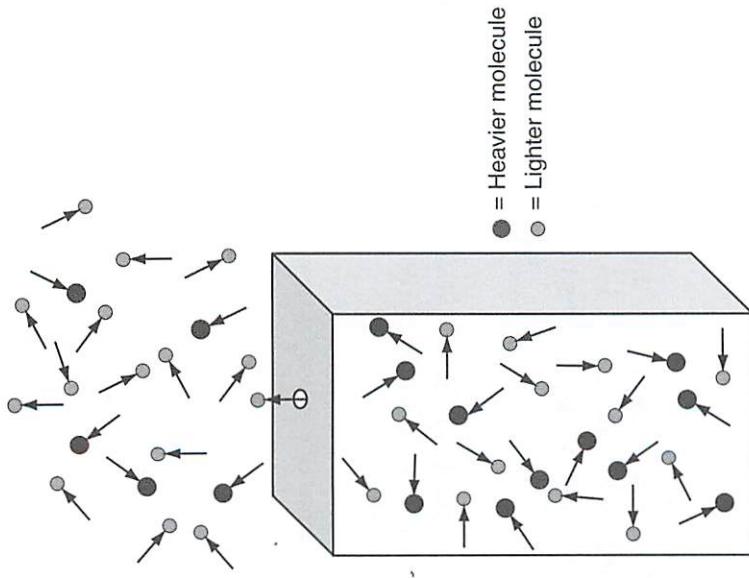


Figure 1.2.3 Effusion of gases through a pinhole in a container.

The quantity  $f = \sqrt{\frac{MM_B}{MM_A}}$  is called the *enrichment factor*.

Consider an example. Suppose we have an equimolar mixture of gases A and B with molar masses  $MM_A$  and  $MM_B$ , respectively. If this mixture is placed into a container with a small pinhole and allowed to effuse for a specific length of time, the gas that escapes will be enriched with the lighter molecules. If gas A is methane,  $\text{CH}_4$  ( $MM = 16.0 \text{ g mol}^{-1}$ ), and gas B is oxygen,  $\text{O}_2$  ( $MM = 32.0 \text{ g mol}^{-1}$ ), the enrichment factor would be:

$$f = \sqrt{\frac{MM_B}{MM_A}} = \sqrt{\frac{32.0}{16.0}} = \sqrt{2} \approx 1.414$$

Note that the heavier  $MM$  (in this case  $O_2$ ) must be in the numerator of the fraction. This number means that the effused gas stream would have 1.414 times as many methane molecules as oxygen molecules.

**Example 1.2.13. Effusion and Enrichment Factor (In-Class Exercise)**

The Manhattan Project was a code name for the top-secret WWII-era US-led undertaking to produce the first nuclear weapons. One of the technological challenges in that project was to collect enough nuclear fission material,  $^{235}U$ , by separating it from the more abundant  $^{238}U$  isotope. To this purpose, a mixture of two uranium hexafluoride gases ( $^{235}UF_6$  and  $^{238}UF_6$ ) was effused repeatedly. Use the atomic mass of  $^{235}U$  (235.04),  $^{238}U$  (238.05), and F (19.00) to determine the enrichment factor for each effusion.

**Example 1.2.14. Effusion and Molar Mass of an Unknown Gas (In-Class Exercise)**

Oxygen effuses into an empty (evacuated) cylinder where the pressure reaches 3.0 kPa at 20 °C after 5 minutes. When the experiment is repeated at the same temperature using the same initial number of moles of an unknown gas, the pressure in the cylinder reaches 3.0 kPa after 10 minutes. Determine the molar mass of the unknown gas.

## Section 1.2 Practice Problems

- At what pressure (in kPa) would the density of oxygen be  $2.86 \text{ g L}^{-1}$  at  $50^\circ\text{C}$ ?
- Assuming ideal gas behaviour, which one of the gases  $\text{N}_2$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CO}_2$ ,  $\text{Kr}$ , and  $\text{SF}_6$  would have the lowest density at  $0^\circ\text{C}$  and 100 kPa?
- A gas has a density of  $1.20 \text{ g L}^{-1}$  at  $27^\circ\text{C}$ . If the gas is heated at constant volume in a sealed container, what is the density, in  $\text{g L}^{-1}$ , at  $127^\circ\text{C}$ ?
- A gas with general formula  $\text{O}_x$  is found to have a density of  $0.189 \text{ g L}^{-1}$  at  $37^\circ\text{C}$  and a pressure of 10.1 kPa. Find the molar mass of the gas and the value of  $x$ .
- Suppose planet Xebon has an atmosphere composed solely of xenon,  $\text{Xe}$ . If the pressure at the surface of the planet was 1.01 kPa, and the temperature was  $20^\circ\text{C}$ , what would the density ( $\text{g L}^{-1}$ ) of the surface atmosphere be?
- Two flasks are connected together by a closed valve. One flask contains 1.0 L He at 200 kPa, while the other contains 2.0 L of Ne at 27 kPa. If the temperature remains constant at  $27^\circ\text{C}$ , find the final pressure after the valve is opened.
- A sample of gas contains  $\text{N}_2(\text{g})$  at 40.0 kPa,  $\text{O}_2(\text{g})$  at 60.0 kPa, and  $\text{CO}_2(\text{g})$  at 10 kPa. Calculate the mole fraction of each gas.
- A mixture of 5.50 g of He, 15.0 g of Ne, and 35.0 g of Kr exerts a total pressure of 100 kPa. What is the partial pressure, in kPa, of He in the mixture?
- A flask contains a mixture of methane,  $\text{CH}_4$ , and ethane,  $\text{C}_2\text{H}_6$ , at partial pressures of 70.0 and 35.0 kPa, respectively. If the gas temperature is  $27^\circ\text{C}$ , what is the average molar mass and density of the mixture?
- Flasks A and B are connected by a stopcock. Initially, flask A contains 500 mL of  $\text{O}_2$  at 100 kPa pressure, while flask B contains 1500 mL  $\text{N}_2$  at 50 kPa pressure, both at  $25^\circ\text{C}$ . The stopcock is opened and the gases are mixed (but DO NOT react). Determine the partial pressure of each gas after mixing, the total pressure, and the mole fraction of  $\text{O}_2$  in the final mixture.
- A flask contains a mixture of helium, He, and neon, Ne, at  $27^\circ\text{C}$ . The partial pressures are 70.0 and 35.0 kPa, respectively. What is the average molar mass, in  $\text{g mol}^{-1}$ , of the gas mixture?

12. An empty balloon is inflated with a mixture of helium and oxygen at 20 °C. He is first added until the volume has reached 10 L at 101 kPa. O<sub>2</sub> is then added until the total volume reaches 30 L, still at 101 kPa. Find, at the final state, the mass and partial pressure of helium, the partial pressure of oxygen, and the mole fraction of each gas.
13. A gaseous mixture of CO and CO<sub>2</sub> exerts a total pressure of 90.0 kPa at 20.0 °C. If the partial pressure of CO is 35.0 kPa, what is the density, in g L<sup>-1</sup>, of the gas mixture?
14. A 2.00 L bottle initially contains air at 25.0 °C and 110 kPa. “Dry ice” is then placed inside the bottle and the bottle is sealed immediately. If the bottle can withstand a maximum pressure of 500 kPa, what is the minimum amount of dry ice, in grams, required to make the bottle explode at 25.0 °C?
15. A sample of nitrogen gas was collected by water displacement at 27 °C and a pressure of 99.3 kPa. If the volume of nitrogen was 535 mL, what was the mass, in g, of nitrogen gas collected? The vapour pressure of water at 27 °C = 3.6 kPa.
16. If 2.00 L of oxygen gas are collected over water at 50 °C and 94.6 kPa, how many grams of oxygen are obtained? The vapour pressure of water at 50 °C is 12.3 kPa.
17. A chemistry professor’s house is heated by the combustion of methane (CH<sub>4</sub>) in air. In one month, he/she used 55.9 m<sup>3</sup> of gas, measured at 15 °C and 101.33 kPa. What is the maximum mass of CO<sub>2</sub> (in g) that the professor contributed to the atmosphere in that month by heating the house?
18. If Kr, Xe, O<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub> are all at the same temperature, which one has the fastest rms speed? If the rms speed of N<sub>2</sub> is 550 m s<sup>-1</sup>, what is that of H<sub>2</sub>?
19. At the same temperature, what is the value of the ratio:
- [average speed of Ar(g)] : [average speed of CH<sub>4</sub>(g)]
20. A glass bulb with a small opening initially contains the same number of moles of N<sub>2</sub> and Cl<sub>2</sub>. The N<sub>2</sub> is effusing at a rate of  $1.5 \times 10^{-4}$  mol hr<sup>-1</sup>. What is the effusion rate of the Cl<sub>2</sub>?

21. A flask containing a 1:1 mixture (by moles) of O<sub>2</sub> and Cl<sub>2</sub> is connected to a second flask, which is initially empty. There is a very small opening between the two flasks such that, after several hours have elapsed, some of the O<sub>2</sub> and Cl<sub>2</sub> have effused into the second flask. Would the second flask contain more O<sub>2</sub> or more Cl<sub>2</sub>? What is the ratio of O<sub>2</sub> to Cl<sub>2</sub> in the second flask?

22. Pentane, C<sub>5</sub>H<sub>12</sub>, burns in oxygen to form carbon dioxide and water. What volume (in L) of O<sub>2</sub>(g) at 100 kPa and 20 °C is required to react completely with 5.00 g of C<sub>5</sub>H<sub>12</sub>?

23. Consider the following gas phase reaction:



The initial partial pressure of each reactant gas is 60.0 kPa, with the volume and temperature held constant. What is the mole fraction of H<sub>2</sub>O in the mixture after the reaction goes to completion?

24. A gaseous compound containing only C, H, and N is mixed with exactly the volume of oxygen required for combustion to CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. Burning nine volumes of this mixture of compound and oxygen produces a gaseous mixture of four volumes CO<sub>2</sub>(g), six volumes H<sub>2</sub>O(g), and two volumes N<sub>2</sub>(g), all gas volumes being measured under the same conditions of temperature and total pressure. Write an equation for the combustion reaction, and find the number of volumes of oxygen required for the combustion and the molecular formula of the compound.

25. In a rigid pressure vessel, a mixture was prepared with only CH<sub>4</sub>(g) and O<sub>2</sub>(g). The mole fraction of the CH<sub>4</sub>(g) was initially 0.50. A spark then initiated combustion to CO<sub>2</sub>(g) and H<sub>2</sub>O(g). What is the mole fraction of CO<sub>2</sub>(g) in the vessel after combustion? (Assume all the H<sub>2</sub>O remains in the gaseous phase.)

26. A mixture of C<sub>2</sub>H<sub>2</sub>(g) and excess Br<sub>2</sub>(g) is allowed to react completely at constant pressure and temperature:



The total volume of the mixture before reaction is 400 L; the total volume after reaction is 200 L. What was the mole fraction of C<sub>2</sub>H<sub>2</sub> in the original mixture before the reaction?



# Chapter 2

## Thermodynamics and Thermochemistry

Richard Gruttmann/Science Source

Scientific discovery and scientific knowledge have been achieved only by those who have gone in pursuit of it without any practical purpose whatsoever in view.

**Max Planck (1858–1947)**

### 2.1 Heat, Work, and Energy

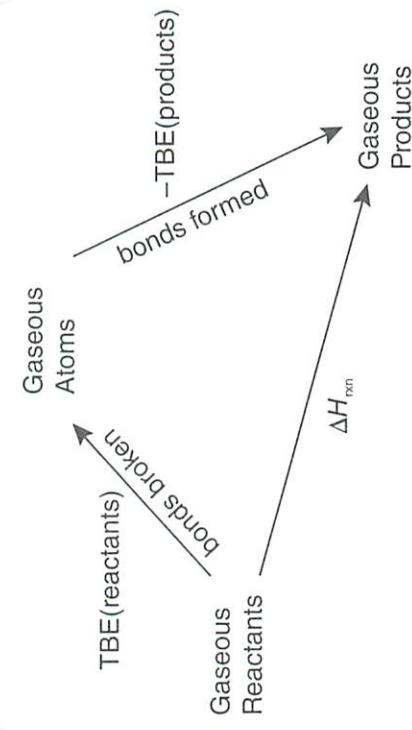
#### OBJECTIVES

After studying this topic, you should be able to:

- Explain, identify, or provide examples of the different types of systems, heat capacity, the meaning of the sign of  $q$ , intrinsic and extrinsic properties, state functions, pressure–volume work, the first law of thermodynamics, and internal energy.
- Determine the temperature change, the energy change, or any other variables for a particular process or reaction, when given the appropriate information.

#### Topics Covered:

- 2.1 Heat, Work, and Energy
- 2.2 Enthalpy
- 2.3 Entropy and Spontaneous Change
- 2.4 Free Energy



#### WHAT IS THERMODYNAMICS?

*Thermodynamics* is the study of the energy changes involved in physical and chemical processes. Physical processes include the heating and cooling of substances, phase changes, and changes in physical parameters such as the volume and pressure of a gas. Chemical processes often involve chemical reactions. *Thermochemistry* is the branch of thermodynamics that investigates the heat flow that occurs during these reactions.

One of the many important applications of thermodynamics is the determination of the energy content of various foods. As you probably know, the nutritional value of a food item is usually stated in terms of energy units called calories. The “food calorie” or “large calorie” (abbreviated Cal), which you typically see on food packages, is actually equal to 1,000 “small calories” (cal) used in thermodynamics. 1 cal = 4.184 J, so 1 Cal is equivalent to 4,184 kJ, which is the amount of energy needed to raise the temperature of 1 kg of water by 1 degree Celsius.

Previously, the energy content of foods was measured directly. A food sample was placed in a calorimeter (see Section 2.2 below) and completely burned. The resulting rise in temperature was recorded and the calorie count of the sample was calculated from it. Nowadays, an indirect method is used, in which one first determines the amounts of three basic nutrient types (proteins, carbohydrates, and fats) present in a food sample and then uses tabulated standard calorie counts per 1 g of each type of nutrient to calculate the total nutritional value of the sample. The standard energy values of proteins, carbohydrates, and fats are still determined by burning. As part of this topic and among many other things, you will learn all the concepts and techniques necessary to perform such calculations and experiments.

### SYSTEMS AND SURROUNDINGS

Many of the energy changes studied in this course take the form of heat flow, which is the transfer of thermal energy in the process being studied. *Heat always flows from the warmer object to the cooler object.*

In any study of heat flow, it is important to distinguish between a system and its surroundings. A system is that part of the universe that one wants to study. For example, when a chemical reaction takes place, chemists consider the reactants and products (or the entire reaction mixture) to be the system. The surroundings are the remaining parts of the universe that can interact (e.g., exchange energy) with a system under study. During a reaction, the surroundings would be the vessel (flask, test tube, etc.) in which the reaction takes place, including the air and any other material making thermal contact with the vessel, such as the solution in which the reaction occurs. The system and its surroundings thus constitute the universe.

#### Types of Systems

Depending on the interactions between a system and its surroundings, there are three common system types defined in chemistry:

1. An **open system**, which can exchange both matter and energy with its surroundings.
2. A **closed system**, which can exchange energy but not matter with its surroundings.
3. An **isolated system**, which exchanges neither matter nor energy with its surroundings.

For example, the unsealed flask in Figure 2.1.1 is partially filled with water and is an open system because gaseous water molecules can escape into the surroundings. The same flask with a stopper is a closed system because the water (matter) cannot escape, although thermal energy can be exchanged between the flask and the surroundings through the glass walls of the flask. If the stoppered flask is placed in an insulated chamber so that there is no heat exchange with the surroundings, it becomes an isolated system.

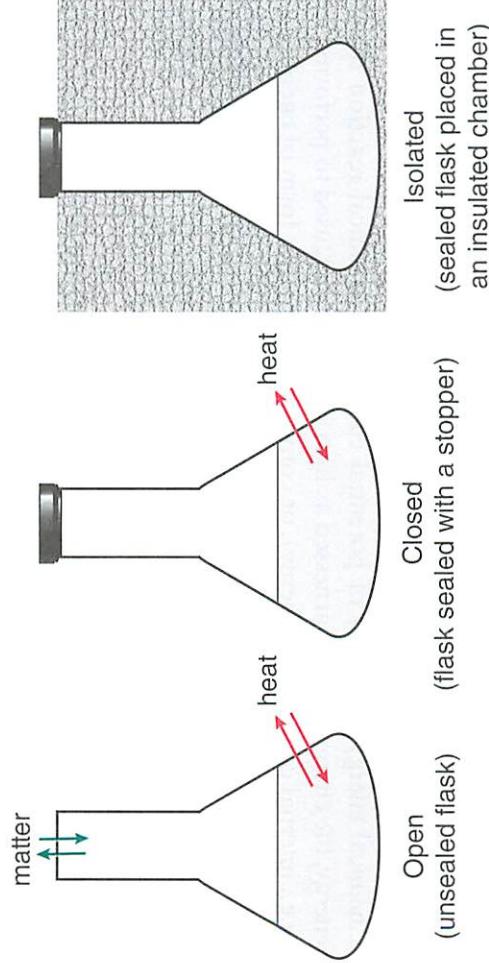


Figure 2.1.1 An open, closed, and isolated system.

### WHAT IS ENERGY?

Energy can take many different forms, and because of this, an all-encompassing definition of energy is not possible. That being said, the most common definition of energy is “the capacity to do work.”

In turn, work,  $w$ , is defined as the product of a force,  $F$ , acting on an object, and the distance,  $d$ , that the object moves in response to the force. That is,  $w = F \times d$ . (The SI units for work are the joule (J) or newton-metre (Nm), where 1 J = 1 Nm.)

Chemists are usually interested in a type of work called *pressure-volume (PV)* work, which is the work involved in the expansion or compression of gases.

Many chemical reactions produce or consume gases, and when gases expand or are compressed, work is involved. Pressure can be measured in kPa, and volume in L, giving rise to the units for  $PV$  work:

$$w = -P \times \Delta V \quad \text{with units of kPa L (where } 1 \text{ kPa L} = 1 \text{ J)}$$

Some types of energy are:

- Heat energy (thermal energy), which is the energy transferred due to a temperature difference between the system and the surroundings.
- Kinetic energy, which is the energy associated with motion.
- Potential energy, which is stored energy or the energy a body possesses due to its position. For instance, a rock on a hill has potential energy and, if it rolls down the hill, the potential energy is converted to kinetic energy.

Chemical energy is a form of potential energy. If a chemical reaction releases energy, the energy can be harnessed as heat (e.g., furnace), used to perform work (e.g., internal combustion energy), or converted to another form of energy.

It is important to realize that while energy cannot be created or destroyed, it can be converted from one form to another.

#### Units of Energy

The joule (J) has already been mentioned as being the SI unit for any form of energy, including heat. What can one do with one joule of energy? Not much at all! In fact, it would take about 4.2 joules of energy to heat up one gram of water by one degree Celsius. A microwave oven must provide about 52,250 J to heat up 250 mL of water from 25 °C to 75 °C. How was this number of joules determined? The heat energy associated with temperature changes can be estimated using a parameter called *heat capacity*, or a related quantity known as *specific heat capacity*.

#### HEAT CAPACITY AND ITS USES

As previously mentioned, heat is the energy transferred between the system and the surroundings, or from one object to another, as a result of a temperature difference. When two objects of different temperature contact each other, heat always flows from the warmer object to the cooler object and stops flowing when

thermal equilibrium is reached (i.e., both objects have the same temperature). The amount of heat transferred,  $q$ , is related to the temperature difference,  $\Delta T$ , and another physical parameter called *heat capacity* or *specific heat capacity*.

Both of these terms are a measure of how many joules are required to change the temperature of a substance or object by one degree ( $^{\circ}\text{C}^{-1}$  or  $\text{K}^{-1}$ ). So why do we need two terms? Heat capacity is usually *used for objects*, like a piece of apparatus used in an experiment. The heat capacity, represented by the symbol  $C$ , is unique to each piece of apparatus and has units of  $\text{J} \cdot ^{\circ}\text{C}^{-1}$ . The relationship between the amount of heat energy ( $q$ ), an object's heat capacity ( $C$ ), and the temperature change ( $\Delta T$ ) is:

$$q = C \times \Delta T$$

Specific heat capacity (lowercase  $c$ ) is similar to heat capacity, but *considers the mass of the substance*. It is the heat needed to warm one *mass unit* (g or kg) of a substance by one degree. The SI units for specific heat capacity are  $\text{J} \cdot \text{kg}^{-1} \cdot ^{\circ}\text{C}^{-1}$ , but the most commonly used are  $\text{J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}$ . It can be used to calculate  $q$ :

$$q = m \times c \times \Delta T$$

An alternative way to express the specific heat capacity is to indicate the energy required to warm 1 mole of substance by one degree. For instance, specific heat capacity expressed in units of  $\text{J} \cdot \text{mol}^{-1} \cdot ^{\circ}\text{C}^{-1}$  describes the heat needed to increase the temperature of one mole of a substance by one degree, and is known as *molar heat capacity*. Another example would be  $\text{J} \cdot \text{cm}^{-3} \cdot ^{\circ}\text{C}^{-1}$ , a quantity known as *volumetric heat capacity*.

Table 2.1.1 lists selected specific and molar heat capacities. Note that  $^{\circ}\text{C}^{-1}$  can be interchanged with  $\text{K}^{-1}$  only because temperature *differences* are used.

TABLE 2.1.1 HEAT CAPACITIES OF SELECTED SUBSTANCES AND MATERIALS

SUBSTANCE	SPECIFIC HEAT CAPACITY $c$ ( $J\text{ g}^{-1}\text{ K}^{-1}$ )	MOLAR HEAT CAPACITY $c$ ( $J\text{ mol}^{-1}\text{ K}^{-1}$ )
Brick	0.840	—
Copper, Cu(s)	0.386	24.47
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}(l)$	2.44	112.0
Graphite, C(s)	0.710	8.53
Oxygen, $\text{O}_2(g)$	0.918	29.38
Glass (Pyrex)	0.753	—
Human tissue	3.5	—
Water, $\text{H}_2\text{O}(s)$ (at -10 °C)	2.114	38.09
$\text{H}_2\text{O}(l)$ (at 25 °C)	4.184	75.40
$\text{H}_2\text{O}(g)$ (at 100 °C)	2.080	37.47
Wood	1.3 to 2.3	—

### Temperature Change

Temperature change ( $\Delta T$ ) is the difference between final and initial temperatures:

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

The value of  $\Delta T$  is the same whether in °C or K. For example, if the initial temperature is 25.0 °C and the final temperature is 14.7 °C, then  $\Delta T$  is -10.3 °C. Using the same example, the initial temperature is 298.2 K, the final temperature is 287.9 K, and  $\Delta T$  is -10.3 K. Make sure that both  $T_{\text{final}}$  and  $T_{\text{initial}}$  are using the same scale before taking the difference. It would be incorrect to determine the difference in Celsius and then add 273.15 to “convert” to Kelvin!

**Example 2.1.1. Energy Required to Warm a Sample of Silver**

Silver has a specific heat capacity of  $0.237 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . How many kJ of energy are needed to warm 100 g of silver from  $25.0 \text{ }^{\circ}\text{C}$  to  $90.0 \text{ }^{\circ}\text{C}$ ?

**Solution:**  $q = m \times c \times \Delta T$

$$\begin{aligned} &= 100 \text{ g} \times 0.237 \text{ J }^{\circ}\text{C}^{-1} \times (90 - 25) \text{ }^{\circ}\text{C} \\ &= 1.54 \text{ kJ} \end{aligned}$$

**Example 2.1.2. Energy Required to Warm Flask and Water (In-Class Exercise)**

An Erlenmeyer flask has a heat capacity of  $175 \text{ J }^{\circ}\text{C}^{-1}$ . 52.0 g of water are added. Assuming there are no heat losses, determine the energy required to raise the temperature of the assembly from  $25.0 \text{ }^{\circ}\text{C}$  to  $40.0 \text{ }^{\circ}\text{C}$ . (Hint: Determine the energy required for the flask and water separately ( $q_{\text{sys}} = q_{\text{flask}} + q_{\text{water}}$ ) and then add the results.)

**Data:**  $c \text{ H}_2\text{O}(l) = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

Now suppose the flask and contents in the above “Flask and Water” In-Class Exercise example are allowed to cool from  $40.0 \text{ }^{\circ}\text{C}$  to  $25.0 \text{ }^{\circ}\text{C}$ . How much heat energy is lost by the flask and the water as they cool down? Logic dictates that it must also be 5.89 kJ. How does one differentiate between energy lost and energy gained? The convention used is that when a system *absorbs* energy from the surroundings, the process is said to be *endothemic* and the change in energy is positive. Conversely, when the system *releases* energy to the surroundings, the process is said to be *exothermic* and the change in energy is negative. In the above “Flask and Water” In-Class Exercise example, the energy change ( $q$ ) for the system (flask plus water), is +5.89 kJ as it heats up, and -5.89 kJ as it cools down.

When a system cools,  $\Delta T$  will be negative. As a result,  $q$  will also be a negative number. Likewise, when a system is warmed,  $\Delta T$  and  $q$  will be positive. In essence, the sign of  $q$  is determined by the sign of  $\Delta T$ .

### Thermal Equilibrium

When heat is transferred between objects, it can be more difficult to distinguish between the system and the surroundings. The warmer object loses heat and cools down, so its  $\Delta T < 0$  and  $q_{\text{lost}}$  are negative. The cooler object gains heat and warms up, so its  $\Delta T > 0$  and  $q_{\text{gained}}$  are positive.

The number of joules lost by the warmer object must equal the number of joules gained by the cooler object. However, this leads to a sign discrepancy between  $q_{\text{lost}}$  and  $q_{\text{gained}}$ . A negative number is obviously not equal to a positive number (e.g.,  $-300 \neq +300$ ). To correct this discrepancy, a negative sign is placed in front of  $q_{\text{lost}}$  in order to make  $-q_{\text{lost}} = q_{\text{gained}}$ .

Once the warmer object has transferred sufficient heat to the cooler object, and both objects reach the same final temperature ( $T_f$ ), the heat flow stops and the objects are said to be in *thermal equilibrium*.

#### Example 2.1.3. Temperature at Thermal Equilibrium (In-Class Exercise)

A piece of aluminum weighing 40.0 g is heated to 80.0 °C and dropped into 100.0 g of water at 25.0 °C. What is the temperature once thermal equilibrium is attained? All of the heat energy lost by the aluminum is gained by the water.

**Data:**  $c_{\text{H}_2\text{O(l)}} = 4.184 \text{ J g}^{-1} \text{ °C}^{-1}$ ;  $c_{\text{Al(s)}} = 0.902 \text{ J g}^{-1} \text{ °C}^{-1}$

### INTENSIVE AND EXTENSIVE PROPERTIES

Suppose you take two samples of the same uniform system, one small and one large, and measure their properties. An *intensive (intrinsic) property* is a property that has the same value regardless of the sample size. Temperature (including melting and boiling points) and density are examples of intensive properties. An *extensive (extrinsic) property* is a physical property whose value increases with the sample size. Mass, volume, energy, enthalpy, and entropy are all examples of extensive properties.

### STATE FUNCTIONS

A *state function* is a property whose value depends only on the current state of the system but not on how that state was reached. Examples of state functions are volume, pressure, and enthalpy. Heat and work are *not* state functions. One can “pump” different amounts of heat into the system, make the system use those different amounts of heat to perform different amounts of work (the more heat, the more work), and still end up in exactly the same final state every time.

To understand this, consider two states of  $n$  moles of an ideal gas: State 1, specified by  $P_1$  and  $V_1$ , and State 2, specified by  $P_2$  and  $V_2$ . There is no need to specify  $T_1$  and  $T_2$  because the temperature of the system is determined by  $P$  and  $V$  through the ideal gas law. Suppose that  $V_2 > V_1$ , that is, that the gas expands.

There are many different ways to change the system from State 1 to State 2. For instance: (a) by letting the gas expand while holding the pressure at  $P_1 = \text{const}$  until the very end and then changing the pressure to  $P_2$ ; (b) by changing the pressure to  $P_2$  right away and holding it constant until the end of expansion (note that the second process would require more heat but would also enable the gas to do more work than in the first process); and (c) by changing the pressure gradually from  $P_1$  to  $P_2$  as the volume increases (see Figure 2.1.2).

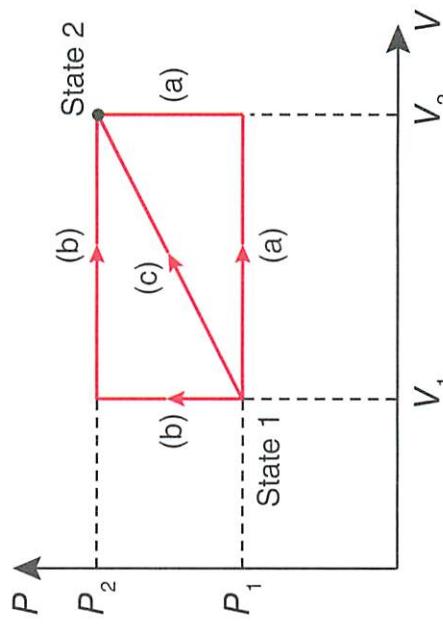


Figure 2.1.2 Different ways of changing the state of an ideal gas. The work done on the system in each case is equal to the area between  $V_1$  and  $V_2$  and under the arrows representing the corresponding path.

Now because it takes different amounts of heat to create different gas pressures for a given  $V$  and because the value of  $P\Delta V$  depends on what  $P = \text{const}$  is, the values of  $q$  and  $w$  will also depend on how the system gets from State 1 to State 2. However, the sum  $\Delta E = q + w$  will be independent of those details. This is the meaning of the statement that  $q$  and  $w$  are not state functions, whereas internal energy is a state function.

The following mechanical analogy may also be useful. Imagine a person flying a small plane from Vancouver to St. John's. The person's initial position in Vancouver is a state function, because how he or she got there is irrelevant. The final position in St. John's is also a state function, because it doesn't matter if the person travelled there via the shortest route or decided to visit northern Canadian cities and towns along the way (Figure 2.1.3). However, the distance traveled from Vancouver and St. John's and the amount of fuel consumed during the trip are not state functions. Heat and work roughly correspond to the amount of fuel consumed and the distance traveled, respectively.

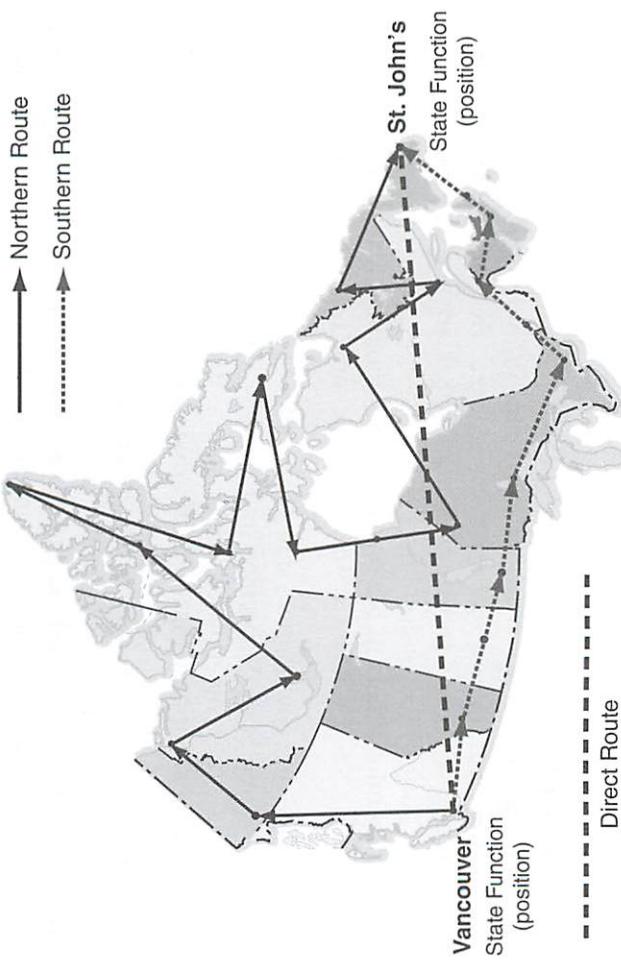


Figure 2.1.3 Position is an example of a state function.

### FIRST LAW OF THERMODYNAMICS

Example 2.1.3 follows the first law of thermodynamics, which states that:

*The total energy of an isolated system is conserved.*

This means that energy can be transferred from one part of the system to another, or converted from one form to another, but it cannot be created or destroyed.

To keep track of the energy of a system, a thermodynamic function called *internal energy*,  $E$ , is used.  $E$  is the sum of all the kinetic and potential energies of all the atoms, ions, and molecules in the system. Internal energy is an extensive property and a state function.

For example, the internal energy of a monoatomic ideal gas is the total kinetic energy of all the atoms. For a gas consisting of molecules,  $E$  would be the total kinetic energy of all the molecules plus their total rotational and vibrational energies. If the gas is not ideal, then the internal energy would also include the potential energy of intermolecular interactions.

We have discussed two methods by which energy may be transferred: heat and work.

Heat is symbolized by  $q$ . If heat is added to a system, the sign of  $q$  is positive, and this signifies an endothermic process. If heat is released by a system, the sign of  $q$  is negative, and this signifies an exothermic process.

Work is symbolized by  $w$ . For a system at constant pressure, work may be calculated using:  $w = -P \times \Delta V$ . The sign of  $w$  tells us whether work is being done on the system, or whether it is the system that does the work. In an expansion, the gas (the system) is said to be doing work on the surroundings, and the value of  $w$  is negative (work energy has been used, so it has been removed from the system). In a compression, the surroundings are said to be doing work on the system, and the value of  $w$  is positive (the system has gained work energy). *However, if a process does not involve a compression or expansion, there is no volume change ( $\Delta V = 0$ ) and the value of w is zero.*

In 1845, English physicist James Joule showed that heat and work are equivalent ways of transferring energy in or out of a system. Joule conducted an experiment in which the same rise in temperature of a sample of water was brought about by transferring a given quantity of energy *either* by electrically heating or by doing mechanical work on the water. His results are consistent with the first law of thermodynamics, which can be expressed mathematically as:

$$\Delta E = q + w$$

If the surroundings do work on, or supply heat to the system, the internal energy of the system increases ( $\Delta E > 0$ ). If the system does work on, or supplies heat to the surroundings, the internal energy of the system decreases ( $\Delta E < 0$ ).

If the system is kept at a constant volume, there is no expansion or compression work performed. That is,  $w = 0$ , assuming there are no other kinds of work done. The relationship then becomes  $\Delta E = q$  and is commonly written as:

$$\Delta E = q_V$$

where the subscript V signifies that the volume of the system remains constant.

*Therefore, the internal energy change of a system is equal to the heat transferred when the volume does not change.*

## Section 2.1 Practice Problems

- The specific heat capacity of Al is  $0.902 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . What is its *molar* heat capacity? Use the molar heat capacity to find the amount of heat needed to warm 3.25 moles of Al from  $24.5 \text{ }^{\circ}\text{C}$  to  $46.5 \text{ }^{\circ}\text{C}$ .
- 250.0 J of heat is supplied to 20.00 g of  $\text{O}_2(\text{g})$ , and the resulting final temperature of the gas is  $36.1 \text{ }^{\circ}\text{C}$ . What was the initial temperature? The specific heat capacity of  $\text{O}_2(\text{g})$  is  $0.918 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ .
- A 355 mL bottle of warm beer at  $25.0 \text{ }^{\circ}\text{C}$  is placed into a fridge. How much energy must the fridge remove from the beer ( $c = 4.06 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ) and the glass bottle ( $c = 250 \text{ J }^{\circ}\text{C}^{-1}$ ) to cool the bottle of beer to a refreshing  $4.0 \text{ }^{\circ}\text{C}$ ?
- An unknown volume of water ( $c = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ) at  $20.0 \text{ }^{\circ}\text{C}$  is added to 50 mL of water at  $40.0 \text{ }^{\circ}\text{C}$ . If the final temperature of the combined volumes is  $24.5 \text{ }^{\circ}\text{C}$ , what was the unknown volume of water at  $20.0 \text{ }^{\circ}\text{C}$ ?
- A 35 g sample of a metal alloy at  $95 \text{ }^{\circ}\text{C}$  is placed in 50 g of water ( $c = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ) at  $20 \text{ }^{\circ}\text{C}$ . At thermal equilibrium, the temperature is  $32 \text{ }^{\circ}\text{C}$ . Find the specific heat capacity of the alloy.
- A piece of copper at  $120 \text{ }^{\circ}\text{C}$  has exactly twice the mass of another piece of copper at  $40 \text{ }^{\circ}\text{C}$ . The two pieces are brought into contact and allowed to reach thermal equilibrium. What is the final temperature?
- A glass with a specific heat capacity of  $0.84 \text{ J g}^{-1} \text{ K}^{-1}$  has a temperature of  $20.0 \text{ }^{\circ}\text{C}$ . It is then filled with 0.300 L of water ( $c = 4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ,  $d = 1.00 \text{ g mL}^{-1}$ ) at  $95.0 \text{ }^{\circ}\text{C}$ . The resulting combined weight of the cup and water is 450 g. What is the temperature of the water at thermal equilibrium?
- When 30.0 g of water at an unknown temperature were mixed with 27.0 g of water at  $15.8 \text{ }^{\circ}\text{C}$ , the final temperature of the mixture was  $29.1 \text{ }^{\circ}\text{C}$ . Heat exchange with the container walls was negligible. What was the initial temperature of the added water ( $^{\circ}\text{C}$ )?
- Explain the difference between intensive and extensive properties. Provide examples of intensive and extensive properties.

10. Are the following quantities state functions? Explain.

- a.  $q$
- b.  $w$
- c.  $\Delta E$
- d. speed

11. When two objects of the same mass reach thermal equilibrium, their final temperatures are the same. However, their  $\Delta T$  values may not be of the same magnitude. Explain. Under what circumstances, if any, would their  $\Delta T$  values be of the same magnitude?

## 2.2 Enthalpy

### OBJECTIVES

After studying this topic, you should be able to:

- Explain the difference between internal energy and enthalpy.
- Describe the possible phase transitions and use latent heats, in various units, to determine the amount of energy required for phase changes.
- Use data from a calorimetry experiment to calibrate a calorimeter, determine the heat of a reaction, or to find other variables.
- Define standard state, identify the standard state of common elements, and write formation reactions.
- Use Hess's law to determine enthalpy change or other variables.
- Write the appropriate reaction to determine the total bond energy (TBE) of a gaseous species, use average bond enthalpies to estimate the enthalpy change of a reaction, and explain why using heats of formation in thermodynamic calculations is more accurate than using average bond enthalpies.

### ENTHALPY

As discussed in the previous topic, the change in internal energy ( $\Delta E$ ) of a system is equal to the heat flow ( $q$ ) if the volume of the system remains constant ( $w = 0$ ). However, many physical processes and chemical reactions of interest often take place at constant (atmospheric) pressure instead of constant volume.

*Enthalpy* ( $H$ ) is a thermodynamic state function defined by

$$H = E + PV$$

where  $E$  is the internal energy,  $P$  is the pressure, and  $V$  is the volume of the system. Like internal energy, the absolute enthalpy of a system cannot be measured, but changes in enthalpy ( $\Delta H$ ) can be. At constant pressure:

$$\Delta H = \Delta E + P\Delta V$$

Recall that  $\Delta E = q + w$  and that  $w = -P\Delta V$ :

$$\Delta H = (q + w) + P\Delta V$$

$$\Delta H = (q - P\Delta V) + P\Delta V$$

$$\Delta H = q_p$$

This shows that, at constant pressure, the  $\Delta H$  of a system is equal to the heat ( $q_p$ ) flowing into or out of a system. Because many processes and reactions take place at constant pressure instead of constant volume, it is much more practical to measure heat flow in terms of  $\Delta H$  instead of  $\Delta E$ . In other words, provided the pressure of the system is kept constant, heat may be treated as if it were a state function, and that state function is known as enthalpy.

### PHYSICAL PROCESSES AND LATENT HEAT

*Latent heat* is the energy change associated with physical processes that involve a change of state (phase). Melting (fusion), boiling (vapourization), and sublimation are endothermic processes (consume energy), while condensation, freezing, and deposition are exothermic (release energy). During any one of these processes, the temperature of the substance remains constant.

For example, when a mole of ice at 0 °C melts into a mole of water at 0 °C, the latent heat of fusion ( $q_{\text{fusion}}$ ) is +6.01 kJ mol<sup>-1</sup>. The positive sign of  $q$  indicates that the process is endothermic. The energy absorbed from the surroundings is used only to change the phase of the substance, not its temperature. Note that chemists often omit the adjective “latent” from the “latent heat of” expression, but it is understood to be there during state changes.

## CHAPTER 2 THERMODYNAMICS AND THERMOCHEMISTRY

2-17

TABLE 2.2.1 MOLAR LATENT HEATS FOR  $\text{H}_2\text{O}$  STATE CHANGES

PROCESS	TERM	VALUE OF $q$
$\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$	melting (fusion)	+6.01 kJ mol <sup>-1</sup> at 0 °C
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$	freezing	-6.01 kJ mol <sup>-1</sup> at 0 °C
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$	boiling (vapourization)	+40.66 kJ mol <sup>-1</sup> at 100 °C
$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	condensation	-40.66 kJ mol <sup>-1</sup> at 100 °C
$\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{g})$	sublimation	+51.06 kJ mol <sup>-1</sup> at 0 °C
$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{s})$	deposition	-51.06 kJ mol <sup>-1</sup> at 0 °C

If the phase changes are carried out at constant pressure, the latent heat values are also  $\Delta H$  values. For example, at constant pressure, the  $\Delta H$  of fusion ( $\Delta H_{\text{fus}}$ ) of ice is +6.01 kJ mol<sup>-1</sup>. This is the difference in enthalpy between the product (liquid water) and the reactant (ice).

Observe that the values listed in Table 2.2.1 are not for standard conditions. If the processes are occurring under standard conditions, the corresponding latent heats (enthalpy changes) would be different. For example, the  $\Delta H_{\text{vap}}$  of water would be +44 kJ mol<sup>-1</sup>.

It is also important to note that the forward and reverse processes have  $q$  values of the same magnitude but of opposite sign. At 0 °C, 6.01 kJ mol<sup>-1</sup> of energy must be added to melt ice, but 6.01 kJ mol<sup>-1</sup> must be removed to freeze water.

### Example 2.2.1. Energy Needed for Phase Change (In-Class Exercise)

How much energy is required to convert 22.0 g of ice at -15.0 °C to water vapour at 120.0 °C? Use the data provided below.

**Data:**  $c(\text{H}_2\text{O}(\text{s})) = 2.06 \text{ J g}^{-1} \text{ K}^{-1}$ ;  $c(\text{H}_2\text{O}(\text{l})) = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$ ;

$$c(\text{H}_2\text{O}(\text{g})) = 1.87 \text{ J g}^{-1} \text{ K}^{-1}; \Delta H_{\text{fus}}(\text{H}_2\text{O} \text{ at } 0^\circ\text{C}) = 6.01 \text{ kJ mol}^{-1};$$

$$\Delta H_{\text{vap}}(\text{H}_2\text{O} \text{ at } 100^\circ\text{C}) = 40.66 \text{ kJ mol}^{-1}$$

### Enthalpy Change Under Standard Conditions ( $\Delta H^\circ$ )

Changes in enthalpy ( $\Delta H$ ) can be measured or determined, but the value of  $\Delta H$  for a given process varies with temperature and pressure. It is therefore important to define a set of *standard conditions*. In the study of thermodynamics, the standard conditions used are 1 atm (101.33 kPa) and 25 °C (298.15 K), unless otherwise stated. Enthalpy changes under standard conditions are reported as  $\Delta H^\circ$ , where the superscript “o” denotes *under standard conditions*.

### $\Delta H$ FOR CHEMICAL REACTIONS

For any reaction occurring under standard conditions, the enthalpy change for that reaction,  $\Delta H_{\text{rxn}}$ , is the difference between the sum of the absolute molar enthalpies of the products and those of the reactants:

$$\Delta H_{\text{rxn}} = \sum H(\text{products}) - \sum H(\text{reactants}) \quad (2.2.1)$$

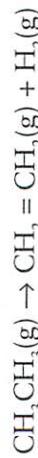
If a reaction releases heat into the surroundings, it is exothermic. That is, the system has lost energy, and the enthalpy has decreased ( $\Delta H < 0$ ).

For example, if one mole of ethylene,  $\text{CH}_2 = \text{CH}_2(\text{g})$ , reacts with  $\text{H}_2(\text{g})$  under standard conditions to form ethane,  $\text{CH}_3\text{CH}_3(\text{g})$ , the system releases 137 kJ mol<sup>-1</sup> of heat to the surroundings. The reaction is exothermic and the  $\Delta H^\circ$  is negative:



Conversely, if a reaction absorbs heat from the surroundings, it is endothermic. In endothermic reactions, the enthalpy of the system increases and the enthalpy change has a positive value ( $\Delta H > 0$ ).

If the reaction above was reversed to give:



the process would be endothermic. The absolute value of  $\Delta H$  is the same for both reactions but the sign is different.

$\Delta H$  for a reaction may be found experimentally by measuring the heat lost or gained when a process is carried out at constant pressure.

$$\Delta H_{\text{rxn}}^\circ = -137 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{rxn}}^\circ = +137 \text{ kJ mol}^{-1}$$

### UNITS OF REACTION ENTHALPIES

From now on we will use the following two ways of reporting enthalpy changes for chemical reactions.

When  $\Delta H^\circ_{\text{rxn}}$  is shown in units of kJ (not  $\text{kJ mol}^{-1}$ ) next to a reaction, it means the enthalpy change for the reaction involving the numbers of moles equal to the stoichiometric coefficients of the balanced equation *as written*. A kJ value of  $\Delta H^\circ_{\text{rxn}}$  is therefore proportional to the stoichiometric coefficients. For instance,



The first of these equations says that, when 1 mol of  $\text{H}_2(\text{g})$  is reacted with 0.5 mol of  $\text{O}_2(\text{g})$ , 242 kJ of heat is produced. The second equation says that, when 2 mol of  $\text{H}_2(\text{g})$  is reacted with 1 mol of  $\text{O}_2(\text{g})$ , 484 kJ of heat is produced.

When  $\Delta H^\circ_{\text{rxn}}$  is shown in  $\text{kJ mol}^{-1}$ , it means the enthalpy change for the reaction per 1 mole of a particular substance that is either stated or implied by the context.  $\Delta H^\circ_{\text{rxn}}$  values expressed in  $\text{kJ mol}^{-1}$  in reference to a particular substance do not change when stoichiometric coefficients are scaled. To avoid confusion with units of  $\text{kJ mol}^{-1}$ , we will always write the reaction in such a way that the substance in question has a stoichiometric coefficient of 1. For instance, if we write



it would mean that the enthalpy change is -242 kJ per 1 mole of  $\text{H}_2\text{O}$  (and, incidentally, of  $\text{H}_2$ ). Note that the enthalpy change for this reaction per 1 mole of  $\text{O}_2$  would be -484  $\text{kJ mol}^{-1}$ .

The above two ways of reporting  $\Delta H^\circ_{\text{rxn}}$  values are equivalent and may be used interchangeably.

### MEASUREMENT OF $\Delta H$

An experimental technique called *calorimetry* is used to study the heat flow of physical and chemical processes. In this technique, the processes are allowed to occur in a piece of apparatus known as a *calorimeter*.

#### Simple Calorimeter

A simple, low-tech calorimeter can be constructed using a low-cost insulated vessel (such as two styrofoam cups, one inside the other, with a lid), thermometer, and stirrer (magnetic stir bar or stirring rod), as shown in Figure 2.2.1. Such calorimeters can be used to study both exothermic and endothermic reactions in solution.

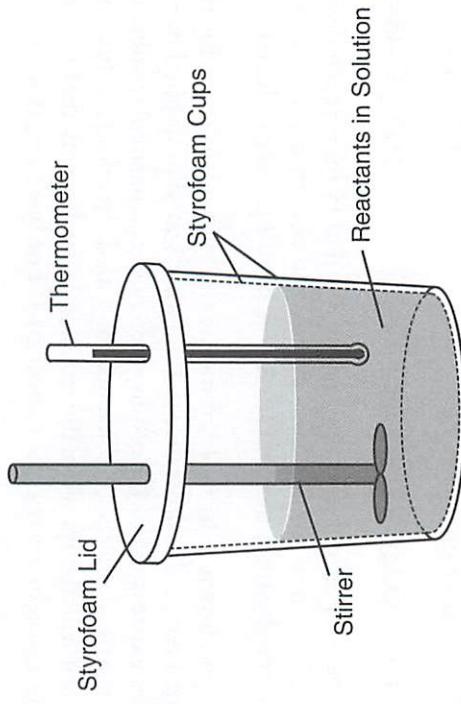


Figure 2.2.1 A simple calorimeter.

In the context of calorimetry, we will define the “system” as the calorimeter assembly (the styrofoam cups, the lid, the stirrer, and the thermometer) and all of its contents. The “surroundings” are the rest of the universe. The styrofoam cups of the simple calorimeter prevent the exchange of heat between the system and the surroundings, so the system can be treated as isolated. The thermometer is used to measure the temperature change of the system that is caused by the chemical reaction (or some other process).

For example, if HCl(aq) and NaOH(aq) are reacted in a calorimeter to produce NaCl(aq), the temperature of the system increases. Knowing the heat capacity of the solution and the heat capacity of the calorimeter assembly, one can use the observed temperature change to calculate the amount of heat produced by the reaction.

The “system” as defined on the previous page consists of three parts: the chemical reactants (the “reaction”), the solvent, and the dry calorimeter assembly. Within the system, heat flows from the reactants to the solvent and to the calorimeter (or in the opposite direction). We will denote the amounts of heat *gained* by these three parts as  $q_{\text{rxn}}$ ,  $q_{\text{sol}}$ , and  $q_{\text{cal}}$ , respectively.

For an isolated system, there is no heat exchange between the system and the surroundings, so we can write

$$q_{\text{surr}} = -q_{\text{sys}} = -(q_{\text{rxn}} + q_{\text{sol}} + q_{\text{cal}}) = 0$$

Therefore,

$$q_{\text{rxn}} = -(q_{\text{sol}} + q_{\text{cal}})$$

If we also assume that the calorimeter assembly has a zero heat capacity, then  $q_{\text{cal}} = 0$  and the above equation reduces to

$$q_{\text{rxn}} = -q_{\text{sol}}$$

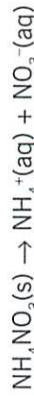
The heat absorbed or released by the solvent can be related to its heat capacity:

$$q_{\text{sol}} = m_{\text{sol}} C_{\text{sol}} \Delta T_{\text{sol}}$$

If the calorimetry experiment is performed at constant pressure, the value of  $q_{\text{rxn}}$  is also the  $\Delta H$  for the reaction being studied. Furthermore, if the experiment is performed under standard conditions (1 atm and 298.15 K), the value of  $q_{\text{rxn}}$  is the standard enthalpy change ( $\Delta H^\circ$ ) for the associated reaction.

**Example 2.2.2.  $\Delta H$  of Reaction from a Simple Calorimeter (In-Class Exercise)**

Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is the compound present in many “instant” cold packs found in first aid kits. The process of dissolving  $\text{NH}_4\text{NO}_3(\text{s})$  in water is endothermic, which causes the cold pack to become cold. The  $\Delta H$  associated with the dissolution of a substance in water is called the *enthalpy of (dissolution)*.



When 1.00 g of  $\text{NH}_4\text{NO}_3$  is dissolved in 50.00 g water in a simple calorimeter, the water cools from 25.00 to 23.32 °C. Assuming that the heat capacity of the solvent is 4.184 J g<sup>-1</sup> °C<sup>-1</sup>, and that the heat released by the calorimeter assembly is negligible, find the enthalpy change for this process.

**Molar Enthalpy of Reaction**

It is often useful to express  $\Delta H$  as an amount of energy per 1 mole of a particular reactant or product. The resultant value for  $\Delta H$  is termed the molar enthalpy of dissolution. Note that this value always refers to a specific species participating in that reaction.

**Example 2.2.3. Molar Enthalpy of Dissolution (In-Class Exercise)**

Using the  $\Delta H$  determined in Example 2.2.2, find the molar enthalpy of dissolution of ammonium nitrate, in units of kJ mol<sup>-1</sup>.

**Calorimeter Calibration**

So far, we have assumed that the calorimeter assembly itself does not absorb or release heat. To obtain more accurate experimental data, the heat absorbed or released by the calorimeter ( $q_{\text{cal}}$ ) needs to be taken into account. Therefore:

$$q_{\text{rxn}} = -q_{\text{sol}} \text{ becomes } q_{\text{rxn}} = -(q_{\text{cal}} + q_{\text{sol}})$$

The  $q_{\text{cal}}$  term can be calculated from  $q_{\text{cal}} = C_{\text{cal}} \times \Delta T$ , but we first require the heat capacity of the calorimeter,  $C_{\text{cal}}$ . The process of determining  $C_{\text{cal}}$  (also called the *calorimeter constant*) is called *calorimeter calibration*.

Two common methods used for calorimeter calibration are:

1. Adding a known amount of hot water, with a known initial temperature, to the calorimeter and then measuring the temperature when the water and calorimeter are at thermal equilibrium. The heat lost by the water is absorbed by the calorimeter. There is no chemical reaction taking place. The calorimeter constant can be found from:

$$q_{\text{water}} = -q_{\text{cal}}$$

$$m_{\text{water}} \times c_{\text{water}} \times \Delta T_{\text{water}} = -(C_{\text{cal}} \times \Delta T_{\text{cal}})$$

$$C_{\text{cal}} = -\frac{m_{\text{water}} c_{\text{water}} \Delta T_{\text{water}}}{\Delta T_{\text{cal}}}$$

2. Carrying out a chemical reaction, with a known heat of reaction, inside the calorimeter. The heat released by the reaction is absorbed by the calorimeter. If there is no solution or water in the calorimeter, the calorimeter constant can be determined from:

$$q_{\text{cal}} = C_{\text{cal}} \Delta T_{\text{cal}} = -q_{\text{rxn}}$$

$$C_{\text{cal}} = -\frac{q_{\text{rxn}}}{\Delta T_{\text{cal}}}$$

**Example 2.2.4.  $\Delta H$  of Reaction from a Calibrated Calorimeter (In-Class Exercise)**

*Calibration (Method 1).* A calorimeter consists of a glass beaker surrounded by a styrofoam insulating jacket. When 25.0 mL of hot water is added to the calorimeter, the temperature of the hot water decreases by 4.5 °C and that of the calorimeter increases by 10.0 °C.

*Actual experiment.* 15.0 mL of 3.00 M HCl and 15.0 mL of 3.00 M NaOH, both initially at 22.6 °C, are mixed inside the calorimeter. After the reaction, the temperature of the solution is 38.2 °C. The mass of the final solution is 31.5 g, and it has a specific heat capacity of 3.79 J g<sup>-1</sup> K<sup>-1</sup>.

Determine the  $\Delta H$  of neutralization per mole of HCl reacted.

**Bomb Calorimeter**

While simple calorimeters are suitable for reactions occurring in liquids, they are not very useful for reactions involving gases or combustion. A *bomb calorimeter* (Figure 2.2.2) is typically used to measure the heat liberated from gaseous or combustion reactions. The reaction takes place in a heavy-duty vessel (the “bomb”) that is immersed in water. The entire bomb calorimeter assembly is therefore comprised of the vessel, the water surrounding it, and any other accessories (stirrer, thermometer, sample tray, etc.).

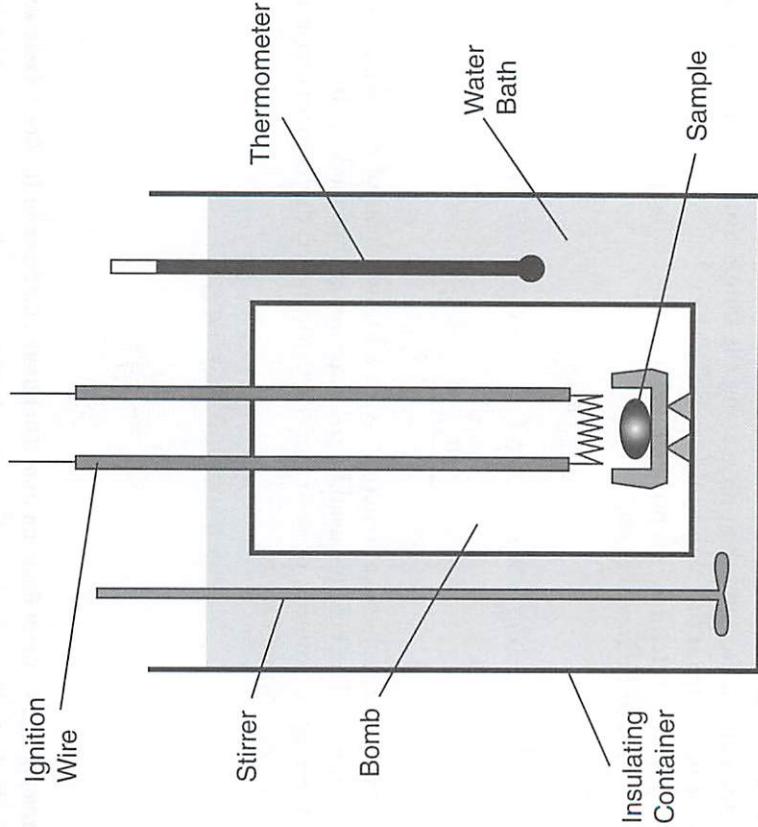


Figure 2.2.2 Bomb calorimeter.

Because of the complexity of the bomb calorimeter, it is necessary to calibrate the bomb calorimeter (determine its  $C_{\text{cal}}$ ) prior to use. Note, however, that the value of  $C_{\text{cal}}$  typically does not include the water around the vessel.

In contrast to the simple calorimeter in the previous section, reactions in a bomb calorimeter take place under constant volume, and thus the measured heat transfer corresponds to  $\Delta E$ . In practice, a bomb calorimeter is filled with a large excess of oxygen, so that the total pressure change due to the combustion is negligible. Since the pressure remains approximately constant, the heat transfer recorded is equal to  $\Delta H$ .

The amount of heat produced by the chemical reaction in a bomb calorimeter can be calculated as follows

$$q_{\text{rxn}} = -(q_{\text{cal}} + q_{\text{water}}) = -(C_{\text{cal}} + c_{\text{water}} m_{\text{water}}) \Delta T$$

where  $\Delta T$  is the change in the temperature of the calorimeter and the water bath.

**Example 2.2.5. Determination of the Calorimeter Constant (In-Class Exercise)**

1.22 grams of benzoic acid ( $C_6H_5COOH$ , 122 g mol<sup>-1</sup>) are placed in a bomb calorimeter along with excess oxygen and burned completely. The heat of combustion of benzoic acid is known to be -3230 kJ mol<sup>-1</sup>. The initial temperature of the water (1500 g) and the bomb calorimeter is 25.0 °C. After combustion, the temperature of the water bath and the bomb calorimeter is 28.2 °C. What is the calorimeter constant,  $C_{\text{cal}}$ ?

**Example 2.2.6. Calorimeter Temperature Change after Reaction (In-Class Exercise)**

Ethanol,  $CH_3CH_2OH$ , is a renewable biofuel and a component of certain beverages. 11.5 g of ethanol are placed into a bomb calorimeter with a heat capacity of 650 J K<sup>-1</sup> and surrounded by 10.0 kg of water. By how many degrees does the water temperature rise when the ethanol is completely burned to produce  $CO_2(g)$  and  $H_2O(l)$ ? The heat of combustion of ethanol is -1366.7 kJ mol<sup>-1</sup>.

### STANDARD ENTHALPY OF FORMATION

*Standard enthalpy of formation*,  $\Delta H_f^\circ$ , also known as the *standard heat of formation*, is the enthalpy change for the reaction in which 1 mole of a substance under standard conditions (1 atm and 298.15 K) is formed from the constituent elements in their reference states under standard conditions. This reaction is called a *formation reaction*:

elements (reference state, standard conditions)  $\rightarrow$  1 mole of a substance (standard conditions)

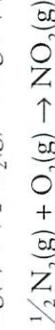
The state of a substance under standard conditions is often called a *standard state*. The *reference state* of an element is that form of the element which is the most stable under standard conditions. The reference states of selected elements are given in Table 2.2.2. Realize that the elemental form need not be an atom; elements can also be molecules.

TABLE 2.2.2 REFERENCE STATES OF SELECTED ELEMENTS

ELEMENT	REFERENCE STATE	ELEMENT	REFERENCE STATE
Hydrogen	H <sub>2</sub> (g)	Sulfur	S(rhombic, s)
Carbon	C(graphite, s)	Bromine	Br <sub>2</sub> (l)
Nitrogen	N <sub>2</sub> (g)	Iodine	I <sub>2</sub> (s)
Oxygen	O <sub>2</sub> (g)	Mercury	Hg(l)

Some chemical elements can exist in two or more different forms called *allotropes*. For instance, the allotropes of carbon include graphite, graphene, diamond, and fullerene (buckyball). Graphite is the most stable allotrope and so it is chosen as the reference state of carbon.

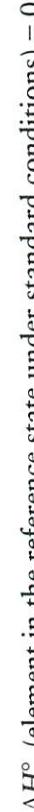
Examples of formation reactions include:



**Example 2.2.7. Writing  $\Delta H_f^\circ$  for Reactions (In-Class Exercise)**

Write formation reactions for  $\text{C}_2\text{H}_5\text{OH}(\text{l})$ ,  $\text{Mg}(\text{NO}_3)_2(\text{s})$ , and  $\text{NH}_4\text{Br}(\text{s})$ .

The standard enthalpy of formation of an element in its reference state under standard conditions is arbitrarily defined as zero, i.e.,



This sets a “reference point” of enthalpies for each chemical element. Note that the standard enthalpy of formation of an element under standard conditions is *not* zero if the element is not in its reference state. For example,



Standard enthalpies of formation of substances that are not in their reference states have to be determined empirically. The experimental values of  $\Delta H_f^\circ$  for common substances are listed in Table 2.2.3.

TABLE 2.2.3 STANDARD ENTHALPIES OF FORMATION (kJ mol<sup>-1</sup>)

AgBr(s)	-100.4	CdCl <sub>2</sub> (s)	-391.5	MgO(s)	-601.7
AgCl(s)	-127.1	CdO(s)	-258.2	Mg(OH) <sub>2</sub> (s)	-924.5
AgI(s)	-61.8	Cr <sub>2</sub> O <sub>3</sub> (s)	-1139.7	MgSO <sub>4</sub> (s)	-1284.9
AgNO <sub>3</sub> (s)	-124.4	CuO(s)	-157.3	MnO(s)	-385.2
Ag <sub>2</sub> O(s)	-31.0	CuS(s)	-53.1	MnO <sub>2</sub> (s)	-520.0
Al <sub>2</sub> O <sub>3</sub> (s)	-1675.7	Cu <sub>2</sub> S(s)	-79.5	N(atomic, g)	+470.5
B(g)	+590	CuSO <sub>4</sub> (s)	-771.4	NH <sub>3</sub> (g)	-46.1
B <sub>2</sub> Cl <sub>4</sub> (g)	-490	F(atomic, g)	+76.5	N <sub>2</sub> H <sub>4</sub> (l)	+50.6
BaCl <sub>2</sub> (s)	-858.6	Fe(OH) <sub>3</sub> (s)	-823.0	NH <sub>4</sub> C(l)s	-314.4
BaCO <sub>3</sub> (s)	-1216.3	Fe <sub>2</sub> O <sub>3</sub> (s)	-824.2	NH <sub>4</sub> NO <sub>3</sub> (s)	-365.6
BaO(s)	-553.5	Fe <sub>3</sub> O <sub>4</sub> (s)	-1118.4	NO(g)	+90.2
BaSO <sub>4</sub> (s)	-1473.2	H(atomic, g)	+218.0	NO <sub>2</sub> (g)	+33.2
Br(atomic, g)	+111.9	HBr(g)	-36.4	N <sub>2</sub> O <sub>4</sub> (g)	+9.2
Br <sub>2</sub> (g)	+30.9	HCl(g)	-92.3	NaCl(s)	-411.2
C(atomic, g)	+715.0	HF(g)	-271.1	NaF(s)	-573.6
CCl <sub>4</sub> (l)	-135.4	H(l)g	+26.5	NaOH(s)	-425.6
CHCl <sub>3</sub> (l)	-134.5	HNO <sub>3</sub> (l)	-174.1	O(atomic, g)	+249.0
CH <sub>4</sub> (g)	-74.8	H <sub>2</sub> O(g)	-241.8	PbBr <sub>2</sub> (s)	-278.7
CHCH(g)	+226.7	H <sub>2</sub> O(l)	-285.8	PbCl <sub>2</sub> (s)	-359.4
CH <sub>2</sub> CH <sub>2</sub> (g)	+52.3	H <sub>2</sub> O <sub>2</sub> (l)	-187.8	PbO(s)	-219.0
CH <sub>3</sub> CH <sub>3</sub> (g)	-84.7	H <sub>2</sub> S(g)	-20.6	PbO <sub>2</sub> (s)	-277.4
C <sub>3</sub> H <sub>8</sub> (g)	-103.8	H <sub>2</sub> SO <sub>4</sub> (l)	-814.0	PCl <sub>3</sub> (g)	-287.0
CH <sub>3</sub> OH(l)	-238.7	HgO(s)	-90.8	PCl <sub>5</sub> (g)	-347.9
C <sub>2</sub> H <sub>5</sub> OH(l)	-277.7	I <sub>2</sub> (g)	+62.4	SiCl <sub>4</sub> (l)	-687.0
Cl(atomic, g)	+122.0	KBr(s)	-393.8	SiO <sub>2</sub> (s)	-910.9
CO <sub>2</sub> (g)	-393.5	KCl(s)	-436.7	SnO <sub>2</sub> (s)	-580.7
CaCl <sub>2</sub> (s)	-798.5	KClO <sub>3</sub> (s)	-397.7	SO <sub>2</sub> (g)	-296.8
CaCO <sub>3</sub> (s)	-1206.9	KClO <sub>4</sub> (s)	-432.8	SO <sub>3</sub> (g)	-395.7
CaO(s)	-635.1	KNO <sub>3</sub> (s)	-494.6	ZnI <sub>2</sub> (s)	-208.0
Ca(OH) <sub>2</sub> (s)	-986.1	MgCl <sub>2</sub> (s)	-641.3	ZnO(s)	-348.3
CaSO <sub>4</sub> (s)	-1434.1	MgCO <sub>3</sub> (s)	-1095.8	ZnS(s)	-206.0

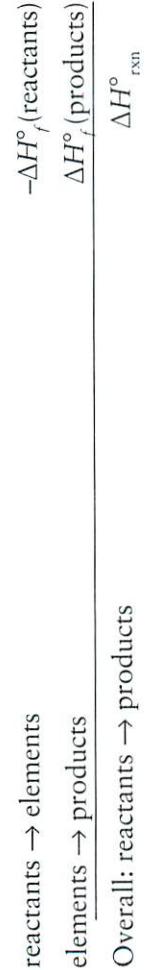
**HESS'S LAW OF THERMOCHEMISTRY**

Standard enthalpies of formation  $\Delta H_f^\circ$  (or any other  $\Delta H^\circ$ , for that matter) may be used to predict the  $\Delta H^\circ$  of a reaction, using Hess's law, which states:

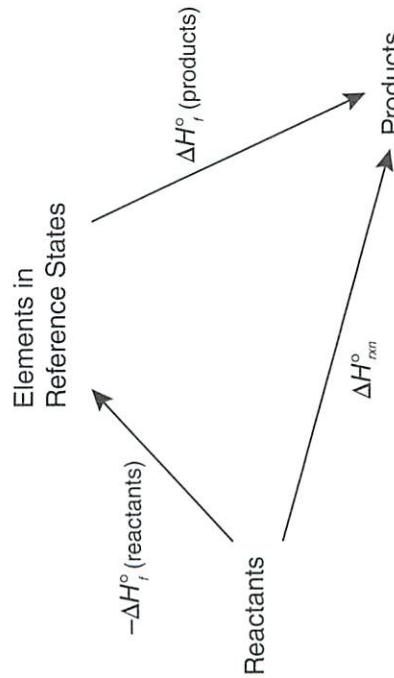
*The enthalpy change for a reaction is the sum of the enthalpy changes for the individual steps of the reaction.*

Consequently, an unknown  $\Delta H^\circ$  can be found for any reaction that is a combination of other reactions for which  $\Delta H^\circ$  is known. For example, if the reaction enthalpies for two reactions are known, the reaction enthalpy for a third related reaction can be derived. This is possible because enthalpy is a state function.

In general, standard enthalpies of formation ( $\Delta H_f^\circ$ ) can be used as shown on the next page to predict the enthalpy change for a reaction. The reactants are hypothetically “unformed” in a reaction that is the reverse of formation, after which the resulting elements combine to form the products.



$$\text{Therefore: } \Delta H^\circ_{\text{rxn}} = \Delta H_f^\circ \text{ (products)} - \Delta H_f^\circ \text{ (reactants)}$$



If there is more than one product or reactant, the enthalpy change for a reaction must be summed over all the products and reactants:

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants})$$

For a generic reaction:  $aA + bB \rightarrow cC + dD$

$$\Delta H_{\text{rxn}}^{\circ} = [c\Delta H_f^{\circ}(C) + d\Delta H_f^{\circ}(D)] - [a\Delta H_f^{\circ}(A) + b\Delta H_f^{\circ}(B)]$$

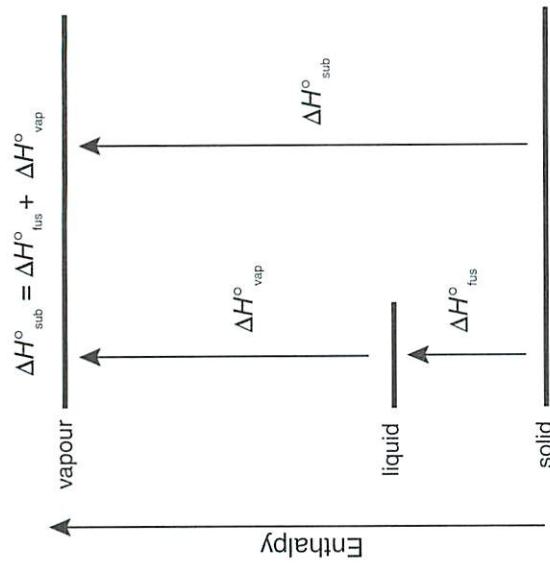
Note that the stoichiometric coefficients are essential in this equation because  $\Delta H$  is an extensive property. Also, remember that elements in their standard state have an enthalpy of formation of zero.

#### **Example 2.2.8. Calculation of $\Delta H_{\text{rxn}}^{\circ}$ from $\Delta H_f^{\circ}$ Values (In-Class Exercise)**

Use the standard enthalpy of formation data from Table 2.2.3 to determine  $\Delta H_{\text{rxn}}^{\circ}$  for the following reaction:



Hess's law is versatile in that it can be used to combine any set of  $\Delta H_f^{\circ}$  values, not just  $\Delta H_f^{\circ}$  values, to determine the  $\Delta H_f^{\circ}$  of another reaction or process. For instance, it can be used to predict enthalpy of sublimation, which is often difficult to measure. Again, the combination of  $\Delta H_f^{\circ}$  values is possible because enthalpy is a state function. The same change in enthalpy must be obtained both in the direct conversion of solid to vapour, and in the indirect conversion of solid to liquid and then to vapour (see the following diagram).

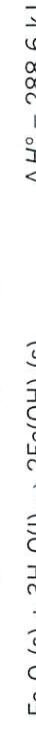
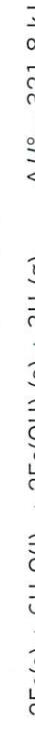


**Example 2.2.9. Calculation of  $\Delta H^\circ_f$  from  $\Delta H^\circ$  Values for Other Reactions (In-Class Exercise)**

The oxidation (rusting) of iron occurs according to the reaction:



Given the following data, what is the heat of reaction for this process? Also note that the  $\Delta H^\circ$  for this process is the  $\Delta H^\circ_f$  of  $\text{Fe}_2\text{O}_3$ .



### Combustion

Hess's law can be used to predict the  $\Delta H^\circ$  of combustion, a very important class of reactions in everyday life. The  $\Delta H^\circ$  for a given combustion reaction is termed the *standard enthalpy of combustion* or more commonly the *heat of combustion*, and it is a useful measure of the energy available from a particular fuel.

The heat of combustion is the energy released when one mole of a fuel in its standard state undergoes *complete combustion* with oxygen to form products in their standard state. Typically, the products formed from the complete combustion of an organic fuel are  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ ; incomplete combustion results in undesirable compounds such as carbon monoxide,  $\text{CO}(\text{g})$ .

Heats of combustion can be expressed as heat per mole of fuel (e.g.,  $\text{kJ mol}^{-1}$ ). For example, the heat of combustion for methane,  $\text{CH}_4$ , is  $890 \text{ kJ mol}^{-1}$ .



Note that the product side of the reaction includes *liquid* water. Although the water will initially be in the vapour form after the reaction, the measurements are taken after the products have cooled to  $25^\circ\text{C}$ .

Table 2.2.4 lists the standard enthalpies of combustion for some compounds.

TABLE 2.2.4 STANDARD ENTHALPIES OF COMBUSTION ( $\text{kJ mol}^{-1}$ )

Benzene, $\text{C}_6\text{H}_6(\text{l})$	-3268	Hydrogen, $\text{H}_2(\text{g})$	-286
Carbon, C(graphite, s)	-394	Methane, $\text{CH}_4(\text{g})$	-890
Carbon monoxide, $\text{CO}(\text{g})$	-283	Ethane, $\text{CH}_3\text{CH}_3(\text{g})$	-1560
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$	-1368	Ethyne, $\text{HCCH}(\text{g})$	-1300
Glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-2808*	Butane, $\text{CH}_3(\text{CH}_2)_2\text{CH}_3(\text{g})$	-2874

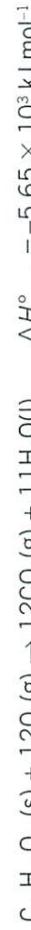
\*When the human body metabolizes glucose, the same amount of energy is released!

**Example 2.2.10. Calculation of  $\Delta H^\circ_{\text{combustion}}$  from  $\Delta H^\circ_f$  Values (In-Class Exercise)**

Propane,  $\text{CH}_3\text{CH}_2\text{CH}_3$ , is the fuel used in most home barbecues. Use the standard enthalpy of formation data from Table 2.2.3 to determine the  $\Delta H^\circ$  for the combustion of propane.

**Example 2.2.11. Calculation of  $\Delta H^\circ_f$  from  $\Delta H^\circ_{\text{combustion}}$  (In-Class Exercise)**

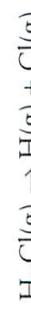
The heat of combustion of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ , is given by:



Determine the standard enthalpy of formation,  $\Delta H^\circ_f$ , for sucrose.

**Bond Enthalpy**

*Bond enthalpy* (BE) is the energy required to break one mole of a specific type of bond (single, double, or triple) between two atoms, provided the reactants and products are both gases. When bonds are formed between atoms in the gas phase, energy is always released (exothermic). Breaking bonds to form atoms, therefore, requires an input of energy (endothermic), so bond enthalpies are always positive: for example, 431 kJ is required to break one mole of the single bond in  $\text{HCl}(\text{g})$ .

**Total Bond Enthalpy**

*Total bond enthalpy* (TBE), also known as the *enthalpy of atomization*, is the energy required to break all of the bonds in one mole of a gaseous compound:

one mole of gaseous compound  $\rightarrow$  gaseous atoms

There are no bonds between any of the gaseous atoms on the product side. For example, the TBE required to break up methane ( $\text{CH}_4$ ) is:



### Average Bond Enthalpy

The average bond enthalpy can be determined by dividing the TBE of a molecule which contains only one type of bonds by the total number of those bonds. For example, given that the TBE of  $\text{CH}_4(\text{g})$  is  $1661.8 \text{ kJ mol}^{-1}$ , the average bond enthalpy of the C–H bond is  $(1661.8 \text{ kJ mol}^{-1})/4 = 415.5 \text{ kJ mol}^{-1}$ .

The following example illustrates how structural differences affect the numerical value for the enthalpy of a particular type of bond:



Both of these reactions involve breaking one mole of O–H bond, but the bond enthalpies, measured experimentally, are obviously different. Therefore, an average bond enthalpy of  $464 \text{ kJ mol}^{-1}$  is listed in Table 2.2.5 for the O–H bond.

TABLE 2.2.5 SELECTED AVERAGE BOND ENTHALPIES ( $\text{kJ mol}^{-1}$ )

	SINGLE BONDS						
	H	C	N	O	S	F	Cl
H	436	414	389	464	339	565	431
C	347	293	351	259	485	331	288
N		159	222		272	201	216
O			138			205	
S				226	285	255	
F					153	255	
Cl						244	
Br							193
I							151

### MULTIPLE BONDS

C≡C	820	S=O	498	N=N	418	C=N	615
C=C	612	O=N	890	N=O	604	O=O	498
C=S	477	C=O	799	N=N	941		

Bond strength increases with bond order. For example, the CC triple bond ( $820 \text{ kJ mol}^{-1}$ ) is stronger than the CC double bond ( $612 \text{ kJ mol}^{-1}$ ), which is stronger than the CC single bond ( $347 \text{ kJ mol}^{-1}$ ). Note the double- and triple-bond values are not double or triple that of a single bond, respectively.

**Example 2.2.12. Writing Total Bond Enthalpy Reactions (In-Class Exercise)**

For each of the following compounds, write the reaction whose  $\Delta H^\circ$  is equal to the TBE:  $\text{NH}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_2\text{CH}_2$ .

**Determination of Total Bond Enthalpies**

There are two methods that can be used to determine the total bond enthalpy of a molecule, and both are shown below for methane.

**Method 1:** The TBE reaction can be treated like any reaction. Determine the  $\Delta H^\circ$  using the standard enthalpy of formation ( $\Delta H_f^\circ$ ) data from Table 2.2.3:

$$\begin{aligned}\text{TBE}_{\text{CH}_4} &= \Delta H_{rxn}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ \text{TBE}_{\text{CH}_4} &= [(1 \times 715.0 \text{ kJ mol}^{-1}) + (4 \times 218.0 \text{ kJ mol}^{-1}) \\ &\quad - (1 \times -74.8 \text{ kJ mol}^{-1})] \\ &= 1661.8 \text{ kJ mol}^{-1}\end{aligned}$$

**Method 2:** Determine the TBE by summing up the enthalpies of all the bonds in the molecule, using the *average bond enthalpies* from Table 2.2.5:

$$\begin{aligned}\text{TBE}_{\text{CH}_4} &= 4 \times \text{BE}(\text{C}-\text{H}) \\ &= 4 \times 414 \text{ kJ mol}^{-1} \\ &= 1656 \text{ kJ mol}^{-1}\end{aligned}$$

Obviously, the first method can only be used if the  $\Delta H_f^\circ$  values for all of the species in the reaction are known. A similar condition applies to the second method, which is suitable only if the average bond enthalpies, as well as the number and types of bonds in the molecule, are known.

Note that the two methods gave slightly different values for the TBE of  $\text{CH}_4$ . This is because molecular structure has an impact on bond enthalpy; that is, the enthalpy of the C–H bond in  $\text{CH}_4$  is expected to be slightly different than the one in, for instance, ethane,  $\text{CH}_3\text{CH}_3$ . The bond enthalpies listed in Table 2.2.5 are *average values* only. Therefore, it is normally more accurate to determine TBE using  $\Delta H_f^\circ$ .

Yet, the differences in TBE obtained using the two methods are usually small enough to allow the following approximation to be made:

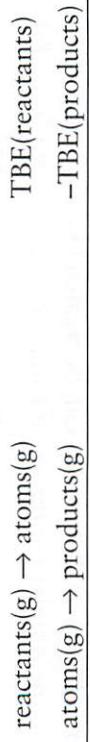
$$\text{TBE} \text{ (using } \Delta H_f^\circ \text{)} \approx \text{TBE} \text{ (using bond enthalpies)}$$

### $\Delta H$ of Gas-Phase Reactions

As previously discussed, the  $\Delta H^\circ$  of reactions can be determined using standard enthalpies of formation ( $\Delta H_f^\circ$ ):

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ \text{ (products)} - \sum \Delta H_f^\circ \text{ (reactants)}$$

If a reaction is one where all of the reactants and products are in the gas phase, it is possible to estimate the enthalpy change of the gas-phase reaction using average bond enthalpies. The gaseous reactants are hypothetically broken up into gaseous atoms, after which the gaseous atoms combine to form new bonds in different arrangements, resulting in products in the gas phase.

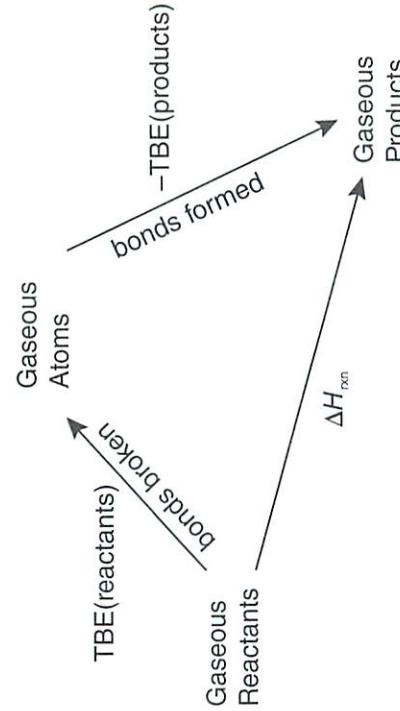


Overall: reactants(g)  $\rightarrow$  products(g)  $\Delta H_{\text{rxn}}$

Therefore:  $\Delta H_{\text{rxn}}^\circ = \text{TBE}_{\text{reactants}} - \text{TBE}_{\text{products}}$

The equation above can be rewritten as:

$$\Delta H_{rxn} = \sum \text{enthalpies of bonds broken} - \sum \text{enthalpies of bonds formed}$$



Remember, this equation works only if all of the reactants and products are in the gas phase!

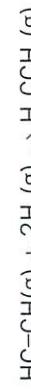
#### Example 2.2.13. Calculation $\Delta H^\circ_{rxn}$ from Average Bond Enthalpies

Using the average bond enthalpies provided in Table 2.2.5, find  $\Delta H^\circ$  for the reaction below.



#### Example 2.2.14. Calculation of Bond Enthalpy from $\Delta H^\circ_{rxn}$ and Other Bond Enthalpies

The hydrogenation reaction of acetylene,  $\text{C}_2\text{H}_2$ , has  $\Delta H^\circ = -311 \text{ kJ mol}^{-1}$ . Use this value and the H–H, C–C, and C–H bond enthalpies from Table 2.2.5 to find the average bond enthalpy of the C≡C bond. Compare it to the value given in Table 2.2.5.



**Using Gas-Phase Reactions**

As seen previously, both enthalpies of formation and bond enthalpies can be used to determine  $\Delta H$  for gaseous reactions. As the  $\Delta H$  values obtained using these two methods are usually very similar, the  $\Delta H$  value may be used interchangeably in the two relationships.

We can make use of this concept to determine enthalpies of formation or bond enthalpies of participant species in gaseous reactions.

**Example 2.2.15. Calculation of  $\Delta H_f^\circ$  from Average Bond Enthalpies and Other  $\Delta H_f^\circ$  Values  
(In-Class Exercise)**

Determine the enthalpy of formation of gaseous methylamine,  $\text{CH}_3\text{NH}_2$ , which has the structure:



Use Enthalpy of Formation values found on Table 2.2.3 and Bond Enthalpies found in Table 2.2.5.

**Example 2.2.16. Calculation of  $\Delta H_f^\circ$  from a Combination of Thermochemical Data (In-Class Exercise)**

Using only the data below, determine the  $\Delta H_f^\circ$  of  $\text{CF}_2\text{Cl}_2$  using the reaction:



**Data:**  $\Delta H_f^\circ$  (kJ mol<sup>-1</sup>):  $\text{CCl}_4(\text{g}) = -96$ ; F(atomic, g) = 76.5

Avg. bond enthalpies (kJ mol<sup>-1</sup>): (C–Cl) = 331; (C–F) = 485; (Cl–Cl) = 244

## Section 2.2 Practice Problems

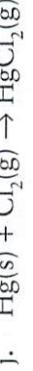
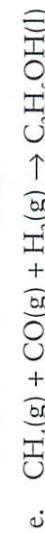
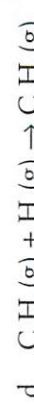
1. A student writes in an essay, “During melting of a pure substance, no heat is absorbed because the temperature does not change.” Is this true? Explain.
2. How many kJ of energy are required to convert 1.00 mol of Hg(l) at 20 °C to Hg(g) at its boiling point of 357 °C? Applicable data are 0.138 J g<sup>-1</sup> K<sup>-1</sup> and 59,400 J mol<sup>-1</sup>. Again, examine the units to determine the relevance of the data.
3. Hg, the only metal that is a liquid under standard conditions, freezes at -39 °C. What is the  $\Delta H^\circ$  when 1.00 mL of Hg at 23 °C is cooled to -39 °C and frozen? Applicable data are 13.6 g mL<sup>-1</sup>, 0.138 J g<sup>-1</sup> K<sup>-1</sup>, and 11 J g<sup>-1</sup>. Hint: Examine the units to determine what the data are.
4. What is the maximum mass of ice at -15.0 °C that can be converted to water vapour at 100.0 °C using  $8.00 \times 10^3$  kJ of energy? Use other necessary data.
5. 505 mg of naphthalene ( $C_{10}H_8$ ) reacts with excess oxygen in a bomb calorimeter. The heat released causes temperature to increase from 25.62 °C to 29.06 °C. The calorimeter constant, which includes the water bath, has been determined to be 5.90 kJ K<sup>-1</sup>. Find the total heat released from the combustion and the molar heat of combustion of naphthalene.



Did you know that naphthalene was once used as an ingredient in mothballs?

6. When 1.00 g of sucrose ( $C_{12}H_{22}O_{11}$ ) was combusted in a calorimeter to give  $CO_2(g)$  and  $H_2O(l)$ , the temperature rose from 25.00 to 27.32 °C. The calorimeter itself had a heat capacity of 837 J °C<sup>-1</sup> and was submersed in 1500.0 g of water. Find the heat of combustion for sucrose.
7. A sample of sulfur, mass 2.56 g, is burned in excess oxygen inside a calorimeter of heat capacity 923 J K<sup>-1</sup> and insulated by 815 g of water. If the sole product of combustion is  $SO_2(g)$ , what is the expected increase in temperature?

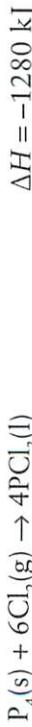
8. Which of these reactions, when performed under standard conditions with the number moles as written, has a  $\Delta H$  of reaction equal to the  $\Delta H_f^\circ$  of the product? Hint: Before punching numbers into the calculator, think about what the question is asking.



9. Use the data below to find the standard heat of formation for  $B_2H_6(g)$ .



10. What is the  $\Delta H$  when  $PCl_3(l)$  reacts with  $Cl_2(g)$  to give  $PCl_5(s)$ ? Use data below.



11. The thermite reaction is highly exothermic and is used to weld large pieces of metal, such as railroad rails, together:



Given the following data, how many kJ of heat are released when 5.00 g  $\text{Fe}_2\text{O}_3(\text{s})$  reacts with excess  $\text{Al}(\text{s})$ ?



12. The enthalpies of the following two processes are known:



Find the following:

- a. The heat is released when 100 g  $\text{H}_2\text{O}_2(\text{l})$  reacts via the first reaction.



13. Consider the reaction below. What is the  $\Delta H_f^\circ$  of  $\text{Cu}_2\text{O}(\text{s})$ , in kJ  $\text{mol}^{-1}$ ?



14. How much heat energy is involved when 5.58 g of Fe metal reacts with excess oxygen to produce  $\text{Fe}_2\text{O}_3$ ? Use the  $\Delta H_f^\circ$  of  $\text{Fe}_2\text{O}_3$ .

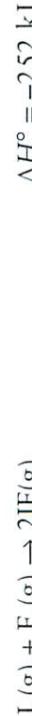
15. Consider the following reaction of hydrazine, a rocket fuel:



Determine how much heat will be released if 32 kg hydrazine is used under standard conditions. Use the necessary  $\Delta H_f^\circ$  values from Table 2.2.3.

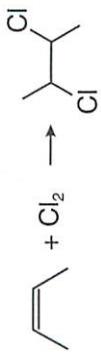
16. The standard heat of combustion for gaseous cyclopropane ( $C_3H_6$ ) is  $-2091 \text{ kJ mol}^{-1}$ . What is its standard enthalpy of formation? Use data from Table 2.2.3 and Table 2.2.4.
17. The standard heat of combustion of gaseous ethylene oxide ( $C_2H_4O$ ) is  $-1264 \text{ kJ mol}^{-1}$ . What is the  $\Delta H_f^\circ$  of gaseous ethylene oxide? Use data from Table 2.2.3 and Table 2.2.4.
18. The complete combustion of a certain quantity of acetylene ( $C_2H_2$ ) at  $25^\circ\text{C}$  releases  $650 \text{ kJ}$  of energy. What was the quantity (in g) of acetylene combusted? Use data from Table 2.2.3.
19. A fuel mixture contains 90.0% octane,  $C_8H_{18}(l)$ , and 10.0% ethanol,  $CH_3CH_2OH(l)$ , by weight. How many kJ of energy are produced when 100.0 g of this mixture burns completely to  $CO_2(g)$  and  $H_2O(l)$ ? The  $\Delta H_f^\circ$  of octane is  $-250 \text{ kJ mol}^{-1}$ . Use other necessary  $\Delta H_f^\circ$  values from Table 2.2.3.
20. The TBE of benzene ( $C_6H_6$ ) is equal to the  $\Delta H$  of which reaction?
- $C_6H_6(l) \rightarrow 6C(s, \text{graphite}) + 3H_2(g)$
  - $C_6H_6(l) \rightarrow 6C(g) + 6H(g)$
  - $C_6H_6(g) \rightarrow 6C(s, \text{diamond}) + 3H_2(g)$
  - $C_6H_6(g) \rightarrow 6C(s, \text{graphite}) + 3H_2(g)$
  - $C_6H_6(g) \rightarrow 6C(g) + 6H(g)$
21. Consider the statement, “The  $\Delta H_f^\circ$  of atomic oxygen,  $O(g)$  is exactly twice the bond energy of  $O_2(g)$ .” Explain whether the statement is true or false.
22. Bond enthalpies reported in the literature are *average* values. Why *average*?
23. If the  $\Delta H_f^\circ$  for ethene gas ( $C_2H_4$ ) is  $+52 \text{ kJ mol}^{-1}$ , what is the TBE (in  $\text{kJ mol}^{-1}$ ) of ethene? Use data from Tables 2.2.3 and 2.2.5.
24. Using the  $\Delta H_f^\circ$  for atomic oxygen,  $O(g)$ , find the bond enthalpy of the oxygen–oxygen bond in  $O_2(g)$ .

25. Ozone gas ( $O_3$ ) has a bent structure with two oxygen–oxygen linkages. If ozone has a  $\Delta H_f^\circ$  of +143 kJ mol<sup>-1</sup>, what is the average oxygen–oxygen bond enthalpy in  $O_3$ ? Does this suggest a reason why ozone is much more reactive than molecular oxygen,  $O_2$ ? Use other necessary data.
26. Consider the reaction below. If the I–I bond enthalpy is 152 kJ mol<sup>-1</sup>, find the I–F bond enthalpy.



27. The  $\Delta H_f^\circ$  values in kJ mol<sup>-1</sup> for the carbon tetrahalides are respectively:  $CF_4(g)$ , −933;  $CCl_4(g)$ , −96;  $CBr_4(g)$ , +79. Use this and data on Table 2.2.3 to find the C–F, C–Cl, and C–Br bond enthalpies.
28. Hexafluoroethane,  $F_3C-CF_3(g)$ , has  $\Delta H_f^\circ = -1343 \text{ kJ mol}^{-1}$ . Find the TBE of this compound and use this in conjunction with the C–F bond energy from the previous problem, plus data on Table 2.2.3, to find the energy of the C–C bond in hexafluoroethane.
29. Given the structure shown below, what is the average bond enthalpy (kJ mol<sup>-1</sup>) of a boron–chlorine bond in  $B_2Cl_4$ ? (Data: Bond enthalpy of  $B-B = 309 \text{ kJ mol}^{-1}$ )
- 
30. Estimate the standard enthalpy of formation ( $\Delta H_f^\circ$ ) of acetaldehyde(g) from the structure and data below.
- 
- Bond energies (kJ mol<sup>-1</sup>): C–H 414; C–C 347; C=O 715  
 $\Delta H_f^\circ$  (kJ mol<sup>-1</sup>): C(g,at) 715; H(g,at) 218; O(g,at) 249

31. The  $\Delta H$  for the reaction below, where all molecules are gases, is  $-152 \text{ kJ mol}^{-1}$ . Using bond energies, calculate the average bond energy for the C-Cl bond.



Bond energies (kJ mol<sup>-1</sup>): C-H 414; C-C 347; C=C 612

$\Delta H_f^\circ$  (kJ mol<sup>-1</sup>): Cl(g,at) 122

## 2.3 Entropy and Spontaneous Change

### OBJECTIVES

After studying this topic, you should be able to:

- Determine the standard molar entropy change of chemical reactions given tabulated values of standard molar entropies for elements and compounds.
- Predict the sign (+ or –) of an entropy change for phase transitions.
- Predict the sign (+ or –) of an entropy change based on the change in the total number of molecules during a chemical reaction.
- Explain and apply the first and second laws of thermodynamics.

### SPONTANEITY

In addition to the determination of enthalpy changes in chemical reactions, thermodynamics allows us to determine whether a process will proceed spontaneously. In the case of a process at equilibrium (rate forward = rate reverse), we can determine whether the equilibrium will favour the reactants or the products.

### SPONTANEOUS PROCESSES

A spontaneous process is one that occurs in the absence of any ongoing outside intervention. The transfer of heat from a hot object to a cold object is spontaneous. Sugar will spontaneously dissolve in hot coffee. Wet laundry will spontaneously dry and a piece of iron will spontaneously rust. The combustion of propane, once ignited, is spontaneous.

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction. A car that is rolling backward does not spontaneously produce gasoline from  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

How can we determine if a process will occur spontaneously? Enthalpy, which is related to internal energy and the first law of thermodynamics, is not sufficient on its own for predicting spontaneity. Rather, we must examine *free energy*, a thermodynamic quantity that encompasses both enthalpy and *entropy*.

### WHY IS THE FIRST LAW OF THERMODYNAMICS INSUFFICIENT?

For a process where no work has been done ( $w = 0$ ),  $\Delta E = \Delta H$ . In our study of thermodynamics, we saw that if  $\Delta E_{\text{sys}}$  or  $\Delta H_{\text{sys}}$  were negative quantities, then energy was released into the surroundings, and the products were at a lower energy than the reactants.

While one might think that a negative  $\Delta E_{\text{sys}}$  or  $\Delta H_{\text{sys}}$  is the only criterion needed for a reaction to occur spontaneously, it is not necessarily so. Sometimes, an exothermic reaction will not occur spontaneously, and sometimes, an endothermic reaction will occur spontaneously.

Clearly, the first law of thermodynamics alone is not enough to predict whether a process will occur spontaneously or not. This is illustrated by the two processes shown in Figure 2.3.1.

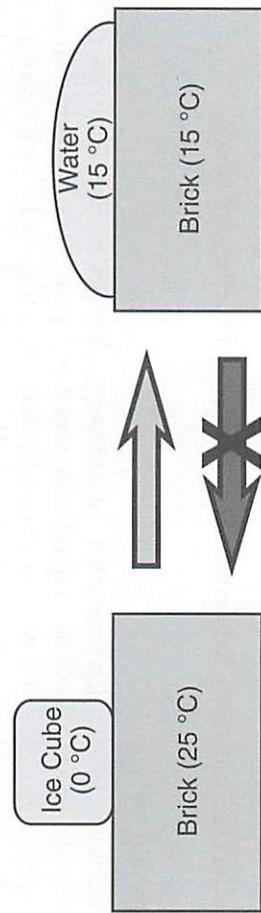


Figure 2.3.1 The melting of ice is a spontaneous process.

1. The forward process. An ice cube (system) placed on a warm brick will melt. The thermal energy provided by the brick disrupts the intermolecular forces that hold the H<sub>2</sub>O molecules in the ice together, thereby turning the solid into a liquid. This lowers the temperature of the brick (say, from 25 °C to 15 °C) such that the overall energy of the two bodies is conserved. The process does not violate the first law, and one knows from experience that it will occur spontaneously.
2. The reverse process. A sample of liquid water is placed on the same brick. Both the water and brick are at an initial temperature of 15 °C. Is it possible for the brick to absorb heat from the water, thereby cooling the water so it turns to ice? This process would not violate the first law, but it will not happen spontaneously.

The previous examples demonstrate that energetic considerations alone are insufficient for predicting the direction of spontaneous change. In order to determine whether a process will occur spontaneously, it is necessary to consider another quantity known as *entropy*.

### ENTROPY

A simple definition of entropy is that it is a measure of the randomness, or the disorder, of a system. The higher the number of possible arrangements of a system, the greater the entropy. For example, Figure 2.3.2 shows a container divided into two equal volumes. The left half of the container is filled with 1 mole of nitrogen, while the right half is filled with 1 mole of oxygen. The gases are at the same temperature and the two halves are initially separated by a barrier. Once the barrier is removed, mixing takes place. After some time, both sides of the container will be filled with a random mixture of the two gases. The final (mixed) state is more disordered than the initial state. Mixing is a spontaneous process because it increases the entropy of the system. The opposite process, namely spontaneous de-mixing, will not occur.

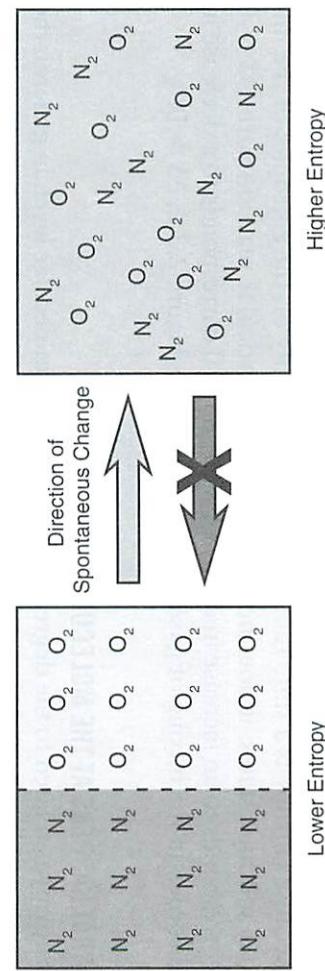


Figure 2.3.2 Mixing of gases is driven by entropy.

Note that processes that occur spontaneously are not necessarily fast. In fact, spontaneity and reaction rate are unrelated. For example, the detonation of an explosive and the corrosion of a piece of metal are both spontaneous processes, but they occur at vastly different rates.

Entropy,  $S$ , is a state function.  $\Delta S$  is the entropy change for a given process:

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

For a chemical reaction,  $S_{\text{final}}$  and  $S_{\text{initial}}$  are the entropies of all products and reactants, respectively.

Because entropy is a state function,  $\Delta S$  depends only on the entropies of the initial and final states; it does not depend on the particular reaction path.  $\Delta S > 0$  corresponds to an increase in disorder, while  $\Delta S < 0$  corresponds to a decrease in disorder. In the mixing of gases example shown in Figure 2.3.2,  $\Delta S > 0$ .

### WHAT HAPPENS AT THE MOLECULAR LEVEL?

Entropy is related to the degree of disorder at the molecular level. In general, the more random the distribution of molecules, the greater the entropy. States that are highly disordered are generally more probable in nature.

Figure 2.3.3 shows four noninteracting gas molecules (A, B, C, D) randomly moving about in a container. Below the figure is a chart showing the possible arrangements that result in 0, 1, 2, 3, or 4 molecules in the left half of the container. For example, there are four possible arrangements in which three molecules are located in the left half and one molecule in the right half. The situation in which there are two molecules in the left half of the container has the highest number of possible arrangements, six. The system with the largest number of possible arrangements is the most probable state of the system. The greater the number of possible arrangements, the greater the entropy.

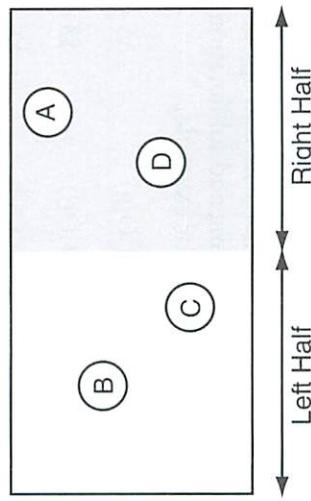


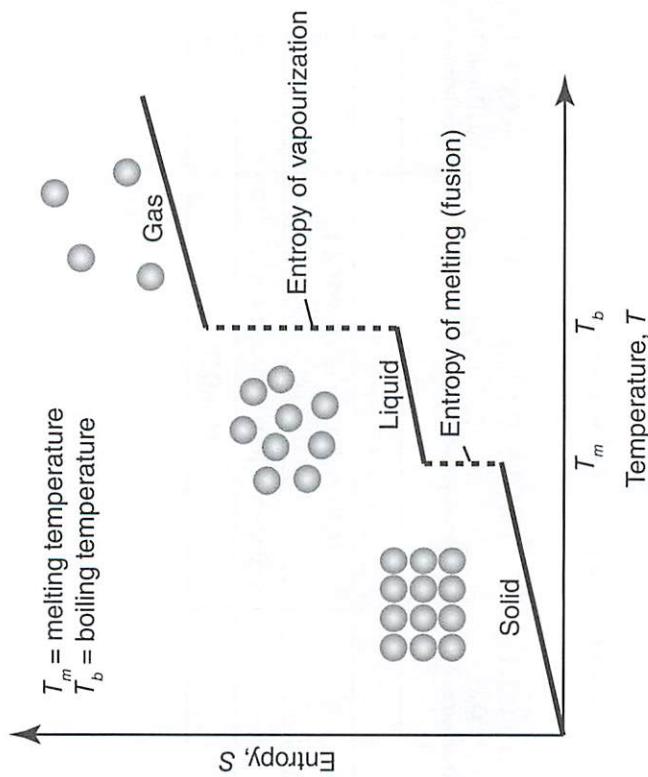
Figure 2.3.3 Random arrangement of four molecules.

# OF MOLECULES IN LEFT HALF	POSSIBLE MOLECULES IN LEFT HALF	# OF POSSIBLE ARRANGEMENTS
0	-	1
1	A or B or C or D	4
2	(A,B) or (A,C) or (A,D) or (B,C) or (B,D) or (C,D)	6
3	(A,B,C) or (A,B,D) or (A,C,D) or (B,C,D)	4
4	(A,B,C,D)	1

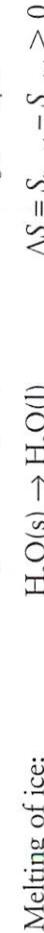
### EFFECT OF HEAT AND CHEMICAL REACTIONS ON ENTROPY

#### Heat

The addition of heat, particularly when associated with a phase change, greatly affects entropy, as shown in the following diagram.



The vapourization of a liquid into a gas increases entropy because the gas is more disordered than the liquid. Similarly, melting and sublimation increase the entropy. For any substance,  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$ . For example:



Note that the change in entropy from a liquid to a gas is much larger than the change in entropy from a solid to a liquid.

Entropy increases with temperature, which is a measure of the kinetic energy of molecular motion in the system. This includes translational, vibrational, and rotational motions. Atoms and molecules can move in straight lines, and they can also vibrate and rotate. While increasing the temperature of a solid does not increase translational motion (the atoms are fixed in a lattice arrangement), there will be an increase in vibrational motion, hence an increase in entropy.

At a temperature of absolute zero, a substance has no translational or rotational motion, but the atoms are still vibrating due to a quantum effect known as *zero-point vibrational energy*. As it is warmed, the molecules in the solid begin to vibrate more. This vibrational motion results in a larger distribution of atomic or molecular positions, hence an increase in entropy.

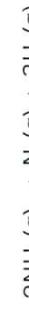
### Chemical Reactions

Chemical reactions can greatly affect entropy if they involve one or more reactants or products in the gas phase. Increasing the number of molecules in the gas phase also increases the entropy because two moles of gas particles have more freedom of motion, and therefore more possible arrangements, than one mole of gas particles. For example, in the decomposition of  $\text{N}_2\text{O}_4$ :



#### Example 2.3.1. Predicting the Sign of $\Delta S$ (In-Class Exercise)

Without any additional data, predict the sign of  $\Delta S^\circ$  for the following reactions:



## THE SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics states that:

*Every spontaneous process increases the entropy of the universe.*

$$\Delta S_{\text{univ}} > 0$$

Because  $\Delta S_{\text{univ}}$  has contributions from both the system and the surroundings, it can also be stated that for any spontaneous process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

To determine if a process occurs spontaneously, one has to determine whether the process is associated with an overall increase of entropy to the universe.

It is possible for a spontaneous process to have  $\Delta S_{\text{sys}} < 0$ , provided that  $\Delta S_{\text{surr}} > 0$  is so large that  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ .

For example, spontaneous condensation of water vapour reduces the entropy of the system but the heat released in this process increases the entropy of the surroundings by a larger amount. The overall entropy of the universe increases as a result.

### Nature and the Second Law of Thermodynamics

The second law dictates an overall trend in nature towards high entropy, which is equivalent to molecular disorder and chaos. Yet, the world is full of highly ordered structures, such as buildings, streets, cars, plants, animals, people, etc. One might get the impression that the very existence of life contradicts the second law.

A simple explanation is that nature tolerates the creation of order in one part of the universe, as long as this is compensated by the formation of chaos somewhere else. Thus, the presence of highly ordered systems in our environment does not violate the second law. The human body can grow because it consumes enormous amounts of relatively ordered substances (sugars, proteins, fats) and turns them into heat,  $\text{CO}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{g})$ . The release of these gases leads to a tremendous increase in the entropy of the surroundings.

### STANDARD MOLAR ENTROPIES

Earlier in this chapter, we mentioned that only the internal energy changes ( $\Delta E$ ) of a system could be determined, nor the absolute internal energy. Likewise, with enthalpy, only the enthalpy changes ( $\Delta H$ ) are measurable, not the absolute enthalpy.

With respect to the entropy of solids, the third law of thermodynamics states:

*The entropy of a perfectly ordered crystalline solid is defined to be zero at a temperature of absolute zero (0 K).*

In the same way that sea level provides a means of determining absolute altitude, this definition of zero entropy allows absolute entropies to be determined.

Using the third law, one can assign a standard molar entropy ( $S^\circ$ ) to all elements and compounds. The  $S^\circ$  values are typically reported in  $J\ mol^{-1}\ K^{-1}$  (not  $\text{kJ}\ mol^{-1}$ ) and refer to standard states, where all gases have partial pressures of 1 atm and all species in solution have a concentration of 1 M. Usually, the listed values are for a temperature of 298.15 K. Note that the  $S^\circ$  values of all elements and compounds are always greater than zero because entropy increases as temperature increases, and  $S^\circ = 0$  at 0 K. In contrast,  $\Delta H_f^\circ$  is zero for elements in their standard states. Standard entropies for selected compounds are shown in Table 2.3.1.

TABLE 2.3.1 STANDARD MOLAR ENTROPIES FOR SELECTED COMPOUNDS

COMPOUND	$S^\circ\ (\text{J}\ \text{mol}^{-1}\ \text{K}^{-1})$	COMPOUND	$S^\circ\ (\text{J}\ \text{mol}^{-1}\ \text{K}^{-1})$
$\text{CO(g)}$	197.7	$\text{CH}_3\text{CH}_2\text{OH(l)}$	160.7
$\text{CO}_2\text{(g)}$	213.7	$\text{H}_2\text{(g)}$	130.6
$\text{CH}_4\text{(g)}$	186.2	$\text{H}_2\text{O(l)}$	69.9
$\text{C}_2\text{H}_4\text{(g)}$	200.8	$\text{H}_2\text{O(g)}$	188.7
$\text{C}_2\text{H}_6\text{(g)}$	219.5	$\text{N}_2\text{(g)}$	191.6
$\text{C}_3\text{H}_8\text{(g)}$	269.6	$\text{NH}_3\text{(g)}$	111.3
$\text{CH}_3\text{OH(l)}$	126.8	$\text{O}_2\text{(g)}$	205.1

Based on tabulated  $S^\circ$  values, the standard entropy change,  $\Delta S^\circ$ , can be determined for any reaction according to:

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

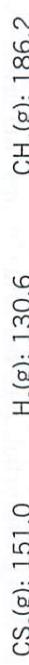
The equation above is analogous to Hess's law, which was used to find  $\Delta H^\circ$  from the tabulated  $\Delta H_f^\circ$  values earlier in the chapter.

### Example 2.3.2. Determination of Standard Entropy Change

Determine the standard entropy change for the following reaction:



based on the following  $S^\circ$  values in  $\text{J mol}^{-1} \text{K}^{-1}$ :



**Solution:** As entropy is an extensive property, it is important that the equation is balanced. Once the equation is correct, then use the standard entropy change equation:

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(1 \text{ mol} \times 186.2 \text{ J mol}^{-1} \text{ K}^{-1}) + (2 \text{ mol} \times 205.6 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$- [(1 \text{ mol} \times 151.0 \text{ J mol}^{-1} \text{ K}^{-1}) + (4 \text{ mol} \times 130.6 \text{ J mol}^{-1} \text{ K}^{-1})]$$

$$\Delta S^\circ = -76.0 \text{ J K}^{-1}$$

The entropy change of this reaction is negative because the number of moles of gas has decreased from 5 to 3.

### Section 2.3 Practice Problems

1. A box contains four coins. (a) Complete the table below to show the number of head (H) and tail (T) arrangements that correspond to all observable states of the coins. (b) If the box is shaken and then stopped, what is the most probable distribution of heads and tails in the box?

OBSERVABLE STATE	ARRANGEMENTS (MICROSCOPIC STATES)	NUMBER OF ARRANGEMENTS	PROBABILITY FOR AN OBSERVABLE STATE
4 heads, 0 tails	HHHH	1	
3 heads, 1 tail	HHHT, HHTH...		

2. A container is separated by a wall into two parts with volumes  $V_1$  and  $V_2$ , respectively. In  $V_1$  there is a gas of mass  $M$  while  $V_2$  is empty. The wall is removed and, as expected, the gas expands. This process is associated with a change in entropy  $\Delta S_1$ . Assume the same setup but instead of  $V_2$ , the volume is  $2 \times V_2$ . The process is the same but now the gas expands in a larger volume. Is the change in entropy for the second process larger or smaller than the change in entropy in the former process?
3. Use the entropy data in Table 2.3.1 to calculate  $\Delta S^\circ$  for each of the following reactions:
- $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$
  - $4\text{NH}_3\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{N}_2\text{(g)} + 6\text{H}_2\text{O(l)}$
  - $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$

4. For the following pairs of substances, all under standard conditions, predict which one of each pair has the larger standard entropy and explain why:
- 2 moles of  $\text{NO}_2$  and 1 mole of  $\text{N}_2\text{O}_4$
  - Hg and Au
  - 1 mole of each of  $\text{He(g)}$  and  $\text{H}_2\text{O(g)}$
  - 1 mole of each of  $\text{S}_6$  and  $\text{S}_8$
5. One mole of ice at  $0.0^\circ\text{C}$  is heated to  $100^\circ\text{C}$  and then is cooled back into ice at  $0.0^\circ\text{C}$ . The pressure of the initial and final state of the system is the same.
- Is the change in the entropy of the system positive, negative, or zero?
  - Does the rapid or slow way that the process may take place affect the answer in (a)?
6. A container holds 1 mole of liquid water at  $25^\circ\text{C}$ , which is subsequently heated to  $50^\circ\text{C}$  at constant pressure. Is the change in entropy of the system positive, negative, or zero?
7. Consider the same system in Problem 6, but instead of heating, work is performed on the system by shaking the container or stirring the water. Can one achieve the same change in entropy as Problem 6 by performing work on the system instead of transferring heat? Justify your answer.
8. What is the entropy change when two moles of water at  $0^\circ\text{C}$  turn into ice at  $0^\circ\text{C}$ ? The  $\Delta H_{\text{fusion}}$  of water is  $6.01 \text{ kJ mol}^{-1}$ .

## 2.4 Free Energy

### OBJECTIVES

After studying this topic, you should to be able to:

- Describe and use the Gibbs free energy relationship to determine the spontaneity of a reaction.
- Explain whether a reaction is enthalpically or entropically driven, or both.
- Apply the Gibbs relationship in the determination of phase change temperatures.

### FREE ENERGY

The second law of thermodynamics states that every spontaneous process increases the entropy of the universe.

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (2.4.1)$$

Because the universe is an isolated system itself, the second law can also be stated as follows: A process in an *isolated* system is spontaneous if

$$\Delta S_{\text{sys}} > 0 \quad (2.4.2)$$

The case of an isolated system is of limited interest in chemistry where one often deals with *closed* systems at *constant temperature and pressure*. It would be useful to have a criterion of spontaneity that would apply to systems under constant  $T$  and  $P$ . Fortunately such a criterion exists, as we will now show.

When a process occurs at *constant pressure and temperature*, the heat change associated with the surroundings is given by  $\Delta H_{\text{surr}}$ . One can show that, under these conditions, the entropy change of the surroundings is:

$$\Delta S_{\text{surr}} = \frac{\Delta H_{\text{surr}}}{T} \quad (2.4.3)$$

In any given process, the amount of heat flowing out of a system and into the surroundings, and vice versa, must be equal in magnitude but opposite in sign. That is,  $\Delta H_{\text{surr}} = -\Delta H_{\text{sys}}$  and so, at constant  $T$  and  $P$ ,

After substituting Equation 2.4.1 into Equation 2.4.3, we obtain:

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad (2.4.4)$$

For processes occurring at constant temperature and pressure, Equation 2.4.4 is equivalent to Equation 2.4.1, but involves only the properties of the system. In the next few expressions, the subscript “sys” will be dropped and it will be assumed that all thermodynamics properties are those of the system.

After multiplying both sides of Equation 2.4.4 by  $(-T)$ , the equation for any spontaneous change becomes:

$$\Delta H - T\Delta S < 0 \quad (2.4.5)$$

Equation 2.4.5 helps introduce a new thermodynamic quantity, the *Gibbs free energy*,  $G$ , which is expressed as:

$$G = H - TS \quad (2.4.6)$$

The Gibbs free energy, named after American scientist J. W. Gibbs, is the amount of energy that is available (or “free”) to enable spontaneous change to occur at constant temperature and pressure. The Gibbs free energy is a state function, and every chemical reaction is associated with a free energy change given by:

$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$$

Combined with Equation 2.4.6, this free energy change can also be expressed as:

$$\Delta G = \Delta H - T\Delta S \quad (2.4.7)$$

This relationship, known as the Gibbs equation, is one of the most important relationships in thermodynamics. With Equations 2.4.7 and 2.4.5, the second law of thermodynamics can be described as “for every process spontaneous at constant temperature and pressure,  $\Delta G < 0$ .”

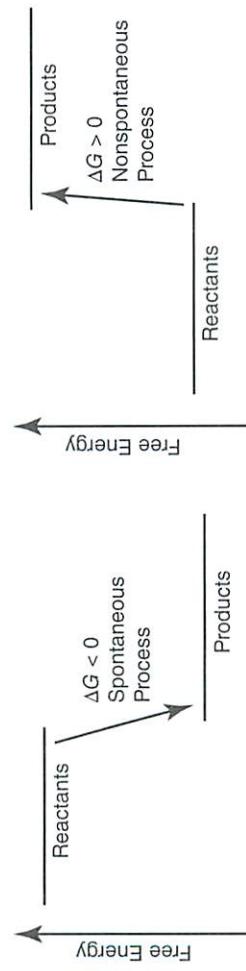
Thus, the criteria of spontaneity of a process at constant temperature and pressure are as follows:

$\Delta G < 0$       The reaction will proceed spontaneously as written.

$\Delta G = 0$       The system is at equilibrium. The numbers of moles of reactants and products do not change over time.

$\Delta G > 0$       The reaction will not proceed spontaneously as written; instead, the reverse process will proceed spontaneously.

A negative value for  $\Delta G$  does not necessarily indicate that the reaction proceeds to completion. When  $\Delta G < 0$ , the reaction *favours* the formation of the products. Similarly, a positive value for  $\Delta G$  does not necessarily indicate there are no products formed. When  $\Delta G > 0$ , the reaction *favours* the reactants, with little or no products formed. The extent of the reaction is determined by the sign and magnitude of  $\Delta G$ .



### WHAT DRIVES A PROCESS?

The sign of  $\Delta G = \Delta H - T\Delta S$  is determined by the signs of  $\Delta H$  and  $\Delta S$ . The four possible sign combinations are summarized in Table 2.4.1.

TABLE 2.4.1 IMPACT OF SIGNS ON  $\Delta G$

$\Delta H$	$\Delta S$	$\Delta G$	COMMENTS
-	+	-	Enthalpically and entropically driven
+	-	+	Enthalpically driven, if spontaneous
-	-	+ or - *	Enthalpically driven, if spontaneous
+	+	+ or - *	Entropically driven, if spontaneous

\* The sign may change with temperature.

### Enthalpically Driven Processes

Most strongly exothermic reactions ( $\Delta H \ll 0$ ) are spontaneous regardless of the sign of  $\Delta S$  because the large negative magnitude of  $\Delta H$  tends to make  $\Delta G$  negative. For example, consider the reaction:



which has  $\Delta H \ll 0$ . Although this process is associated with an entropy decrease ( $\Delta S < 0$ , which is unfavourable),  $\Delta G = (\Delta H - T\Delta S) < 0$ . The free energy change of this spontaneous process can be harnessed by hydrogen fuel cells in the form of electricity. Spontaneous processes with  $\Delta H < 0$  and  $\Delta S < 0$  are said to be *enthalpically driven*.

### Entropically Driven Processes

Endothermic reactions ( $\Delta H > 0$ ) can only be spontaneous if they are associated with a large entropy increase ( $\Delta S \gg 0$ ) such that  $\Delta G = (\Delta H - T\Delta S) < 0$ . These processes are said to be *entropically driven*. One example is the evaporation of water:



Water that evaporates from the palm of a human hand makes it feel cold because the process absorbs heat from the skin. For the same reason, the production of sweat is an effective way to reduce body temperature.

It is not a bad approximation to assume that  $\Delta H$  and  $\Delta S$  are independent of temperature. Then Equation 2.4.7 provides a simple means to predict how changes in temperature will affect the spontaneity of chemical reactions.

For example, why does candle wax melt at an elevated temperature? Candle wax is mainly composed of a long-chain alkane,  $\text{C}_{20}\text{H}_{42}$ . The phase change is:

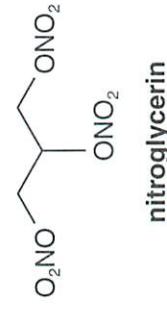


The individual alkane chains in the solid are held together by intermolecular forces. Breaking these interactions requires energy, so  $\Delta H > 0$ . Furthermore, it is known that  $\Delta S > 0$ , as it is for any solid-to-liquid phase transition. At room temperature,  $T\Delta S$  is small, so  $\Delta G = (\Delta H - T\Delta S) > 0$  and the candle wax remains in the solid state. As temperature increases, the magnitude of  $T\Delta S$  increases, eventually causing  $\Delta G$  to become negative. Melting is therefore entropically driven.

There is a point where the temperature gives a  $\Delta G$  of zero. This temperature is the melting point temperature ( $T_m$ ), and at this temperature,  $\Delta G = 0$ , so  $\Delta H_{\text{fus}} = T_m \Delta S_{\text{fus}}$ . Analogously, for a liquid-to-gas transition, the boiling temperature ( $T_b$ ) is defined as  $\Delta H_{\text{evap}} = T_b \Delta S_{\text{evap}}$ .

### Enthalpically and Entropically Driven Processes

Some processes are spontaneous because they are associated with favourable enthalpy and entropy changes ( $\Delta H < 0$  and  $\Delta S > 0$ ). For example, the decomposition of an explosive, such as nitroglycerin:



is highly exothermic ( $\Delta H \ll 0$ ) and produces an increase of entropy ( $\Delta S \gg 0$ ) such that  $\Delta G = (\Delta H - T\Delta S) < 0$ . Reactions of this type are said to be both *enthalpically and entropically driven*.

### STANDARD FREE ENERGY CHANGE

Like  $\Delta H$ , the sign and magnitude of  $\Delta G$  is affected by temperature, pressure, and the concentrations of reactants and products. It is often useful to focus on standard conditions, where all gases are present at a partial pressure of 1 atm, all species in solution have a concentration of 1 M, and the system temperature is 298.15 K. The free energy change under standard conditions is denoted as  $\Delta G^\circ$ . Equation 2.4.7 becomes:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.4.8)$$

where  $\Delta S^\circ$  is the standard entropy change and  $\Delta H^\circ$  is the standard enthalpy change, both of which were discussed in previous topics.

**Example 2.4.1. Spontaneity of a Reaction (In-Class Exercise)**

Use the data below to determine if the oxidation of ethanol to acetic acid is spontaneous under standard conditions at 25 °C.



$\Delta H^\circ_f$ (kJ mol <sup>-1</sup> )	-288.3	0	-485.8	-285.8
$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	148.5	205.0	178.7	69.9

Is this process enthalpically or entropically driven, or both?

**STANDARD FREE ENERGY OF FORMATION**

As with enthalpy, the absolute free energy of a substance cannot be determined.  $\Delta G^\circ_f$ , the *standard free energy of formation*, is the standard free energy change that occurs when 1 mol of a compound is made from elements in their standard states. This definition is analogous to that of  $\Delta H^\circ_f$ .

Likewise, the  $\Delta G^\circ_f$  of any element in its standard state is defined as zero:

$$\Delta G^\circ_f(\text{element in standard state}) = 0$$

For example, the reaction:



has a  $\Delta G^\circ$  of -237.2 kJ mol<sup>-1</sup>. Thus, the  $\Delta G^\circ_f$  of  $\text{H}_2\text{O(l)}$  is -237.2 kJ mol<sup>-1</sup>, because  $\text{H}_2\text{(g)}$  and  $\text{O}_2\text{(g)}$  are elements and are defined as having with  $\Delta G^\circ_f = 0$ .

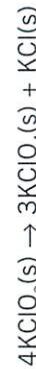
Because free energy is a state function it can be stated that:

$$\Delta G^\circ = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants}) \quad (2.4.9)$$

Equation 2.4.9 is analogous to Hess's law. Therefore,  $\Delta G^\circ$  for any reaction can be determined based on tabulated data that lists the standard free energy of formation ( $\Delta G^\circ_f$ ) of the reactants and products.

**Example 2.4.2. Determination of Standard Free Energy**

Determine  $\Delta G^\circ$  for the following reaction:



based on the following  $\Delta G^\circ_f$  (kJ mol<sup>-1</sup>):



Using Equation 2.4.9:

$$\begin{aligned}\Delta G^\circ &= [(3 \text{ mol KClO}_4 \times -303.2 \text{ kJ mol}^{-1}) + (1 \text{ mol KCl} \times -409.2 \text{ kJ mol}^{-1})] \\ &\quad - [(4 \text{ mol KClO}_3 \times -296.3 \text{ kJ mol}^{-1})] \\ &= -133.6 \text{ kJ}\end{aligned}$$

## Section 2.4 Practice Problems

1. Determine  $\Delta G^\circ$  for the reaction:  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$  at 25 °C based on the following data:

	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	0	0	90.2
$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	191.5	205.0	210.7

Will this reaction occur spontaneously?

2. Determine  $\Delta G^\circ$  for the reaction:



Data:  $\Delta G_f^\circ$  (kJ mol<sup>-1</sup>):  $\text{Fe}^{2+}(\text{aq}) = -78.9$ ;  $\text{CrO}_4^{2-}(\text{aq}) = -727.8$ ;  $\text{H}^+(\text{aq}) = 0$ ;  $\text{Fe}^{3+}(\text{aq}) = -4.7$ ;  $\text{H}_2\text{O}(\text{l}) = -228.6$

3. The oxidation of ethanol releases energy. Does the oxidation of 1 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , produce more or less Gibbs free energy than the oxidation of 1 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ ? Write a balanced equation for each reaction. Based on the results, which reaction occurs faster?

Data:  $\Delta G_f^\circ$  (kJ mol<sup>-1</sup>):  $\text{C}_2\text{H}_5\text{OH}(\text{l}) = -174.8$ ;  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) = -917.2$ ;  $\text{H}_2\text{O}(\text{l}) = -120.4$ ;  $\text{CO}_2(\text{g}) = -394.4$

4. Consider a reaction where  $\Delta H^\circ = 150$  kJ and  $\Delta S^\circ = 400$  J K<sup>-1</sup>.

- Will this reaction occur spontaneously at 25 °C?
- What is the minimum temperature at which the reaction will occur spontaneously?
- Estimate the boiling point of  $\text{Br}_2$  based on the following data:
 

$S^\circ \text{ Br}_2(\text{l}) = 152.2 \text{ J mol}^{-1} \text{ K}^{-1}$	$S^\circ \text{ Br}_2(\text{g}) = 245.4 \text{ J mol}^{-1} \text{ K}^{-1}$
$\Delta H_f^\circ \text{ Br}_2(\text{g}) = 30.91 \text{ kJ mol}^{-1}$	

6. Organ pipes in unheated churches develop “tin disease,” in which white tin is converted to grey tin. What is the minimum temperature at which the church must be maintained in order to prevent the reaction from occurring?

	White Sn	Grey Sn
$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )	0	-2.09
S° (J mol <sup>-1</sup> K <sup>-1</sup> )	51.55	44.14

7. Which of the following is/are true?

- A formation reaction is one in which one mole of compound is made from its constituents in their most stable thermodynamic state, at 25 °C, 1 atm.
- Entropy and energy are equivalent.
- Under standard conditions,  $\Delta G^\circ$  for a reaction can be used as a criterion for spontaneity.



# Chapter 3

## Chemical Equilibrium



### 3.1 The Equilibrium Constant

#### OBJECTIVES

After studying this topic, you should be able to:

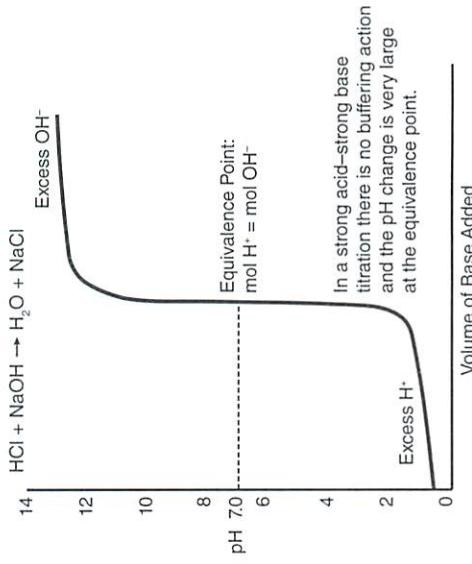
- Write an equilibrium constant expression ( $K$ ) for a given chemical equilibrium and vice versa.
- Determine equilibrium concentrations of reactants and products for an equilibrium, given the  $K$  value and vice versa.
- Determine the reaction quotient ( $Q$ ) and the direction in which a reaction will proceed to achieve equilibrium.
- Describe Le Châtelier's principle, and apply the principle to determine the direction a reaction will shift when subjected to a stress.
- Identify the relationship between the Gibbs free energy ( $\Delta G^\circ$ ) and  $K$ , and use this relationship to determine the standard enthalpy and entropy of a reaction ( $\Delta H_{rxn}^\circ$  and  $\Delta S_{rxn}^\circ$ ).
- Describe and apply the van't Hoff relationship between  $K$  and temperature.

We may fairly judge the commercial prosperity of a country by the amount of sulfuric acid it consumes.

**Justus Von Liebig (1803–1873)**

#### Topics Covered:

- 3.1 The Equilibrium Constant
- 3.2 Solubility of Ionic Compounds
- 3.3 Weak Acids and Bases
- 3.4 Buffer Solutions



#### INTRODUCTION

So far, the study of chemical reactions has focused on reactions that proceed in one direction, to completion. The amount of product made, or reagent remaining, was determined using the limiting reagent. However, there are many chemical reactions that are reversible. When these reactions are complete (have reached equilibrium), the system contains both reactants and products.

**WHAT IS EQUILIBRIUM?**

If a container is half-filled with water and then sealed, some, but not all, of the liquid water molecules will vapourize:



After some length of time, there will be sufficient water vapour that the reverse reaction can also occur:



At some point, the number of liquid and gaseous water molecules in the system (the sealed flask) becomes constant. At this stage, the system is said to have reached or established *equilibrium*. This process is written as:



Although the number of liquid and gaseous molecules remains constant at equilibrium, there is in fact a great deal of liquid-to-gas and gas-to-liquid conversion taking place (see Figure 3.1.1). Therefore, a system that is at equilibrium is dynamic and not static. The liquid will continue to evaporate, and the gas will continue to condense.

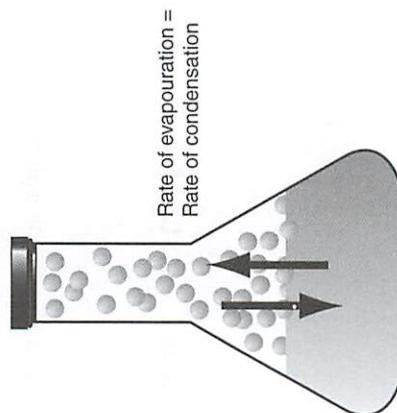
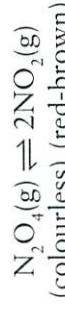


Figure 3.1.1  $\text{H}_2\text{O}(g)$  in equilibrium with  $\text{H}_2\text{O}(l)$ .

Figure 3.1.1 shows an equilibrium involving physical states, but the same principles can be applied to chemical processes.

In chemical processes, equilibrium is defined as the condition where the rate of the forward reaction is equal to the rate of the reverse reaction.

For example, what happens when a system at equilibrium involves the type of reaction shown in the following equation?



If the system initially contains only  $\text{N}_2\text{O}_4$ , then the system is colourless. As the reaction proceeds, a red-brown colour is seen ( $\text{NO}_2$  gas). When the system reaches equilibrium, the colour of the gas mixture is yellow and there are measurable amounts of both  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the gas. Once the system attains equilibrium, the amount of each gas does not change, neither does the colour of the gas mixture. At the molecular level, however, both the forward and the reverse processes are still occurring.

Alternatively, this equilibrium system could be obtained by starting with only  $\text{NO}_2$  gas. Initially the system would have a red-brown colour. As the reaction proceeds in the reverse direction, the colour will “fade” to yellow as  $\text{N}_2\text{O}_4$  is produced.

Table 3.1.1 shows the results of three equilibrium experiments. Experiment 1 began with  $\text{N}_2\text{O}_4$  only, Experiment 2 began with  $\text{NO}_2$  only, and Experiment 3 began with a mixture of both gases. All three experiments were carried out at a constant temperature of  $100^\circ\text{C}$ . Once the systems reached equilibrium, the final partial pressure of each gas was recorded. At the end of the three experiments, regardless of the initial composition of each species in the system, both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  were present.

TABLE 3.1.1 THREE EQUILIBRIUM EXPERIMENTS WITH  $\text{N}_2\text{O}_4$  AND  $\text{NO}_2$ 

EXPERIMENT	SPECIES	$P_{\text{initial}}$ (atm)	$P_{\text{final}}$ (atm)
1	$\text{N}_2\text{O}_4$	1.000	0.226
	$\text{NO}_2$	0	1.548
2	$\text{N}_2\text{O}_4$	0	0.047
	$\text{NO}_2$	0.800	0.706
3	$\text{N}_2\text{O}_4$	1.000	0.431
	$\text{NO}_2$	1.000	2.138

What is the relationship between the equilibrium pressures? At first glance, it seems that all these experiments have one thing in common. In the equilibrium mixture, it appears that there is more  $\text{NO}_2$  than  $\text{N}_2\text{O}_4$ . However, it turns out that there is a consistent mathematical relationship between the equilibrium pressures of the reactants and products in all three of the above experiments. For this equilibrium this relationship is:

$$\frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \text{constant}$$

For any equilibrium, there is a mathematical relationship between the pressures or concentrations of the reactants and products. The symbol used for this relationship is  $K$ , which is known as the *equilibrium constant*.  $K$  sometimes includes a subscript that provides a bit more information about the equilibrium situation. For the previous example, the constant would be  $K_p$ . The subscript  $P$  indicates that the amounts of the species participating in the equilibrium were measured as pressures. If these amounts were measured in concentration units (e.g., mol L<sup>-1</sup>), then the subscript would be  $C$ , as in  $K_C$ .

### Effect of Temperature

Equilibrium constants are temperature dependent. If the temperature of the system changes, the numerical value of the equilibrium constant changes. Whether the value of  $K$  increases or decreases depends on whether the temperature is increased or decreased, and whether the reaction is endothermic or exothermic.

### Homogeneous and Heterogeneous Equilibria

An equilibrium system may have all of its components in the same phase (physical state) or the components may be in different phases. If all the components are in the same phase, the system is a *homogeneous equilibrium*. If they are in different phases, the system is a *heterogeneous equilibrium*. The  $\text{N}_2\text{O}_4 \rightleftharpoons \text{NO}_2$  system shown in Table 3.1.1 is an example of a homogeneous equilibrium in the gas phase.

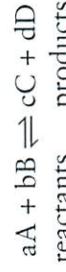
The equilibrium  $\text{C(s)} + \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)}$  is an example of a heterogeneous equilibrium because carbon is a solid while oxygen and carbon dioxide are gases. The equilibrium constant expression for this system would be:

$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{O}_2}}$$

Note that the solid is not included in the equilibrium constant expression. This is a general rule that will be explained further in the next section.

### THE EQUILIBRIUM CONSTANT EXPRESSION

A general equilibrium reaction is written as:



and the general form of the equilibrium constant expression for this reaction, using concentrations, is:

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (3.1.1)$$

In Equation 3.1.1 the  $[\text{C}]$  and  $[\text{D}]$  denote the products (numerator), and the  $[\text{A}]$  and  $[\text{B}]$  denote the reactants (denominator). The coefficients (a, b, c, d) in the balanced reaction have become the exponents in the concentrations. The  $K$  expression is unique to the chemical equation associated with it. The concentration of any solid, or of any solvent, is considered to be constant and is therefore omitted from the equilibrium constant expression.

**Example 3.1.1. Writing Equilibrium Constant Expressions (In-Class Exercise)**

Write equilibrium constant expressions for the following reactions:

- $\text{H}_2\text{S}(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) + \text{S}(\text{s})$
- $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$
- $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightleftharpoons \text{BaSO}_4(\text{s})$
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

The next several examples show how the equilibrium constant expression is affected by the way the equilibrium reaction is written. In other words, how is  $K$  affected by reversing a reaction, multiplying or dividing a reaction, or the combination of multiple reactions?

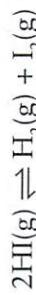
**Reversing an Equilibrium Reaction**

If the chemical equation for an equilibrium reaction is reversed, the expression for the equilibrium constant must be inverted. For example, in the equilibrium:



The equilibrium constant expression would be written as:  $K' = \frac{(P_{\text{H}_2} P_{\text{I}_2})^2}{(P_{\text{HI}})^2}$

If the equilibrium is written in the reverse direction:

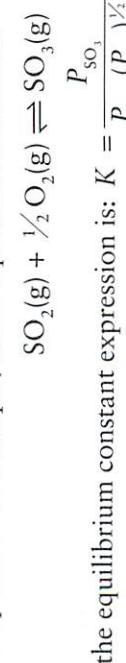


The equilibrium constant expression would be written as:  $K' = \frac{P_{\text{H}_2} P_{\text{I}_2}}{(P_{\text{HI}})^2} = \frac{1}{K}$

Thus, when reversing an equilibrium reaction, the new  $K$  value is  $1/K_{\text{original}}$ .

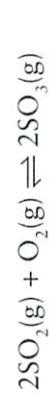
**Multiplying or Dividing an Equilibrium Reaction**

If the chemical equation for an equilibrium is multiplied by two, the  $K$  expression is squared. For example, in the equilibrium reaction:



the equilibrium constant expression is:  $K = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} (P_{\text{O}_2})^{\frac{1}{2}}}$

If the reaction is multiplied by two, giving:



then the equilibrium constant expression is:  $K' = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 P_{\text{O}_2}} = K^2$

Conversely, if the chemical equation is divided by two (multiplied by  $\frac{1}{2}$ ), then the  $K$  expression is the square root of the original expression,  $K' = K^{\frac{1}{2}}$ .

So, the general rule is that when an equilibrium reaction is multiplied by some coefficient,  $m$ , the new  $K$  value is  $K^m$ .

### Combining Equilibria

If two or more equilibria are combined to produce an overall equilibrium, the equilibrium constant for the overall equilibrium can be determined.

For example:

1.  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$   
 $K_1 = 2.2$
2.  $\text{NO}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$   
 $K_2 = 4.0$

These equilibria may be added together to give the overall equation:



To determine how to find  $K_3$ , take a look at the expressions for  $K_1$ ,  $K_2$ , and  $K_3$ :

$$K_1 = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2}(P_{\text{O}_2})^{\frac{1}{2}}} \qquad K_2 = \frac{P_{\text{NO}}(P_{\text{O}_2})^{\frac{1}{2}}}{P_{\text{NO}_2}} \qquad K_3 = \frac{P_{\text{SO}_3}P_{\text{NO}}}{P_{\text{SO}_2}P_{\text{NO}_2}}$$

Multiplying  $K_1 \times K_2$  will produce  $K_3$ , and the numerical value is 8.8.

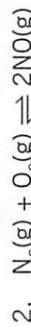
Thus, when adding reactions, multiply the  $K$  values:  $K_{\text{new}} = K_1 \times K_2$ .

**Example 3.1.2. Determination of  $K$  Using Manipulation Rules (In-Class Exercise)**

Given the following:



$$K_1 = 2.70 \times 10^{-18}$$



$$K_2 = 4.70 \times 10^{-31}$$

Determine the value of  $K_3$  for:

**Significance of the Magnitude of  $K$** 

The numerical value of the equilibrium constant for a given reaction can range from very large to very small. The magnitude of the equilibrium constant is an indication of the relative amount of product or reactant present at equilibrium. If  $K$  is greater than 1, the equilibrium lies toward the right (product side) of the equation. This indicates that there are more products than reactants. If  $K$  is less than 1, the equilibrium lies toward the left (reactant side) of the equation. This indicates that there are more reactants than products.

**Units for  $K$ , the Equilibrium Constant**

Sometimes we write an equilibrium constant as  $K_p$  or  $K_c$ , where the subscript indicates whether the amounts of the species involved are expressed in atm or  $\text{M} = \text{mol L}^{-1}$ . But then we go on to say that equilibrium constants do not normally have units associated with them. How can this be?

The proper thermodynamic definition of the equilibrium constant is given in terms of properties called *activity* (for molecules in a solution) and *fugacity* (for gas-phase molecules). Both activity and fugacity are related to concentration and partial pressure, respectively, but carry no units (i.e., they are dimensionless).

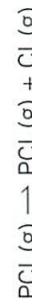
For the examples we cover in this course, activity may be approximated as concentration in units of M; whereas fugacity may be approximated as partial pressure in units of atm (but not kPa). For this reason, only the units of M and atm should be used in calculations of  $K_c$  and  $K_p$ . The resulting equilibrium constants are to be treated as dimensionless quantities.

**Determining  $K$  and Amounts**

A numerical value for an equilibrium constant may be found if the equilibrium amounts of each species involved are known. Conversely, if the  $K$  is known, the stoichiometry of the reaction may allow the amounts of some species to be determined.

**Example 3.1.3. Determining  $K$** 

In the reaction:



the equilibrium pressures are as follows:  $P_{\text{PCl}_3} = 0.832 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.712 \text{ atm}$ , and  $P_{\text{PCl}_5} = 0.276 \text{ atm}$ . Determine  $K$  for the reaction.

Solution:

$$K = \frac{P_{\text{Cl}_2} \times P_{\text{PCl}_3}}{P_{\text{PCl}_5}} = \frac{(0.832)(0.712)}{(0.276)} = 2.15$$

**Example 3.1.4. Determining Equilibrium Amounts and  $K$  (In-Class Exercise)**

Consider the reaction:



Suppose the reaction begins with only 1.00 atm each of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$ . At equilibrium, the system was found to contain 0.2125 atm each of  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$ . Determine the equilibrium pressure of  $\text{HI}(\text{g})$  and a value of the equilibrium constant.

**THE REACTION QUOTIENT,  $q$** 

A system can be studied at any time during the course of a reaction, not just initially or at equilibrium. If the amounts of products and reactants can be determined, a quantity known as the *reaction quotient* may be calculated. This number indicates whether the system is at equilibrium, *and* the direction in which the reaction must proceed to attain equilibrium.

For the general reaction:  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

Using concentrations, the expression for the reaction quotient,  $Q$ , is:

$$Q_C = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q_P = \frac{P_C^{c'} P_D^{d'}}{P_A^a P_B^b}$$

The expression for the reaction quotient in terms of pressures would be similar:

The reaction quotient expression is the same as the equilibrium constant expression except that the concentrations (or pressures) used to calculate  $Q$  are not necessarily the equilibrium concentrations (or pressures). Comparing the numerical value of  $Q$  to that of  $K$  will indicate if the reaction is at equilibrium and, if not, whether more products or more reactants must be made to attain equilibrium.

Consider the equilibrium for the production of ammonia:



At some point in the reaction, the following measurements are made:

$$P_{\text{NH}_3} = 0.913 \text{ atm}, P_{\text{N}_2} = 0.131 \text{ atm}, P_{\text{H}_2} = 0.0518 \text{ atm}$$

Is this system at equilibrium? If not, in which direction must the reaction proceed to attain equilibrium? The reaction quotient expression for the reaction is:

$$Q = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.913)^2}{(0.131)(0.0518)^3} = 4.57 \times 10^4$$

A system is at equilibrium only when  $Q = K$ . The value of  $Q$  is less than the value of  $K$  in this case, so the system is not at equilibrium. The smaller  $Q$  value means the system either does not have enough product(s) or has too much reactant, and the reaction must proceed in a forward ( $\rightarrow$ ) direction to attain equilibrium.

If the numerical value of  $Q$  is greater than  $K$ , the system must proceed in the reverse ( $\leftarrow$ ) direction to attain equilibrium, because there is either too much product or not enough reactant.

### LE CHÂTELIER'S PRINCIPLE

Once a system has reached equilibrium, the concentrations or pressures of the reactants and products remain constant. This does not mean that the system has stopped reacting, only that the forward and reverse rates are equal. Changing the temperature or the pressure, or adding or removing one of the chemical species, will disturb the equilibrium. The system will react in one direction or the other to re-establish equilibrium. After this occurs, the concentrations or pressures at equilibrium will be different than they were before the system was disturbed. The phrase used is “the position of the equilibrium will change.” The value of the equilibrium constant does not change unless the temperature changes.

The manner in which these changes are accomplished was summed up in a famous principle originated by French chemist Henri Le Châtelier in 1884:

*If a chemical system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of a participant in the equilibrium, the equilibrium will shift in such a way as to minimize the disturbance.*

Some of the applications of this principle may be illustrated using the equilibrium:



The numerical value of the equilibrium constant will not change, unless the temperature changes, so at 298.15 K,  $K_p = 3.6 \times 10^8$ .

### Concentration Changes

Suppose that the concentration of  $\text{H}_2$  is increased in the reaction above. The system will attempt to use some of this additional  $\text{H}_2$ . The reaction will proceed to the right, also using some of the  $\text{N}_2$ , resulting in an increase in the concentration of  $\text{NH}_3$ . The overall effect is that the concentration of  $\text{H}_2(\text{g})$  will be larger, the concentration of  $\text{N}_2(\text{g})$  will be smaller, and the concentration of  $\text{NH}_3(\text{g})$  will be larger.

Now suppose that some of the  $\text{NH}_3(\text{g})$  is removed by condensing it into  $\text{NH}_3(\text{l})$ . The system will attempt to make more  $\text{NH}_3$ . Once again, the reaction will proceed in the forward direction, decreasing the amounts of  $\text{N}_2$  and  $\text{H}_2$ .

If  $\text{NH}_3$  is added, the opposite effect is seen and the reaction will proceed in the reverse direction toward the reactants. The amounts of both  $\text{N}_2$  and  $\text{H}_2$  will increase. These changes can be observed mathematically using the equilibrium constant expression, and comparing  $K$  with  $Q$ . At equilibrium:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

If the concentration of  $\text{H}_2$  is increased,  $Q$  will be smaller than  $K$ . Therefore, the reaction will proceed in the forward direction until  $Q = K$  again. If the concentration of  $\text{NH}_3$  is increased,  $Q$  will be larger than  $K$ . The reaction must proceed in the reverse direction until  $Q = K$ .

### Pressure Changes

Another way of disturbing a gaseous equilibrium system is to change the total pressure of the system. If the equilibrium pressure of a reactant or product is changed, the result is the same as a change in concentration. (The pressure of a particular species is directly proportional to the number of moles of that species.)

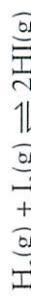
The pressure of a system involving gases may be disturbed by changing the volume of the system. Increasing the volume of a system results in a drop in pressure of each gas. If the volume of a system is increased the reaction will proceed in the direction that produces more moles of gas, if that is possible. This will increase the pressure. If the volume of a system is decreased, pressures will increase and the reaction will proceed in the direction that will produce fewer moles of gas.

For example, if there are four moles of gas on the reactant side and two moles of gas on the product side of an equilibrium reaction, an increase in the volume of the container would result in the reaction proceeding in the reverse direction. Decreasing the volume of the container would result in the reaction proceeding in the forward direction.



Thus, the reaction will proceed in a direction that produces more gas or less gas, depending on whether the volume is increased or decreased. If an inert gas is added to the gaseous equilibrium system, the result will be an increase in the total pressure, but there will not be any changes to the partial pressures of the reactant and product gases. Therefore, there will be no change in the position of the equilibrium.

Systems involving just solids and liquids are not affected by changing the volume of a container. Systems that involve both gases and solids or liquids will be affected. If the number of moles of reactant gases and product gases are the same, as in:



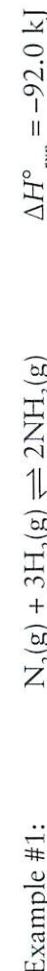
then changing the volume will not effect the position of the equilibrium.

All of the above changes have been accomplished by changing some condition of the equilibrium system at a constant temperature, which means that the numerical value of  $K$  has not changed.

#### Relationship Between Temperature and $K$ Values

If the temperature of the system is changed, the value of the equilibrium constant will change. The explanation for this involves looking at the change in enthalpy ( $\Delta H$ ) that accompanies a reaction. If  $\Delta H$  for a reaction is positive, the reaction is endothermic and heat is absorbed from the surroundings. If  $\Delta H$  for a reaction is negative, the reaction is exothermic and heat is released to the surroundings.

To understand how temperature changes affect the position of the equilibrium, one has to include the enthalpy change as a reactant or product in the equation.



can be written as:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + 92.0 \text{ kJ}$

This reaction produces heat and the temperature of the surroundings will rise.



can be written as:  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 181 \text{ kJ} \rightleftharpoons 2\text{NO}(\text{g})$

This reaction requires or absorbs heat, resulting in a drop in the temperature of the surroundings. For each of these reactions, one could either increase or decrease the system temperature.

In an exothermic reaction, increasing the temperature has the same effect as increasing the amount of one of the products. Le Châtelier's principle indicates that this will result in a shift of the equilibrium to the left, increasing the amounts of the reactants and decreasing the value of  $K$ . The reverse is true if the temperature is lowered. This would be similar to removing one of the products. The equilibrium

will shift to the right, increasing the amounts of the products and increasing the value of  $K$ .

Adding heat in an endothermic reaction has the same effect as increasing the amount of one of the reactants. Therefore, increasing the temperature leads to an increase in the amounts of the products. The equilibrium will shift to the right, resulting in an increase in  $K$ . Removing heat is similar to decreasing the amount of one of the reactants. To offset this disturbance, the equilibrium will shift to the left, increasing the amounts of the reactants and decreasing  $K$ .

### GIBBS FREE ENERGY AND THE EQUILIBRIUM CONSTANT

Recall that the Gibbs free energy change ( $\Delta G$ ) can be used to determine whether a reaction proceeds spontaneously at constant temperature and pressure. In summary, when:

$\Delta G < 0$       The reaction will proceed spontaneously as written.

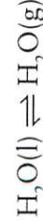
$\Delta G = 0$       The system is at equilibrium. The number of moles of reactant and product will not change over time.

$\Delta G > 0$       The reaction will not occur spontaneously as written; instead, the reverse process will occur spontaneously.

$\Delta G^\circ$  is the free energy change under standard conditions. This means that the temperature is 298.15 K (25 °C), all gases are at pressure of 1 atm and all species in solution have a concentration of 1 M. A positive value for  $\Delta G^\circ$  indicates that a process is nonspontaneous *under standard conditions*. This does not mean that a reaction does not proceed at all, only that it proceeds to a very small extent.

$\Delta G^\circ$  is also related to equilibrium. If  $\Delta G^\circ$  is positive, the equilibrium lies to the left (reactant side) and  $K$  is small. Conversely, if  $\Delta G^\circ$  is negative, the equilibrium lies to the right (product side) and  $K$  is large.

A familiar example of equilibrium is the vapourization of water:



$$\Delta G^\circ = 8.590 \text{ kJ mol}^{-1}$$

Even though the  $\Delta G^\circ$  is positive, some water does evaporate but the  $\text{H}_2\text{O(g)}$  produced has a vapour pressure less than 1 atm. At 25 °C the equilibrium lies far to the left, in favour of the reactants.

What is the relationship between  $\Delta G^\circ$  and  $K$ ? First, the relationship between  $\Delta G$  and  $\Delta G^\circ$  (i.e., free energy under nonstandard and standard conditions) is:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (3.1.2)$$

where  $Q$  is the reaction quotient. Because  $\Delta G = 0$  and  $Q = K$  at equilibrium, Equation 3.1.2 can be rearranged to show the relationship between  $\Delta G^\circ$  and  $K$ :

$$\Delta G^\circ = -RT \ln K \quad (3.1.3)$$

In Equation 3.1.3:

- $\Delta G^\circ$  is the standard Gibbs free energy for the reaction in joules per mole
- $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
- $T = 298.15 \text{ K}$  (since  $\Delta G^\circ$  values are at  $298.15 \text{ K}$ )
- $K$  is the equilibrium constant ( $K_p$  for gas-phase reactions,  $K_c$  for reactions in solution)

Note that for Equation 3.1.3 to be used correctly,  $\Delta G^\circ$  must be in joules per mole ( $\text{J mol}^{-1}$ ) because  $R$ , the gas constant, is in units of  $\text{J mol}^{-1} \text{ K}^{-1}$ . (Do not confuse the  $K$  for Kelvin with the italicized  $K$  used for the equilibrium constant..)

#### **Example 3.1.5. Determining $K$ from $\Delta G^\circ$ (In-Class Exercise)**

Determine the equilibrium constant for the vapourization of water.

The standard free energy change for a reaction is also related to enthalpy and entropy changes:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3.1.4)$$

By substituting for  $\Delta G^\circ$  from Equation 3.1.3, the following relationship emerges:

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\text{Dividing both sides by } -RT: \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3.1.5)$$

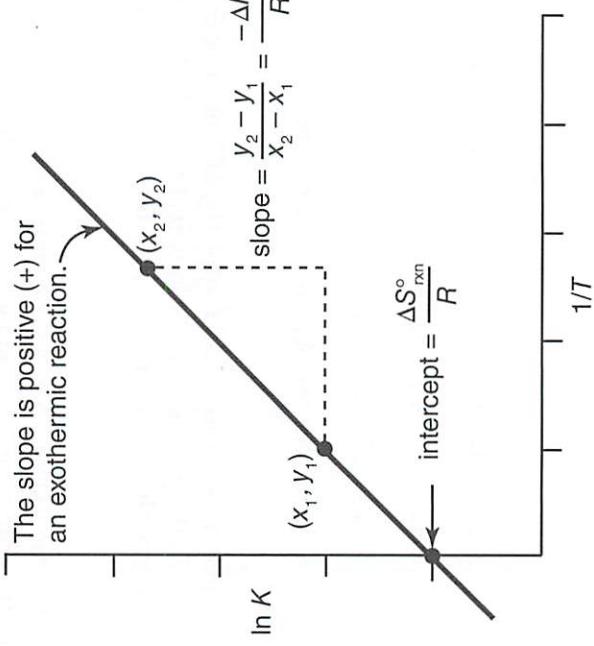
While  $\Delta G^\circ$  varies with temperature as shown in Equation 3.1.4, both  $\Delta H^\circ$  and  $\Delta S^\circ$  vary little over the temperature range of most reactions. Equation 3.1.5 can therefore be used to find  $K$  values at temperatures other than  $298.15 \text{ K}$ .

Equation 3.1.5 can be rearranged to correspond with the general equation for a straight line,  $y = mx + b$  ( $m$  = slope;  $b$  = intercept point on y-axis):

$$\ln K = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (3.1.6)$$

$$y = m \quad x + b$$

Thus, a plot  $\ln K$  versus  $1/T$  gives a straight line with a slope of  $-\Delta H^\circ_{\text{rxn}}/R$  and a y-intercept of  $\Delta S^\circ_{\text{rxn}}/R$ .



#### Example 3.1.6. Determining $\Delta H^\circ_{\text{rxn}}$ from $K$ and $T$ (In-Class Exercise)

For a given reaction, a series of  $K$  values were determined at various temperatures. If the values of  $K$  were 6.0 and 330 at 1333 K and 800 K respectively, what is the value of  $\Delta H^\circ_{\text{rxn}}$ ?

### THE VAN'T HOFF EQUATION

In the late 19th century, Dutch chemist Jacobus Henricus van't Hoff used a derivative of Equation 3.1.6 to determine  $K$  values at different temperatures.

Writing Equation 3.1.6 for two sets of points,  $(\ln K_1, 1/T_1)$  and  $(\ln K_2, 1/T_2)$ :

$$\ln K_1 = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_1} \right) + \frac{\Delta S^\circ}{R} \quad \text{and} \quad \ln K_2 = \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} \right) + \frac{\Delta S^\circ}{R}$$

Then subtracting  $\ln K_2 - \ln K_1$ :

$$\begin{aligned} \ln K_2 - \ln K_1 &= \left[ \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} \right) + \frac{\Delta S^\circ}{R} \right] - \left[ \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_1} \right) + \frac{\Delta S^\circ}{R} \right] \\ &= \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} \right) + \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} \right) \end{aligned}$$

Thus,

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3.1.7)$$

Equation 3.1.7, known as the van't Hoff equation, can be used to determine  $K$  at a second temperature,  $T_2$ , given  $\Delta H_{\text{rxn}}^\circ$ ,  $K_1$  and  $T_1$ . If  $K$  is known at two different temperatures, the equation may also be used to calculate  $\Delta H_{\text{rxn}}^\circ$ . Another practical use for the van't Hoff equation is to determine the appropriate temperature at which to carry out a reaction.

For example, in the reaction:



$$\Delta G^\circ = 4.78 \text{ kJ}$$

$K_C = 4.61 \times 10^{-3}$  at  $25^\circ\text{C}$ , and  $\Delta H_{\text{rxn}}^\circ = +57.2 \text{ kJ}$ . From the magnitude of  $K_C$ , the equilibrium lies to the left at this temperature; there is much, much more  $\text{N}_2\text{O}_4$  than there is  $\text{NO}_2$ . If the desired species is  $\text{NO}_2$ , the equilibrium must be shifted to the right in favour of the product. To accomplish this, the numerical value of  $K$  must be increased to reflect the greater amount of product.

Since  $\Delta H^\circ_{\text{rxn}}$  is positive, this is an endothermic reaction so an increase in temperature will cause the equilibrium to shift in the forward direction. How much of a temperature increase will be necessary? Suppose one wants a  $K$  value of 2.00, which would clearly result in more product. The temperature necessary to achieve this value of  $K$ , using the van't Hoff equation, is found by:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ_{\text{rxn}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$
$$\ln \frac{2.00}{4.61 \times 10^{-3}} = \frac{57,200 \text{ J}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{298.15 \text{ K}} - \frac{1}{T_2} \right)$$

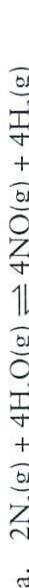
Note that the value of  $\Delta H^\circ_{\text{rxn}}$  was converted to joules to match the units of  $R$ , the gas constant, and the temperature was converted to Kelvin, also to match the units of the gas constant. Solving,  $T_2 = 404 \text{ K}$  or  $131^\circ\text{C}$ .

#### Example 3.1.7. Predicting $K$ at Different $T$ (In-Class Exercise)

A reaction has  $\Delta H^\circ = -41.2 \text{ kJ mol}^{-1}$ . If  $K = 201$  at  $250 \text{ K}$ , what is  $K$  at  $725 \text{ K}$ ?

### Section 3.1 Review Problems

1. Write the equilibrium constant expressions for the following equilibria:

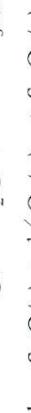


2. Write the chemical equations for the equilibrium systems that would lead to the following equilibrium constant expressions:

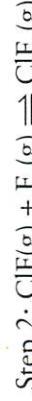
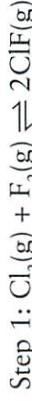
$$\text{a. } K = \frac{(P_{\text{H}_2\text{O}})^2(P_{\text{Cl}_1})^2}{(P_{\text{HCl}})^4 P_{\text{O}_2}}$$

$$\text{b. } K = \frac{(P_{\text{H}_2\text{O}_2})^2}{(P_{\text{H}_2\text{O}})^2 P_{\text{O}_2}}$$

3. Write the equilibrium constant expression for each of the following reactions. Classify each as homogeneous or heterogeneous. For gaseous equilibria, use partial pressures.



4. The two-step fluorination of chlorine gas produces  $\text{ClF}_3$  as the only product.



What is the correct equilibrium constant expression for the overall reaction?

a.  $K = \frac{(\text{P}_{\text{ClF}})^2}{\text{P}_{\text{Cl}_2}\text{P}_{\text{F}_2}}$

b.  $K = \frac{\text{P}_{\text{ClF}_3}}{\text{P}_{\text{ClF}}\text{P}_{\text{F}_2}}$

c.  $K = \frac{(\text{P}_{\text{ClF}})^2}{\text{P}_{\text{Cl}_2}(\text{P}_{\text{F}_2})^3}$

- d.  $K = \frac{\text{P}_{\text{ClF}_3}}{\text{P}_{\text{Cl}_2}\text{P}_{\text{F}_2}}$
- e.  $K = \frac{\text{P}_{\text{ClF}_3}}{(\text{P}_{\text{ClF}})^2\text{P}_{\text{F}_2}}$
5. In each of the following examples, three related chemical reactions are shown, with equilibrium constants  $K_1$ ,  $K_2$ , and  $K_3$ . In each case, express  $K_3$  as a function of  $K_1$  and  $K_2$ .

- a. i.  $\text{Mg}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{MgO}(\text{s}) + \text{H}_2(\text{g}) \quad K_1$   
ii.  $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad K_2$   
iii.  $\text{Mg}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{MgO}(\text{s}) \quad K_3$
- b. i.  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad K_1$   
ii.  $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons 2\text{HNO}_3(\text{g}) \quad K_2$   
iii.  $4\text{HNO}_3(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 3\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \quad K_3$
- c. i.  $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g}) \quad K_1$   
ii.  $\text{NO}(\text{g}) + \text{Cl}(\text{g}) \rightleftharpoons \text{NOCl}(\text{g}) \quad K_2$   
iii.  $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g}) \quad K_3$
6. Given:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ;  $K_p = 49$  at 730 K,  
Determine  $K_p$  for:  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$  at 730 K.

7. Given:  $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ ;  $K_p = 0.77$  at 1020 K,  
Determine  $K_p$  for:  $3\text{H}_2\text{O}(\text{g}) + 3\text{CO}(\text{g}) \rightleftharpoons 3\text{H}_2(\text{g}) + 3\text{CO}_2(\text{g})$  at 1020 K.
8. Methanol,  $\text{CH}_3\text{OH}$ , can be produced from the reaction of hydrogen gas,  $\text{H}_2$ , and carbon monoxide gas,  $\text{CO}$ , if a suitable catalyst is used. This process is a chemical equilibrium.

- Write a balanced equation for this equilibrium.
- Write the equilibrium constant expression for this equilibrium.
- At 227 °C, the equilibrium partial pressures of  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CH}_3\text{OH}$  are as follows: 0.711 atm, 0.177 atm, and 0.00136 atm. Determine  $K_p$  for this reaction.
- What would the equilibrium constant be at 227 °C for the decomposition reaction of 2.0 moles of  $\text{CH}_3\text{OH}$  to  $\text{CO}$  and  $\text{H}_2$ ?

9. Use the van't Hoff equation to determine the  $\Delta H_{\text{rxn}}^\circ$  for the following equilibrium reaction given the  $K$  and  $T$  values at right:



$$K_2 = 4.0 \times 10^{-1} \quad T_2 = 1100 \text{ K}$$

10. Given:  $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ ;  $K_c = 0.77$  at 1020 K,  
Determine  $K_p$  at 850 K using the data below.

$$\Delta H_f^\circ (\text{kJ mol}^{-1}): \text{CO}_2(\text{g}) = -393.5 \text{ kJ}; \text{H}_2\text{O}(\text{g}) = -241.8; \text{CO}(\text{g}) = -110.5$$

11. In an equilibrium reaction, the following values of  $\ln K$  versus  $1/T$  were recorded and plotted to give a straight line:

$\frac{1}{T}$	$\ln K$
$8.0 \times 10^{-4} \text{ K}^{-1}$	-2.0
$9.0 \times 10^{-4} \text{ K}^{-1}$	0
$10.0 \times 10^{-4} \text{ K}^{-1}$	2.0
$11.0 \times 10^{-4} \text{ K}^{-1}$	4.0

Given these data, what was the  $\Delta H_{\text{rxn}}^\circ$  and  $\Delta S_{\text{rxn}}^\circ$ ?

12. Determine the  $\Delta H_{\text{rxn}}^\circ$  in kJ for an equilibrium reaction which has  $K_1 = 2.5 \times 10^2$  at 25 °C and  $K_2 = 6.5$  at 95 °C.
13. An equilibrium reaction has  $K_1 = 6.5 \times 10^{-2}$  at 85 °C and  $\Delta H_{\text{rxn}}^\circ = -46.5 \text{ kJ mol}^{-1}$ . What is  $K$  at 235 °C?
14. An equilibrium reaction has  $K_1 = 4.5 \times 10^{-2}$  at 110 °C and  $\Delta H_{\text{rxn}}^\circ = -65.2 \text{ kJ mol}^{-1}$ . At what temperature, in K, is  $K = 6.50$ ?

## 3.2 Solubility of Ionic Compounds

### OBJECTIVES

After studying this topic, you should to be able to:

- Use  $K_{sp}$  to find the solubility of a compound in water or in an aqueous solution containing a common ion.
- Given a  $K_{sp}$  value, determine the pH of a solution and how the solubility of a substance changes with pH.
- Given  $K_{sp}$  values, identify and determine the concentrations of the ions that will remain in solution when two different solutions are mixed.

### WHY IS SOLUBILITY IMPORTANT?

It would be difficult to overestimate the importance of solution processes and precipitation reactions as there are numerous examples encountered in our daily lives. Processes involving the solubility of ionic compounds are important in many areas of scientific endeavour, from biology, biochemistry, and medicine, to earth sciences, as well as in industrial chemistry.

Calcium, for example, is an extremely important mineral both in and out of solution in our bodies. In our bloodstream, its ionic form ( $\text{Ca}^{2+}$ ) participates in nerve transmission, muscle contraction, blood clotting, blood pressure regulation, and hormone secretion. The main component in bones and teeth is a highly insoluble calcium complex known as hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . The solubility of this complex may be affected by large amounts of acid which, in the case of tooth enamel, will lead to tooth decay.

There is a delicate balance between the calcium that exists as a solid ionic compound in bones and teeth, and the calcium in our bloodstream. If blood levels of this element are too low, processes come into play that release calcium from bones and allow it to dissolve into the ionic form. If an excess of phosphate ion is also present, calcium phosphate may form and produce kidney stones.

In this topic, the solubility of relatively insoluble ionic compounds is examined.

### A BRIEF REVIEW OF SOLUBILITY AND PRECIPITATION

The *solubility* of a substance is the amount of that substance that will dissolve in a certain volume of a specific solvent, and is usually expressed in grams per litre or in moles per litre. The degree of solubility is roughly defined as:

- Soluble compound: 10 g or more can dissolve in a litre of solvent.
- Slightly soluble compound: 0.1 to 10 g can dissolve in a litre of solvent.
- Insoluble compound: less than 0.1 g can dissolve in a litre of solvent.

The figures above apply at room temperature. In general, ionic compounds become more soluble as the temperature increases.

Table 3.2.1 provides guidelines that can be used to predict if an ionic compound (salt) will be soluble or insoluble.

TABLE 3.2.1 SOLUBILITY GUIDELINES FOR IONIC SOLIDS

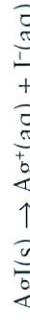
PRIORITY	GUIDELINES Salts of...	EXCEPTIONS
1st	Group 1 cations, $\text{NH}_4^+$ are soluble	$\text{LiF}, \text{Li}_2\text{CO}_3$ are insoluble
2nd	$\text{NO}_3^-$ , $\text{CH}_3\text{COO}^-$ , $\text{HCO}_3^-$ , $\text{ClO}_4^-$	are soluble
3rd	$\text{Ag}^+$ , $\text{Pb}_2^+$ , $\text{Hg}_2^{2+}$	are insoluble
4th	$\text{F}^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$	$\text{AgF}$ is soluble
5th	$\text{CO}_3^{2-}$ , $\text{PO}_4^{3-}$ , $\text{CrO}_4^{2-}$ , $\text{S}^{2-}$ , $\text{O}^{2-}$ , $\text{OH}^-$	Group 2 fluorides are insoluble $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , and $\text{Ba}^{2+}$ hydroxides are soluble
6th	$\text{SO}_4^{2-}$	$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , and $\text{Ba}^{2+}$ sulfates are insoluble

Salts of ions in the top left section of Table 3.2.1 are all *soluble* unless they are salts of one of the ions listed as an exception. Conversely, salts of ions in the bottom left section are all *insoluble* unless they are salts of one of the ions listed as an exception.

### THE SOLUBILITY PRODUCT

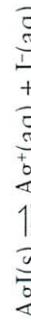
A *solvent* is a liquid or a gas that dissolves another solid, liquid, or gas. The substances that dissolve in a solvent are called the *solutes* of the resultant solution. *Solubility* is defined as the amount of a given substance that dissolves in a given volume of solvent at a given temperature, and may be expressed in g L<sup>-1</sup> or mol L<sup>-1</sup>.

When an ionic solid dissolves in water, it dissociates into hydrated (solvated) ions. For example, suppose one slowly added small amounts of an ionic solid such as silver iodide, AgI(s), to a beaker of pure water. The following reaction would start to occur:



As the dissolution proceeds, the concentration of ions would increase little by little as more and more of the silver iodide was added. Eventually, no more additional silver iodide would dissolve in the solution.

At this point an equilibrium is established between the undissolved solid and the free ions, and the solution is said to be *saturated*. An equilibrium expression can be written for this process:



and an equilibrium constant can be defined as:

$$K_{sp} = [\text{Ag}^+][\text{I}^-]$$

where [Ag<sup>+</sup>] and [I<sup>-</sup>] are the concentrations of the ions in mol L<sup>-1</sup> and K<sub>sp</sub> is an equilibrium constant called the *solubility product* or the *solubility product constant*.

Salts that are very soluble have a very large K<sub>sp</sub> value. These dissolutions essentially go to completion and are denoted by a one-way arrow (→). For compounds with low solubility, an equilibrium may be established and the familiar equilibrium arrow (⇄) is used.

In general, for the dissolution of an ionic solid of composition  $A_xB_y$ , the equilibrium reaction is written as:



and the  $K_{sp}$  expression for this heterogeneous equilibrium is written as:

$$K_{sp} = [A^{a+}]^x[B^{b-}]^y$$

Note that the pure solid is not included in the equilibrium expression. This is because excess solid does not affect the position of the equilibrium. More solid provides more surface area from which dissolution can occur, but reformation of solid also occurs at the surface. Doubling the surface area doubles the rate of dissolution but also the rate of precipitation, thus there is no effect on the equilibrium position.

#### Example 3.2.1. Writing $K_{sp}$ Expressions (In-Class Exercise)

Write the  $K_{sp}$  expressions for  $\text{CaCO}_3$ ,  $\text{Mg(OH)}_2$ , and  $\text{Sr}_3(\text{PO}_4)_2$ .

It is also important to distinguish between the concepts of *solubility* and the *solubility product constant*. The solubility product constant is an equilibrium constant and is thus always the same for a given solid at a given temperature.  $K_{sp}$  values vary only with temperature, and the ones shown in Table 3.2.2 are at 25 °C. On the other hand, at a given temperature the amount of solid that will dissolve will vary depending on other conditions such as the presence of ions in solution, thus giving an infinite number of possible values.

#### Saturated and Unsaturated Solutions

The term *saturated* implies that there is an equilibrium between the solid and the ions in solution. If the quantity of a species in solution is less than that required for equilibrium with the solid, the solution is said to be *unsaturated*. If more solid is added to an unsaturated solution, it dissolves until the solution is saturated (at which point there is solid in equilibrium with solvated ions).

**Example 3.2.2. Solubility of AgCl**

Find the solubility of AgCl ( $K_{sp} = 1.7 \times 10^{-10}$ ) in water.

**Solution:** The equation for dissolution of AgCl is:



Initial:	solid	0	0
Δ:	-x	+x	+x
Equil:	solid - x	x	x

where x is the amount of AgCl that dissolves (mol L<sup>-1</sup>). x also equals [Ag<sup>+</sup>] and [Cl<sup>-</sup>] at equilibrium.

$$\begin{aligned}K_{sp} &= 1.7 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] \\&= (x)(x)\end{aligned}$$

Therefore:  $x = \sqrt{1.7 \times 10^{-10}} = 1.3 \times 10^{-5} M$  = solubility of AgCl.

### CHAPTER 3 ■ CHEMICAL EQUILIBRIUM

3-28

TABLE 3.2.2  $K_{sp}$  VALUES FOR SELECTED COMPOUNDS AT 25 °C

CATEGORY	FORMULA	$K_{sp}$	CATEGORY	FORMULA	$K_{sp}$
Bromides	$PbBr_2$	$4.6 \times 10^{-5}$	Hydroxides (cont'd)	$Fe(OH)_2$	$1.8 \times 10^{-15}$
	$Hg_2Br_2$	$1.3 \times 10^{-22}$		$Fe(OH)_3$	$1.0 \times 10^{-38}$
	$AgBr$	$5.0 \times 10^{-13}$		$Pb(OH)_2$	$4.2 \times 10^{-15}$
	$BaCO_3$	$1.6 \times 10^{-9}$		$Mg(OH)_2$	$8.9 \times 10^{-12}$
Carbonates	$CaCO_3$	$4.7 \times 10^{-9}$	Iodides	$PbI_2$	$8.3 \times 10^{-9}$
	$CuCO_3$	$2.5 \times 10^{-10}$		$Hg_2I_2$	$4.5 \times 10^{-29}$
	$FeCO_3$	$2.1 \times 10^{-11}$		$AgI$	$8.5 \times 10^{-17}$
	$MgCO_3$	$1.0 \times 10^{-15}$		$Ba_3(PO_4)_2$	$6.0 \times 10^{-39}$
Chlorides	$Ag_2CO_3$	$8.2 \times 10^{-12}$	Phosphates	$Ca_3(PO_4)_2$	$1.3 \times 10^{-32}$
	$PbCl_2$	$1.7 \times 10^{-5}$		$Ag_3PO_4$	$1.8 \times 10^{-18}$
	$Hg_2Cl_2$	$1.1 \times 10^{-18}$		$Sr_3(PO_4)_2$	$1.0 \times 10^{-31}$
	$AgCl$	$1.7 \times 10^{-10}$		$BaSO_4$	$1.5 \times 10^{-9}$
Fluorides	$BaF_2$	$2.4 \times 10^{-5}$	Sulfates	$CaSO_4$	$2.4 \times 10^{-5}$
	$CaF_2$	$3.4 \times 10^{-11}$		$PbSO_4$	$1.3 \times 10^{-8}$
	$PbF_2$	$4.0 \times 10^{-8}$		$Ag_2SO_4$	$1.2 \times 10^{-5}$
	$MgF_2$	$8.0 \times 10^{-8}$		$SrSO_4$	$7.6 \times 10^{-7}$
Hydroxides	$SrF_2$	$7.9 \times 10^{-10}$	Sulfides	$CuS$	$8.0 \times 10^{-37}$
	$Al(OH)_3$	$5.0 \times 10^{-33}$		$FeS$	$6.3 \times 10^{-18}$
	$Ba(OH)_2$	$5.0 \times 10^{-3}$		$PbS$	$7.0 \times 10^{-29}$
	$Ca(OH)_2$	$1.4 \times 10^{-6}$		$HgS$	$1.6 \times 10^{-54}$
	$Cu(OH)_2$	$1.6 \times 10^{-19}$		$Ag_2S$	$5.5 \times 10^{-51}$

**Example 3.2.3. Solubility of  $\text{PbCl}_2$  (In-Class Exercise)**

Find the solubility of  $\text{PbCl}_2$  ( $K_{\text{sp}} = 1.7 \times 10^{-5}$ ) in water at 25 °C.

**Example 3.2.4. Solubility of  $\text{Sr}_3(\text{PO}_4)_2$  (In-Class Exercise)**

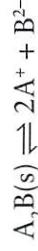
Find the solubility of  $\text{Sr}_3(\text{PO}_4)_2$  in water at 25 °C given its  $K_{\text{sp}} = 1.0 \times 10^{-31}$ . How many litres of water are required to dissolve 0.25 mol of  $\text{Sr}_3(\text{PO}_4)_2$ ?

**Example 3.2.5. Solubility and  $K_{\text{sp}}$  of  $\text{PbI}_2$  (In-Class Exercise)**

The solubility of lead iodide ( $\text{PbI}_2$ ) in water at 25 °C is 0.588 g L<sup>-1</sup>. What is the  $K_{\text{sp}}$  of  $\text{PbI}_2$ ?

**The Reaction Quotient,  $Q$** 

Suppose one dissolves the compound  $A_2B$  to produce a saturated solution:



The  $K_{sp}$  expression may be used for the system at equilibrium. The reaction quotient,  $Q$ , also known as the *ion product*, would be written:

$$Q = [A^+]^2 [B^{2-}]$$

For a saturated solution,  $Q = K_{sp}$  (the system is at equilibrium). As discussed in the previous topic, the reaction quotient expression is the same as the equilibrium constant expression except that the concentrations used to determine  $Q$  are not necessarily the equilibrium concentrations. At given concentrations of ions in solution, the  $K_{sp}$  value and the  $Q$  value can be compared to determine whether a solid (precipitate) will be present:

1. When  $Q < K_{sp}$ , no solid will be present. All ions will remain in solution.
2. When  $Q = K_{sp}$ , the system is in equilibrium (saturated).
3. When  $Q > K_{sp}$ , a solid will be formed from the ions in solution. This is a precipitation reaction and the solution is said to be *supersaturated* (i.e., the solution has an ion concentration greater than the equilibrium values).

The reaction quotient is especially useful when the ions that react to form a salt come from two different sources.

**Example 3.2.6. Precipitation of  $PbCl_2$  (In-Class Exercise)**

If 100 mL of 0.030 M  $Pb(NO_3)_2$  and 150 mL of 0.040 M  $KCl$  are mixed, does precipitation of  $PbCl_2$  ( $K_{sp} = 1.7 \times 10^{-5}$ ) occur?

**Example 3.2.7. Precipitation of  $\text{PbSO}_4$  (In-Class Exercise)**

How much solid  $\text{Pb}(\text{NO}_3)_2$  must be added to 10.0 L of 0.0010 M  $\text{Na}_2\text{SO}_4$  for a precipitate of  $\text{PbSO}_4$  ( $K_{\text{sp}} = 1.3 \times 10^{-8}$ ) to form? Assume no change in volume when the solid is added.

**Example 3.2.8. Determination of  $K_{\text{sp}}$  (In-Class Exercise)**

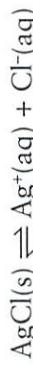
When 133 mL of 0.0500 M KF is added to 200 mL of 0.0100 M  $\text{Ba}(\text{NO}_3)_2$ , the first trace of  $\text{BaF}_2$  precipitate is seen. What is the  $K_{\text{sp}}$  for  $\text{BaF}_2$ ?

### THE COMMON ION EFFECT

Thus far the solubility of ionic solids in pure water has been discussed. Often the situation is more complex and the solution may already contain an ion in common with the dissolving salt. This *common ion effect* can significantly reduce the solubility of the solid relative to that in pure water.

In a previous example, the solubility of AgCl in pure water at 25 °C was found to be  $1.3 \times 10^{-5}$  M. How does one determine the solubility of AgCl in a solution where the  $[NaCl] = 0.20$  M? (NaCl is completely soluble; therefore,  $[Cl^-] = 0.20$  M.)

Let  $x$  be the number of moles of AgCl that must dissolve per litre (the solubility) to establish equilibrium. The equation for the dissolution of AgCl is:



Initial:	solid	0	0.20
Δ:	$-x$	$+x$	$+x$
Equil:	solid - $x$	$x$	$0.20 + x$

Now, at equilibrium:

$$K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10}$$

$$x(0.20 + x) = 1.7 \times 10^{-10}$$

This equation yields the quadratic  $x^2 + 0.20x = 1.7 \times 10^{-10}$ . This may be solved as is, or an approximation (simpler method) may be used. According to Le Châtelier's principle, adding  $Cl^-$  to the equilibrium will cause the reaction to shift to the left, toward the reactant (AgCl) side. Thus, very little extra  $Cl^-$  will be produced as a result of dissolution of AgCl and the value for  $x$  will be smaller than in pure water. In addition, AgCl is already only sparingly soluble ( $K_{sp} = 1.7 \times 10^{-10}$ ).

In this case it is reasonable to assume that  $x \ll 0.20$  or that:

$$0.20 + x \approx 0.20, \text{ therefore:}$$

$$x(0.2) = 1.7 \times 10^{-10}$$

$$x = 8.5 \times 10^{-10} M = \text{solubility of AgCl in } 0.20 \text{ M NaCl.}$$

The solubility of  $\text{AgCl}$  has been very substantially reduced over that in pure water (from  $1.3 \times 10^{-5} \text{ M}$  to  $8.5 \times 10^{-10} \text{ M}$ ). This reduction in solubility is the result of the common ion effect.

**Example 3.2.9. Solubility of  $\text{PbCl}_2$  in Aqueous KCl (In-Class Exercise)**

Find the solubility of  $\text{PbCl}_2$  ( $K_{\text{sp}} = 1.7 \times 10^{-5}$ ) in  $0.20 \text{ M}$  KCl. Compare your answer to that obtained in the "Solubility of  $\text{PbCl}_2$ " In-Class Exercise example on page 3-29.

**Example 3.2.10. Precipitation of  $\text{SrCrO}_4$  (In-Class Exercise)**

Find the concentrations of  $\text{Sr}^{2+}$  and  $\text{CrO}_4^{2-}$  remaining in solution after mixing  $50.0 \text{ mL}$  of  $0.30 \text{ M}$   $\text{Sr}(\text{NO}_3)_2$  with  $100 \text{ mL}$  of  $0.40 \text{ M}$   $\text{K}_2\text{CrO}_4$ .

$$K_{\text{sp}} \text{ for } \text{SrCrO}_4 = 3.6 \times 10^{-5}$$

### Section 3.2 Review Problems

- If the solubilities of  $\text{AgBr}$  and  $\text{SrF}_2$  are  $1.3 \times 10^{-4} \text{ g L}^{-1}$  and  $0.13 \text{ g L}^{-1}$  respectively, determine their  $K_{\text{sp}}$  values.
- What are the solubilities in  $\text{mol L}^{-1}$  of  $\text{MgCO}_3$  ( $K_{\text{sp}} = 1.0 \times 10^{-15}$ ) and  $\text{Mn}(\text{OH})_2$  ( $K_{\text{sp}} = 2.0 \times 10^{-13}$ )? What is the pH of a saturated solution of  $\text{Mn}(\text{OH})_2$ ?
- The solubility of strontium fluoride ( $\text{SrF}_2$ ) in water is  $0.109 \text{ g L}^{-1}$ . What is the  $K_{\text{sp}}$  of  $\text{SrF}_2$ ?
- For an ionic compound in solution, define the terms *ion product* (or *reaction quotient*,  $Q$ ) and *solubility product*,  $K_{\text{sp}}$ . Under what circumstances does  $Q$  equal the solubility product?
- The pH of a saturated solution of  $\text{Cd}(\text{OH})_2$  in pure water is 9.56.
  - How many grams of  $\text{Cd}(\text{OH})_2$  are dissolved in 1 L of this solution?
  - What volume of pure water would be needed to dissolve 1.0 g of  $\text{Cd}(\text{OH})_2$ ?
  - What is the  $K_{\text{sp}}$  for  $\text{Cd}(\text{OH})_2$ ?
- Which of the following statements is/are correct?
  - If solid AB is in equilibrium with an aqueous solution already containing  $[\text{A}^+]$  and  $[\text{B}^-]$  ions,  $[\text{A}^+]$  and  $[\text{B}^-]$  must always be equal.
  - $\text{PbCl}_2$  is less soluble in  $\text{KCl}$  solution than in pure water because the presence of  $\text{Cl}^-$  reduces the  $K_{\text{sp}}$  value of  $\text{PbCl}_2$ .
  - A slightly soluble metal hydroxide,  $\text{M}(\text{OH})_2$ , will dissolve more readily as the pH of the solution is increased.
- Manganese sulfide ( $\text{MnS}$ ) has  $K_{\text{sp}} = 5 \times 10^{-14}$ . What mass of solid manganese chloride ( $\text{MnCl}_2$ ) would have to be added to 100 mL of a  $0.025 \text{ M Na}_2\text{S}$  solution to cause precipitation of  $\text{MnS}$  to begin?
- A  $0.0010 \text{ M}$  solution of barium nitrate,  $\text{Ba}(\text{NO}_3)_2$ , is added gradually to 200 mL of  $0.040 \text{ M NaF}$ . Precipitation of  $\text{BaF}_2$  begins after 35 mL of the  $\text{Ba}(\text{NO}_3)_2$  solution have been added. What is the  $K_{\text{sp}}$  for  $\text{BaF}_2$ ?

9. When solid barium fluoride,  $\text{BaF}_2$ , equilibrates with pure water at  $25^\circ\text{C}$ , the fluoride concentration is  $0.015\text{ M}$ . Determine  $K_{\text{sp}}$  for  $\text{BaF}_2$ . What volume of water would be required to dissolve  $1.00\text{ g}$  of  $\text{BaF}_2$ ?
10. Lead hydroxide,  $\text{Pb}(\text{OH})_2$ , has  $K_{\text{sp}} = 4.2 \times 10^{-15}$ . What is the  $[\text{Pb}^{2+}]$  in a saturated solution of  $\text{Pb}(\text{OH})_2$  at a fixed pH of  $5.30$ ?
11. Joe Student is trying to make a very dilute  $\text{AgNO}_3$  solution by diluting  $1.0\text{ mL}$  of  $0.010\text{ M AgNO}_3$  to  $1.0\text{ L}$ . Carelessly, Joe uses tap water instead of distilled water for the dilution. If the tap water has a chloride ion concentration of  $2.0 \times 10^{-4}\text{ M}$ , will  $\text{AgCl}$  precipitate? ( $K_{\text{sp}}$  for  $\text{AgCl} = 1.7 \times 10^{-10}$ )
12.  $1 \times 10^{-4}\text{ M}$  potassium chromate ( $\text{K}_2\text{CrO}_4$ ) is added drop-by-drop to  $200\text{ mL}$  of  $0.0020\text{ M AgNO}_3$  solution. Precipitation of silver chromate ( $\text{Ag}_2\text{CrO}_4$ ) begins after  $0.50\text{ mL}$  of  $\text{K}_2\text{CrO}_4$  have been added. What is the  $K_{\text{sp}}$  for  $\text{Ag}_2\text{CrO}_4$ ?
13. In attempting to precipitate silver chloride,  $K_{\text{sp}} = 1.7 \times 10^{-10}$ , Jill Student adds  $50.0\text{ mL}$  of  $0.10\text{ M NaCl}$  solution to  $50.0\text{ mL}$  of  $0.050\text{ M AgNO}_3$  solution.
- How many milligrams of  $\text{AgCl}(\text{s})$  are precipitated?
  - What is the final  $[\text{Ag}^+]$  in the solution?
14. Calcium fluoride,  $\text{CaF}_2$ , has  $K_{\text{sp}} = 3.4 \times 10^{-11}$ .  $\text{CaF}_2$  will be used to fluoridate a municipal water supply in a hard-water area where  $[\text{Ca}^{2+}] = 0.070\text{ M}$ . What is the maximum  $\text{F}^-$  concentration, in  $\text{mol L}^{-1}$ , that can be achieved in this area by dissolving  $\text{CaF}_2$ ?
15. Silver hydroxide,  $\text{AgOH}$ , has  $K_{\text{sp}} = 2 \times 10^{-8}$ .
- What is the pH of a saturated solution of  $\text{AgOH}$ ?
  - What is the maximum pH possible for a solution in which  $[\text{Ag}^+] = 0.50\text{ M}$ ?
16. Ferric hydroxide,  $\text{Fe}(\text{OH})_3$ , is extremely insoluble, with  $K_{\text{sp}} = 1.0 \times 10^{-38}$ . What is the maximum pH that is possible in a solution of  $[\text{Fe}^{3+}] = 0.10\text{ M}$  before  $\text{Fe}(\text{OH})_3$  precipitates?



### 3.3 Weak Acids and Bases

#### OBJECTIVES

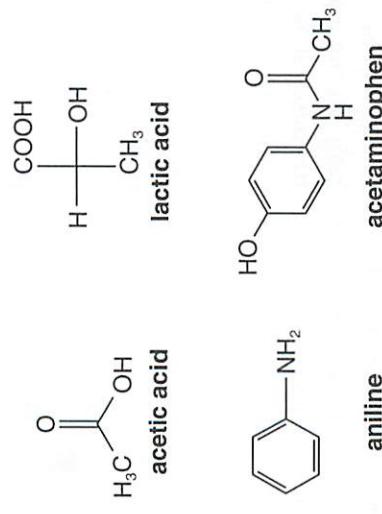
After studying this topic, you should to be able to:

- Explain the differences between the Arrhenius, Brønsted-Lowry, and Lewis acid-base theories.
- Predict the acid–base behaviour of a compound based on its structure.
- Identify conjugate species of acids and bases.
- Perform calculations using equilibrium constants for various weak acid and weak base solutions.
- Predict the acid–base properties of salt solutions and determine their pH.
- Use structural factors to predict the relative strengths of weak acids.

#### INTRODUCTION

Acids are often defined as substances that increase hydrogen ion concentration,  $[H^+]$ , in solution, while bases are often defined as those substances that increase hydroxide ion concentration,  $[OH^-]$ , in solution. The terms *strong* and *weak* are used to described the behaviour of acids and bases, and have nothing to do with “hole burning” power or acid/base concentration. Strong acids and bases completely ionize in solution, whereas weak acids and bases do not ionize completely. Weak acid and weak base reactions proceed until an equilibrium is achieved between the reactants and products.

Weak acids and weak bases are encountered almost everywhere. Acetic acid, for example, is a well-known weak acid formed during the fermentation of ethanol. At approximately 5% to 8% concentration by volume, it is sold worldwide as table vinegar; at higher concentrations it is used in home and commercial food pickling. Lactic acid is a weak acid prevalent in sour dairy products, sausages, and fermenting fruit and vegetables. It is found in most living organisms, including bacteria, and has been consumed by humans throughout history. Lactic acid is also a by-product of anaerobic energy production in muscle tissue and has a crucial role related to the supply of that energy. Acetaminophen, an analgesic, is another weak acid.



Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution is a common weak base and among other things, is an effective cleaning product (pungent odour notwithstanding). Another important weak base, aniline, is used in the production of commercial dyes, polyurethane, and acetaminophen. In this topic, the behaviour of weak acids and bases is examined.

## ACID–BASE TERMINOLOGY

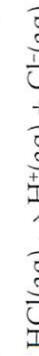
### Strong Acids and Bases

As previously mentioned, strong acids and bases are those that completely ionize in solution. Acids increase  $[\text{H}^+]$  while bases increase  $[\text{OH}^-]$ . Since  $\text{H}^+$  is really just a proton, it cannot exist in solution as such. Thus when an acid is in an aqueous solution, the  $\text{H}^+$  released from the acid combines with water to form  $\text{H}_3\text{O}^+$ . However, for convenience, the terms  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  are used interchangeably.

HCl is an example of a strong acid. When dissolved in water, 1 mol HCl produces 1 mol  $\text{H}^+$  ( $\text{H}_3\text{O}^+$ ) and 1 mol  $\text{Cl}^-$ :

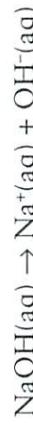


Often, the water in this equation is omitted and the equation is simply written as:



with the (aq) designation indicating that the reaction takes place in water. Other examples of strong acids include  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$ .

NaOH is an example of a strong base. 1 mol of NaOH provides 1 mol of Na<sup>+</sup> and 1 mol of OH<sup>-</sup> as shown in the following equation:



Other examples of strong bases include KOH, Mg(OH)<sub>2</sub>, and Ca(OH)<sub>2</sub>.

### Arrhenius and Brønsted-Lowry Acids and Bases

In the equations above, a unidirectional arrow ( $\rightarrow$ ) was used to indicate that the reactions proceed completely to the product side. In other words, strong acids and bases ionize completely in solution.

The two examples above also illustrate the Arrhenius theory of acids and bases, which states:

- An acid produces H<sub>3</sub>O<sup>+</sup> ions in water.
- A base produces OH<sup>-</sup> ions in water.

The Brønsted-Lowry theory of acid-base behaviour is more general than the Arrhenius theory, and is especially useful for weak acids and bases:

- An acid is a proton donor.
- A base is a proton acceptor.

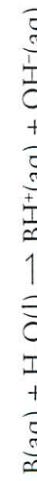
Recall that weak acids and bases do not ionize completely in solution; the reactions proceed until an equilibrium is achieved between reactants and products. When a weak acid (HA) ionizes, it donates a hydrogen ion to water (proton donor) as shown in the equilibrium reaction below.



The weak acid equilibrium equation is often simplified to:



When a weak base (B) ionizes, it accepts a hydrogen ion (proton acceptor) from water or another compound acting as an acid. The weak base equilibrium reaction is written as:



For weak acids, the subscript ‘a’ is added to the equilibrium constant symbol, which becomes  $K_a$ . For weak bases, the subscript ‘b’ is added and the equilibrium constant symbol becomes  $K_b$ .

### Lewis Acids and Bases

The Arrhenius and Bronsted-Lowry definitions of acids and bases are very useful for many applications. In some cases, however, it is advantageous to generalize the concept of acids and bases to include even those reactions where no  $H^+$  and  $OH^-$  species are involved. This generalization was proposed by Gilbert Lewis.

A *Lewis acid* is a substance that can accept a pair of electrons from another atom to form a bond. A *Lewis base* is a substance that donates a pair of electrons to another atom to form a bond. The species formed in this reaction is called an acid–base *adduct* as shown in the generic equation:



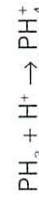
where A represents the acid, B represents the base and  $B \rightarrow A$  represents the acid–base adduct. Note that in this context, the arrow in  $B \rightarrow A$  indicates the species donating the pair of electrons (it is not a reaction arrow). The reaction between the hydrogen ion and water is of this type:



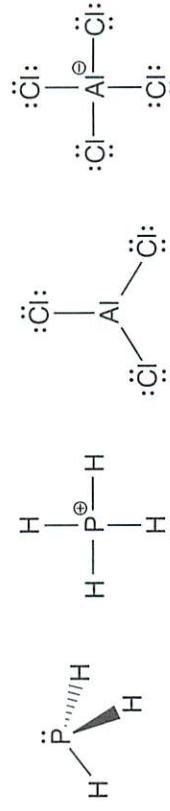
Here, the hydrogen ion acts as a Lewis acid, the water (with two nonbonding pairs of electrons on the oxygen) acts as a Lewis base, and the hydronium ion is the adduct.

**Example 3.3.1. Identifying Lewis Acids and Bases**

Identify  $\text{PH}_3$  and  $\text{AlCl}_3$  as either a Lewis acid or a Lewis base in the following reactions:



**Solution:** The Lewis structure for each molecule is shown below:



The phosphorous atom in  $\text{PH}_3$  bears a nonbonding pair of electrons, which is used to form a bond in  $\text{PH}_4^+$ . Hence  $\text{PH}_3$  is a Lewis base.

In  $\text{AlCl}_3$  the central Al atom has an incomplete octet. It readily accepts electrons from another species and in doing so, acts as a Lewis acid:

**Ammonia and Amines**

The nitrogen atom of  $\text{NH}_3$  carries a nonbonding pair of electrons. Therefore, the  $\text{NH}_3$  molecule can act as a Lewis base. In particular, when ammonia reacts with water, the nonbonding pair of electrons attracts the partially positive hydrogen of water and, in the subsequent reaction, forms a new N–H bond. The overall reaction is



Amines may be viewed as ammonia molecules in which one or more of the H atoms are substituted by alkyl groups. The simplest amine is methylamine,  $\text{CH}_3\text{NH}_2$ . The reaction of amines with water is analogous to that of ammonia. For example, methylamine reacts with water as follows:



### Metal Cations

Metal cations are another group of species that can act as Lewis acids. These ions form complex ions, known as *coordination complexes*, when they react with Lewis bases such as water ( $\text{H}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), or the hydroxide ion ( $\text{OH}^-$ ). For example:



### Oxides of Nonmetals

Some compounds, especially the oxides of nonmetals, behave as Lewis acids when they react with hydroxide. For example, carbon dioxide ( $\text{CO}_2$ ) reacts with  $\text{OH}^-$  to form bicarbonate ( $\text{HCO}_3^-$ ),



This reaction is currently investigated as a potential method to remove carbon dioxide from the atmosphere.

### EQUILIBRIUM CONSTANTS, pH, AND PERCENT IONIZATION

Weak acid and weak base equilibrium reactions are governed by the equilibrium constant expression,  $K$ , with subscripts a for weak acids and b for weak bases.

For  $\text{HA}$  (weak acid):



For  $\text{B}$  (weak base):



Recall that the magnitude of the equilibrium constant is a measure of the extent of the forward reaction: if  $K > 1$ , the equilibrium lies to the right and if  $K < 1$ , the equilibrium lies to the left.

In the case of weak acids and bases, their  $K_a$  and  $K_b$  values are, by definition, much less than one. Some weak acids and bases are stronger than others, and this is reflected in their respective  $K_a$  or  $K_b$  values (the larger the  $K$  value, the greater the ionization).

For example, acetic acid ( $\text{CH}_3\text{COOH}$ ) is a weak acid ( $K_a = 1.8 \times 10^{-5}$ ), and trichloroacetic acid ( $\text{CCl}_3\text{COOH}$ ) is a much stronger weak acid ( $K_a = 2.0 \times 10^{-1}$ ). Note that  $\text{CCl}_3\text{COOH}$  is a stronger weak acid, but it still isn't a strong acid. “Stronger” merely refers to the fact that it ionizes to a greater extent.

Similarly, ammonia ( $\text{NH}_3$ ) is a weak base ( $K_b = 1.8 \times 10^{-5}$ ), and methylamine ( $\text{CH}_3\text{NH}_2$ ) is a slightly stronger weak base ( $K_b = 6.4 \times 10^{-4}$ ).

$K_a$  and  $K_b$  values are often expressed using a logarithmic scale as follows:

$$\text{p}K_a = -\log K_a \quad \text{and} \quad \text{p}K_b = -\log K_b$$

Thus for acetic acid:  $\text{p}K_a = 4.74$ , and for trichloroacetic acid:  $\text{p}K_a = 0.70$

A comparison of the  $\text{p}K_a$  values for the two acids above shows that the numerical value of  $\text{p}K_a$  becomes smaller as the strength of the acid ( $K_a$ ) increases. The  $K_a$  and  $K_b$  for a selection of weak acids and bases, along with the corresponding  $\text{p}K_a$  and  $\text{p}K_b$  values, are shown in Table 3.3.1 and Table 3.3.2, respectively.

Although all weak acids have  $K_a$  values that are much less than one, weak acids vary considerably in strength. Some weak acids are stronger (larger  $K_a$ ), while others are weaker (smaller  $K_a$ ). Therefore, “stronger” and “weaker” are relative terms.

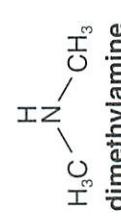
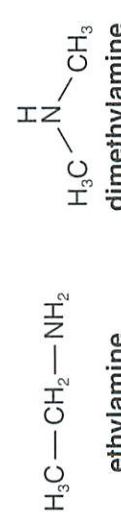
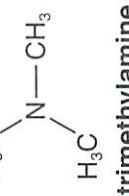
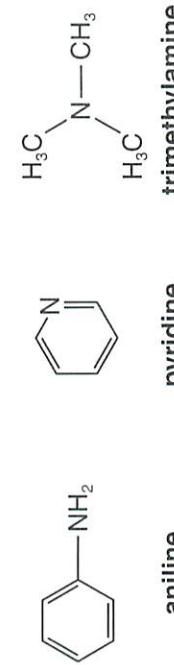
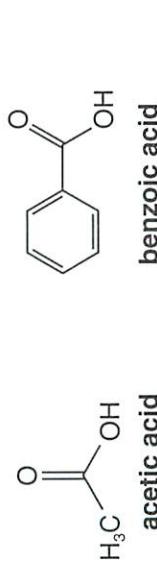


TABLE 3.3.1 EQUILIBRIUM CONSTANTS FOR SELECTED BRØNSTED-LOWRY WEAK ACIDS

WEAK ACID	$K_a$	$pK_a$
Hydrocyanic acid, HCN	$4.0 \times 10^{-10}$	9.40
Hypochlorous acid, HClO	$3.5 \times 10^{-8}$	7.46
Acetic acid, $\text{CH}_3\text{COOH}$	$1.8 \times 10^{-5}$	4.74
Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$	$6.3 \times 10^{-5}$	4.20
Formic acid, HCOOH	$1.9 \times 10^{-4}$	3.72
Nitrous acid, $\text{HNO}_2$	$4.5 \times 10^{-4}$	3.35
Hydrofluoric acid, HF	$6.7 \times 10^{-4}$	3.17
Trichloroacetic acid, $\text{Cl}_3\text{CCOOH}$	$2.0 \times 10^{-1}$	0.70

TABLE 3.3.2 EQUILIBRIUM CONSTANTS FOR SELECTED BRØNSTED-LOWRY WEAK BASES

WEAK BASE	$K_b$	$pK_b$
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	$7.4 \times 10^{-10}$	9.13
Pyridine, $\text{C}_5\text{H}_5\text{N}$	$1.5 \times 10^{-9}$	8.82
Ammonia, $\text{NH}_3$	$1.8 \times 10^{-5}$	4.74
Trimethylamine, $(\text{CH}_3)_3\text{N}$	$7.4 \times 10^{-5}$	4.13
Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$	$4.3 \times 10^{-4}$	3.37
Methylamine, $\text{CH}_3\text{NH}_2$	$6.4 \times 10^{-4}$	3.19
Dimethylamine, $(\text{CH}_3)_2\text{NH}$	$7.4 \times 10^{-4}$	3.13



### Weak Acid and Weak Base Calculations

Determination of the pH for solutions of strong acids and strong bases was straightforward (see the General Review in Chem 1301A). Because dissolved strong acids and strong bases are completely ionized, the concentration of  $\text{H}^+$  in a solution of a strong acid is simply the total concentration of the acid times the number of protons in each acid molecule. Similarly, the concentration of  $\text{OH}^-$  in a solution of a strong base such as NaOH is the total concentration of NaOH.

Determination of the pH for solutions of weak acids and bases is more involved because only a fraction of the dissolved molecules will ionize to form  $\text{H}^+$  (acid) or  $\text{OH}^-$  (base).

The method for determining the pH for solutions of weak acids and weak bases is explained below. Note that the following three relations still apply:

$$\text{pH} = -\log[\text{H}^+] \quad \text{pOH} = -\log[\text{OH}^-]$$

### pH and Percent Ionization of Weak Acids

The  $K_a$  for acetic acid ( $\text{CH}_3\text{COOH}$ ) is  $1.8 \times 10^{-5}$ . In a solution of  $\text{CH}_3\text{COOH}$  the initial concentration may be represented by  $c$ , and the amount of  $\text{CH}_3\text{COO}^-$  that ionizes may be represented by  $x$  because it is in a 1:1 ratio. The concentrations of  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  that result from this ionization are also represented by  $x$ . The equilibrium for this reaction is written as:



Initial:	$c$	0	0
Equilibrium:	$c - x$	$x$	$x$

The equilibrium constant expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{c - x}$$

To solve for  $x$ ,  $K_a = \frac{x^2}{c - x}$  has to be expanded into a quadratic equation:

$$x^2 + K_a x - K_a c = 0$$

which corresponds to  $ax^2 + bx + d = 0$  and can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ad}}{2a} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_a c}}{2}$$

*Because of the  $\pm$  sign, the quadratic formula will give two values of  $x$ , but only a positive concentration is possible.*

If the initial concentration (denoted by  $c$ ) of  $\text{CH}_3\text{COOH}$  is  $0.100\text{ M}$ , this value and the value of  $K_a$  may be substituted into the quadratic formula.

The result is:  $x = 1.33 \times 10^{-3}\text{ M} = [\text{H}_3\text{O}^+]$ , and the  $\text{pH} = 2.875$

Percent ionization,  $\alpha$ , is the amount of the weak acid ionized (or dissociated) expressed as a percent of the original concentration of the acid, using the relationship:

$$\alpha = \frac{x}{c} \times 100\%$$

Therefore, in this example  $\alpha = \frac{1.33 \times 10^{-3}}{0.100} \times 100\% = 1.33\%$ .

To simplify the arithmetic, if  $\alpha$  is less than 5%, the approximation that  $x$  is much smaller than  $c$  is used. This makes  $c - x \approx c$  and therefore:

$$K_a \approx \frac{x^2}{c} \text{ or } x = \sqrt{cK_a} = [\text{H}_3\text{O}^+]$$

With  $c = 0.100\text{ M}$  and  $K_a = 1.8 \times 10^{-5}$ ,  $x = [\text{H}_3\text{O}^+] = 1.342 \times 10^{-3}\text{ M}$  and the pH = 2.872. The percent ionization in this case is 1.342%.

When the two results in the example are compared, it is apparent that there is little difference between the exact answer obtained using the quadratic formula and the answer obtained using the approximation. In fact, the “error” in the approximated answer is less than 1%. Using the simpler method will save time, but there may be instances where the approximation will be poor. How does one know when it is OK to use the approximation  $c - x \approx c$ ? You may use either of the following tests.

1. Calculate the ratio for  $c/K_a$ . If the result is greater than about 400, then the approximation  $c - x \approx c$  is acceptable. If the result is less than 400, then the approximation is too crude and the quadratic formula should be used.
2. If  $\alpha$  is less than 5%, the approximation  $c - x \approx c$  is acceptable. This test is less helpful, however, because you normally do not know  $\alpha$  until after you have solved for  $x$ .

If the equilibrium concentrations of all species are known, a value for  $K_a$  may be calculated. It is also possible to calculate the initial concentration of the weak acid. For these calculations, the exact form of the equilibrium constant expression should always be used. Simply put: Do not neglect  $x$  with respect to  $c$  if you know what  $x$  is. In other words, if you know  $x$ , use it!

#### Example 3.3.2. Percent Ionization and $K_a$ of a Weak Acid (In-Class Exercise)

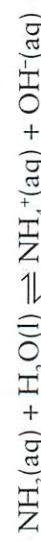
A 0.0250 M solution of a weak acid, HA, has a pH of 2.75. Determine the percent ionization of the acid and its  $K_a$ .

**Example 3.3.3. Concentration of Nitrous Acid (In-Class Exercise)**

Nitrous acid,  $\text{HNO}_2$ , has  $K_a = 4.5 \times 10^{-4}$ . Determine the initial concentration of  $\text{HNO}_2$  if a solution of this acid has a pH of 3.65.

**pH and Percent Ionization of Weak Bases**

Up to this point, the focus has been on the ionization of weak acids. The same principles apply to the reactions of weak bases with water. Consider a solution of 0.100 M  $\text{NH}_3$ . The  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ . The equilibrium is written as:



Equilibrium:  $\begin{array}{ccc} c-x & & x \\ x & & x \end{array}$

$$\text{and } K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{c-x}$$

Solving for  $x$  using the  $K_b$  expression follows the same steps as solving for  $x$  using the  $K_a$  expression. (The approximation that  $c - x \approx c$  can be made, etc.)

When solving for  $x$  using the  $K_b$  expression, the  $[\text{OH}^-]$  is determined. Therefore, if the pH of the solution is required, it can be calculated from the pOH.

**Example 3.3.4. Concentration and Percent Ionization of Methylamine (In-Class Exercise)**

A solution of methylamine ( $\text{CH}_3\text{NH}_2$ ) has a pH of 10.45 and the  $K_b$  for  $\text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}$ . Calculate the initial concentration of methylamine and the % ionization of methylamine.

**Effect of Dilution on Percent Ionization**

The results contained in the previous “Methylamine” In-Class Exercise example indicate that for a solution of  $\text{CH}_3\text{NH}_2$  with an initial concentration of  $4.06 \times 10^{-4} \text{ M}$ , the percent ionization is 69.4%. If the initial concentration of  $\text{CH}_3\text{NH}_2$  was 0.400 M, the percent ionization is 4.0% and the pH of the solution is 12.20. A comparison of these results seems to indicate that the more dilute the solution of a weak acid or base, the greater the *percent* ionization.

Because the  $K_a$  or  $K_b$  for the weak acid or base does not change, there must be changes to the concentrations of the products at equilibrium when the initial concentration of acid or base is decreased by dilution. This trend is shown in Table 3.3.3 for HF. Be sure to understand the *chemical basis behind this trend*.

TABLE 3.3.3 EFFECT OF DILUTION ON PERCENT IONIZATION AND pH

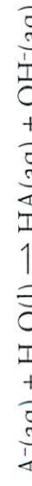
INITIAL [HF]	EQUILIBRIUM $[H^+]$	$\alpha$	pH
1.0	$2.6 \times 10^{-2}$	2.6%	1.59
0.10	$7.9 \times 10^{-3}$	7.9%	2.10
0.010	$2.3 \times 10^{-3}$	22%	2.64

### CONJUGATE SPECIES

The *conjugate base* of an acid is the species formed when the acid has donated a proton. Conversely, the *conjugate acid* of a base is the species formed when the base has accepted a proton. For example, in the equation describing the ionization of a weak acid in solution:



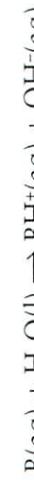
$A^-$  is the *conjugate base* of the weak acid HA. The conjugate base will behave like a weak base when in solution:



This solution will be basic due to the hydroxide ion produced in the reaction. As this is an equilibrium reaction, the conjugate base will have an equilibrium constant expression:

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Similarly, in the equation describing the dissociation of a weak base B,



the species  $BH^+$  is the *conjugate acid* of the weak base B. The conjugate acid will behave like a weak acid in solution:



and will have an equilibrium constant expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{B}]}{[\text{BH}^+]}$$

This solution will be acidic due to the hydronium ion produced in the reaction.

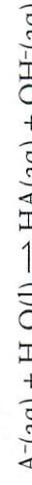
### Equilibrium Constant $K_w$

The equilibrium constant for the ionization of water:

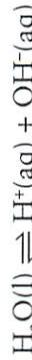


$$\text{is } K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C).}$$

Now consider the ionization equilibria of a weak acid (HA) and its conjugate base:



There is an important relationship between the  $K_a$  for a weak acid and  $K_b$  for its conjugate base. Addition of the two equations above yields:



When two equations are added, the equilibrium constants are multiplied in order to determine the equilibrium constant for the resultant equation. Therefore:

$$K_a \times K_b = K_w$$

and this result holds for any conjugate acid–base pair. ( $K_w$  is also known as the *ion product of water*.) Another way to illustrate the  $K_a$ ,  $K_b$ , and  $K_w$  relationship is:

$$K_w = K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{Alternatively: } \text{p}K_a + \text{p}K_b = 14$$

The relationship between equilibrium constants shows that the stronger the weak acid is, the weaker the weak conjugate base will be. Acetic acid, for example, has  $K_a = 1.8 \times 10^{-5}$  while its conjugate base (the acetate ion) has a  $K_b = 5.6 \times 10^{-10}$ . Formic acid is stronger (has a larger  $K_a$  value) than acetic acid, so it follows that formate is a weaker base than acetate.

By the same token, strong acids have extremely weak conjugate bases. In fact, their bases are so weak that they are called *spectator ions* and do not affect pH at all. When HCl ionizes, the Cl<sup>-</sup> produced is a spectator ion.

### Salts

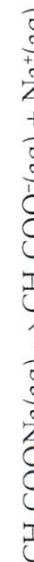
A salt is an ionic solid containing cations (other than just H<sup>+</sup>) and anions. When a salt dissolves in water, its cation and anion separate from each other. The salt may not be very soluble, but whatever dissolves is completely ionized.

Cations that do not have any effect on pH (i.e., do not react with water) are spectator ions. Most monovalent and divalent metal ions such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup> act as spectator ions. Similarly, many anions act as spectator ions and do not affect pH. This is the case for the conjugate bases of strong acids (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). Some cations, such as NH<sub>4</sub><sup>+</sup> and related ammonium species, act as weak acids:



NH<sub>4</sub><sup>+</sup> is the conjugate acid of the weak base NH<sub>3</sub>; therefore, a solution of ammonium chloride (NH<sub>4</sub>Cl) is acidic.

Anions that are the conjugate bases of weak acids act as weak bases (F<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, etc.). For example, sodium acetate (CH<sub>3</sub>COONa) will ionize in water according to:



Because CH<sub>3</sub>COO<sup>-</sup> is the conjugate base of CH<sub>3</sub>COOH and, as stated, Na<sup>+</sup> ions have no effect on pH, it follows that a solution of CH<sub>3</sub>COONa will be basic due to the reaction of acetate, CH<sub>3</sub>COO<sup>-</sup>, with water (hydrolysis):



In the examples considered so far, only one of the ions had an effect on pH, while the other one was a spectator ion. What if the cation AND anion can affect the pH? If K<sub>a</sub> > K<sub>b</sub>, the salt is acidic. A solution of NH<sub>4</sub>F is acidic:



Conversely, if K<sub>b</sub> > K<sub>a</sub> the salt is basic. A solution of NH<sub>4</sub>ClO is basic:



A similar argument can be used to decide if an *amphiprotic anion* (a species that can act as both an acid or a base) will be acidic or basic.



A solution of  $\text{NaHCO}_3$  (sodium bicarbonate or baking soda) is basic since  $K_b + K_a$ . This is why  $\text{NaHCO}_3$  is often used to neutralize acid spills.

### Calculations with Conjugate Species and Salts

Because a conjugate base behaves like a weak base, and a conjugate acid behaves like a weak acid, the approach to finding the pH (or other properties) of these solutions is similar to the examples already shown. However, it may be necessary to determine which, if any, species will set up an equilibrium.

#### Example 3.3.5. pH of KCN (In-Class Exercise)

Determine the pH of a 0.100 M solution of KCN.

Data:  $K_a$  for HCN =  $4.0 \times 10^{-10}$

#### Example 3.3.6. Determination of $K_a$ from pH of Salt (In-Class Exercise)

A 0.285 M solution of the sodium salt, NaA, of the weak monoprotic acid, HA, has a pH of 9.65. Determine  $K_a$  for the acid HA.

### THE COMMON ION EFFECT

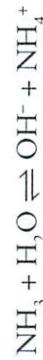
The effect of a *common ion* with respect to the solubility of an ionic solid was previously discussed in the *Solubility of Ionic Compounds* section. The common ion effect may also come into play when discussing the ionization of weak acids and bases. In this section, the effect of an additional source of  $\text{H}_3\text{O}^+$  (in the case of acids) or  $\text{OH}^-$  (in the case of bases) on the ionization of a weak acid or base is examined.

In a solution of a weak acid and a strong acid, there are two sources of the  $\text{H}_3\text{O}^+$  ion. For example, if a strong acid such as HCl is added to a weak acid such as  $\text{CH}_3\text{COOH}$ , both the HCl and  $\text{CH}_3\text{COOH}$  produce  $\text{H}_3\text{O}^+$ . The  $\text{H}_3\text{O}^+$  is therefore a common ion. In the equilibrium reaction shown below, when  $\text{H}_3\text{O}^+$  is added the equilibrium shifts in the reverse direction and the concentration of the anion,  $\text{CH}_3\text{COO}^-$ , is reduced. This is known as the *common ion effect* and is really just an example of Le Châtelier's principle. Note that the amount of  $\text{H}_3\text{O}^+$  produced by the dissociation of the weak acid is negligible when compared to that produced by the strong acid.



$\leftarrow \text{H}_3\text{O}^+$  added from HCl

In a similar fashion, when a strong base such as NaOH is put in solution with a weak base such as  $\text{NH}_3$ , the addition of the common ion  $\text{OH}^-$  shifts the equilibrium in the reverse direction, away from  $\text{NH}_4^+$  production.



$\leftarrow \text{OH}^-$  added from NaOH

### Example 3.3.7. Common Ion Effect

Determine the pH and percent ionization of a 0.10 M  $\text{CH}_3\text{COOH}$  solution ( $K_a = 1.8 \times 10^{-5}$ ) that also contains 0.050 M HCl.

**Solution:** First consider the equilibrium without the HCl:

$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
Initial:	0.10	0
Equilibrium:	$0.10 - x$	$x$

Now consider the equation for the ionization of HCl:

$\text{HCl}(\text{aq}) + \text{H}_2\text{O}(l)$	$\rightarrow$	$\text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
Initial:	0.050	0
After:	0	0.050 0.050

The easiest way to deal with the addition of the HCl is to assume that the  $\text{H}_3\text{O}^+$  is present in the solution before the  $\text{CH}_3\text{COOH}$  starts to ionize. Since the initial concentration of  $\text{CH}_3\text{COO}^-(\text{aq})$  is 0, the reaction must proceed to the right.



Initial:	0.10	0	0
Equilibrium:	$0.10 - x$	$0.050 + x$	$x$

The equilibrium constant expression is:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Substituting the equilibrium concentrations:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.050 + x)(x)}{0.10 - x}$$

Inspection of the initial concentration of the weak acid and  $K_a$  indicates that the approximation  $0.10 - x \approx 0.10$  is valid. Can the same be said about the concentration of  $\text{H}_3\text{O}^+$ ? Is it safe to say that  $0.050 - x \approx 0.050$ ? Since there is no mathematical test that can be performed, a little logic is required. If the approximation  $0.10 - x \approx 0.10$  is valid, then  $x$  must be a small number. The presence of the common ion means that even less weak acid will ionize. Therefore,  $x$  is smaller in the presence of a common ion. It follows then that the approximation  $0.050 - x \approx 0.050$  is valid.

The equilibrium constant expression is now simplified:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.050)(x)}{0.10}$$

$$\text{So } x = 3.6 \times 10^{-5} \text{ M} = [\text{CH}_3\text{COO}^-]$$

Note that in this example,  $x \neq [\text{H}_3\text{O}^+]$  because there is also  $\text{H}_3\text{O}^+$  present from the ionization of HCl. Strictly speaking,  $[\text{H}_3\text{O}^+] = 0.050 + 3.6 \times 10^{-5}$ , but it should be apparent that the small amount of  $\text{H}_3\text{O}^+$  that is produced by the ionization of  $\text{CH}_3\text{COOH}$  is negligible with respect to 0.050 M.

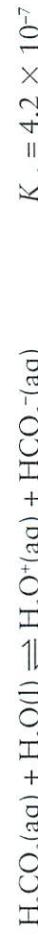
If  $[\text{H}_3\text{O}^+] = 0.050$ , then  $\text{pH} = 1.30$ . To solve for percent ionization, the expression is:

$$\alpha = \frac{x}{C} \times 100\% = \frac{3.6 \times 10^{-5}}{0.10} \times 100\% = 0.036\%$$

Compare this result with the percent ionization calculated for the 0.100 M solution of CH<sub>3</sub>COOH in water (1.33%). The difference in the two results clearly shows the effect of the common ion — it suppresses the ionization of the weak acid quite dramatically. As with all previous examples, what holds true for a weak acid will also hold true for a weak base. Adding a strong base will suppress the ionization of the weak base.

### POLYPROTIC WEAK ACIDS

Some weak acids are *polyprotic*, which means that they contain more than one ionizable hydrogen atom. When these acids ionize, they do so in stages, each with a different K<sub>a</sub> value. One example is the weak *diprotic* acid, carbonic acid (H<sub>2</sub>CO<sub>3</sub>):



Note that K<sub>a1</sub> is quite a bit larger than K<sub>a2</sub>. This means that the amount of H<sub>2</sub>CO<sub>3</sub> ionized is considerably greater than the amount of HCO<sub>3</sub><sup>-</sup> dissociated. It follows, then, that although H<sub>3</sub>O<sup>+</sup> is produced in both steps, the pH of the solution is overwhelmingly due to the H<sub>3</sub>O<sup>+</sup> produced in the first step. K<sub>a2</sub> is much smaller because the conjugate base from the second ionization has two negative charges and is therefore less stable than the conjugate base from the first ionization.

This is an example of a simultaneous equilibria (both reactions are happening at the same time). As a result, both the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) and the carbonate ion (CO<sub>3</sub><sup>2-</sup>) are present in the equilibrium mixture. In order to determine the equilibrium concentrations of these species, each equilibrium must be analyzed separately.

**Example 3.3.8. pH of  $\text{H}_2\text{CO}_3$  Solution**

Find the pH,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$  for a 0.250 M solution of  $\text{H}_2\text{CO}_3$  with the  $K_a$  values from above.

**Solution:** This is a diprotic acid, so each step must be considered separately.



Initial:	0.250	0	0
Equilibrium:	$0.250 - x$	$x$	$x$

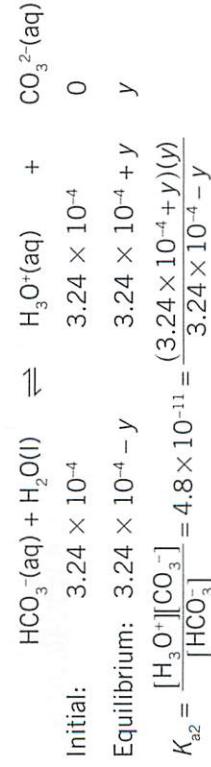
$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.2 \times 10^{-7} = \frac{x^2}{0.250 - x}$$

Comparing 0.250 and  $K_1$  shows that the approximation  $0.250 - x \approx 0.250$  is valid, so solving for  $x$  gives:

$$x = \sqrt{0.250 \times 4.2 \times 10^{-7}} = 3.24 \times 10^{-4} = [\text{H}_3\text{O}^+] = [\text{HCO}_3^-]$$

$$\text{The percent ionization in Step 1: } \alpha = \frac{3.24 \times 10^{-4}}{0.250} \times 100\% = 0.13\%$$

**Step 2:** In the second step, the equilibrium is set up the same way as in Step 1, but the initial concentrations used in Step 2 are the equilibrium concentrations of those species determined in Step 1. In Step 2, the variable  $y$  is used to denote the amount of  $\text{HCO}_3^-$  ionized.



This is another example of a common ion equilibrium ( $\text{H}_3\text{O}^+$  is common to both Step 1 and Step 2). The concentration of this common ion is the sum of the amounts produced in both steps:

$$3.24 \times 10^{-4} \text{ from Step 1 and } y \text{ from Step 2.}$$

Due to the common ion effect, the value of  $y$  will be quite small, even relative to  $3.24 \times 10^{-4}$ . The approximation  $3.24 \times 10^{-4} - y \approx 3.24 \times 10^{-4}$  may therefore be used. This approximation can be validated by comparing the initial concentration of  $\text{HCO}_3^-$  and  $K_{a2}$  from Step 2.

If the approximation that  $3.24 \times 10^{-4} - y \approx 3.24 \times 10^{-4}$  is valid, then the approximation that  $3.24 \times 10^{-4} + y \approx 3.24 \times 10^{-4}$  must also be valid.

$$\text{Therefore: } 4.8 \times 10^{-11} = \frac{(3.24 \times 10^{-4})(y)}{3.24 \times 10^{-4}} = y = [\text{CO}_3^{2-}]$$

Note that this is a general result for a weak polyprotic acid. The concentration of the  $2-$ -species ( $\text{CO}_3^{2-}$  in this case) is numerically equal to  $K_{a2}$ . No calculation is needed.

$$\text{The percent ionization in Step 2: } \alpha = \frac{4.8 \times 10^{-11}}{3.24 \times 10^{-4}} \times 100\% = 1.48 \times 10^{-5}\%$$

The concentrations of all species at equilibrium are:

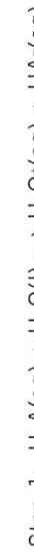
$$[\text{H}_2\text{CO}_3] = 0.250 \text{ M} - 3.24 \times 10^{-4} \text{ M} \approx 0.250 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 3.24 \times 10^{-4} \text{ M} + 4.8 \times 10^{-11} \text{ M} \approx 3.24 \times 10^{-4} \text{ M}$$

$$[\text{HCO}_3^-] = 3.24 \times 10^{-4} \text{ M} - 4.8 \times 10^{-11} \text{ M} \approx 3.24 \times 10^{-4} \text{ M}$$

$$[\text{CO}_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$$

The results of these calculations lead to the following general statement about weak diprotic acids ( $\text{H}_2\text{A}$ ) in water: For diprotic acids with  $K_{a2} \ll K_{a1}$ , the  $[\text{A}^{2-}]$  is equal to  $K_{a2}$ , and the pH of the solution is primarily determined by the  $\text{H}_3\text{O}^+$  obtained from the first ionization (Step 1).



#### Example 3.3.9. pH of $\text{Na}_2\text{CO}_3$ Solution (In-Class Exercise)

The method used for carbonic acid is also applicable to the conjugate bases of polyprotic acids that could only act as bases, that is, the conjugate base formed from the last ionization of the acid. Determine the pH of a  $0.165 \text{ M}$  solution of  $\text{Na}_2\text{CO}_3$ . Use  $K_{a1}$  and  $K_{a2}$  for  $\text{H}_2\text{CO}_3$  as required.

The previous examples involved a solution of  $\text{H}_2\text{CO}_3$ , which could only act as an acid, and a solution of  $\text{CO}_3^{2-}$ , which could only act as a base. How about species such as  $\text{HCO}_3^-$ , which could act as a base and as an acid? Will a solution of  $\text{NaHCO}_3$  (baking soda) be acidic or basic? When baking soda is dissolved in water, two reactions are possible.

If bicarbonate acts as an acid:



If bicarbonate acts as a base:



$$K_b \text{ of } \text{HCO}_3^- = \frac{K_w}{K_a \text{ of } \text{H}_2\text{CO}_3} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-7}} = 2.38 \times 10^{-8}$$

A comparison of the  $K_a$  and  $K_b$  values for  $\text{HCO}_3^-$  shows that the  $K_b$  is approximately three orders of magnitude greater than the value of  $K_a$ . That is,  $\text{HCO}_3^-$  is much more likely to act as a base than as an acid. That is why solutions of sodium bicarbonate are frequently used in labs to neutralize acid spills, and also why baking soda reacts with vinegar!

#### Example 3.3.10. pH of $\text{KH}_2\text{PO}_4$ Solution (In-Class Exercise)

Predict whether a solution of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) will be acidic or basic.

The  $K_a$  values for phosphoric acid,  $\text{H}_3\text{PO}_4$  are:

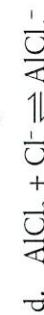
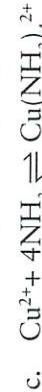
$$\text{H}_3\text{PO}_4 : K_{a1} = 7.1 \times 10^{-3}$$

$$\text{H}_2\text{PO}_4^- : K_{a2} = 6.3 \times 10^{-8}$$

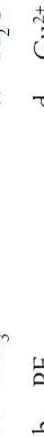
$$\text{HPO}_4^{2-} : K_{a3} = 4.5 \times 10^{-13}$$

### Section 3.3 Review Problems

1. Identify the Lewis acid and base in each of the following reactions.



2. Identify the following molecules as Lewis acids and/or bases:



3. Determine the pH and percent ionization in the following aqueous solutions:



Each of the species in (a) through (d) above is one-half of a conjugate acid-base pair. In each case, provide the name and formula of the other half of the pair and calculate its  $K_a$  or  $K_b$  value.

4. What mass of propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ ,  $pK_a = 4.87$ , should be dissolved in water to 2.00 L volume in order to produce a pH of 2.50?

5. When acid HA is dissolved in water to 0.200 M concentration, the solution has a pH = 1.40. What is the  $K_a$  of this acid?

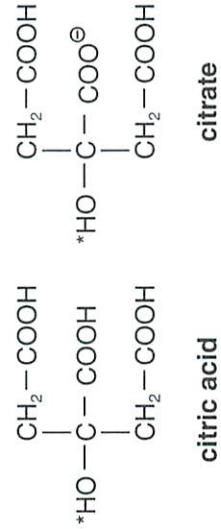
6. Hypochlorous acid, HOCl, is very weak, with  $K_a = 3.5 \times 10^{-8}$ . Calculate the value of  $[\text{H}^+]$ , the pH, and the percent ionization of this acid in concentrations of (a) 1.00 M (b) 0.0100 M.

Based on the results, indicate what happens to a weak acid solution on dilution: Does  $[\text{H}^+]$  increase or decrease? Does the pH increase or decrease? Does the percent ionization increase or decrease?

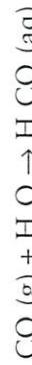
7. Trimethylamine,  $(\text{CH}_3)_3\text{N}$ , is an organic base slightly stronger ( $K_b = 7.4 \times 10^{-5}$ ) than ammonia. Calculate the  $\text{pOH}$ , the  $\text{pH}$ , and the percent ionization of a  $0.35\text{ M}$  solution.
8. For the following three weak acids: formic,  $\text{HCOOH}$  ( $K_a = 1.9 \times 10^{-4}$ ), hydrofluoric,  $\text{HF}$  ( $K_a = 6.7 \times 10^{-4}$ ), hydrogen oxalate ion,  $\text{HC}_2\text{O}_4^-$  ( $K_a = 5.2 \times 10^{-5}$ ).
- Determine the  $\text{p}K_a$  value of each acid.
  - Arrange these three in order of decreasing acid strength.
  - Give the name and formula of the conjugate base of each acid.
  - Determine the  $K_b$  value of each conjugate base and arrange them in order of decreasing base strength.
9. A moderately weak acid is 25% ionized in  $0.15\text{ M}$  concentration. What is its  $K_a$  value?
10. What mass of ammonia ( $K_b = 1.8 \times 10^{-5}$ ) should be dissolved in water to  $10\text{ L}$  volume in order to provide a pH of 11.18?
11. Determine the pH and percent hydrolysis in the following solutions (use  $K$  data from Tables 3.3.1 and 3.3.2).
  - $0.500\text{ M}$  potassium formate,  $\text{HCOOK}$
  - $0.250\text{ M}$  ammonium bromide,  $\text{NH}_4\text{Br}$
12. When  $50.0\text{ mL}$  of  $0.100\text{ M}$   $\text{NH}_3(\text{aq})$  ( $K_b = 1.8 \times 10^{-5}$ ) solution is mixed with  $20.0\text{ mL}$  of  $0.250\text{ M}$   $\text{HCl}$  solution, what is the pH after reaction?
13. When  $0.020\text{ mol}$  of weak acid HA is dissolved in water to  $100\text{ mL}$  volume, the ratio dissociated to undissociated,  $[\text{A}^-] / [\text{HA}]$ , at equilibrium is  $0.30$ . What is the  $K_a$  of this acid?
14.  $33.0\text{ g}$  of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , is dissolved in water to  $1.00\text{ L}$  volume. What is the pH of this solution?  $\text{NH}_3(\text{aq})$  has  $K_b = 1.8 \times 10^{-5}$ .
15. What concentration of formic acid,  $\text{HCOOH}$ , ( $K_a = 1.9 \times 10^{-4}$ ) in water would produce a pH of 4.5? What would the percent dissociation of the acid be in this solution?

16. Ethylamine ( $\text{CH}_3\text{CH}_2\text{NH}_2$ ,  $K_b = 4.3 \times 10^{-4}$ ) and ethanolamine ( $\text{HOCH}_2\text{CH}_2\text{NH}_2$ ,  $K_b = 2.8 \times 10^{-4}$ ) are weak bases.

- Which of these is the stronger base?
- For the stronger base, calculate the pH and percent ionization in 0.50 M solution.
- The acidity of lemon juice is due to the presence of citric acid, a triprotic acid (MM 192 g mol<sup>-1</sup>,  $pK_{a1} = 3.1$ ). The pH of lemon juice is 2.3. Determine:
  - The molar concentration of  $\text{H}^+$ , citrate ion, and undissociated citric acid.
  - The total molar concentration of citric acid, dissociated and undissociated.
  - The percent ionization of citric acid.
  - The mass percent of citric acid present (lemon juice density = 1.13 g mL<sup>-1</sup>).



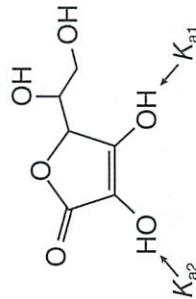
18. Carbonic acid is the result of dissolving  $\text{CO}_2$  in water as follows:



It is a weak diprotic acid with  $K_{a1} = 4.2 \times 10^{-7}$  and  $K_{a2} = 4.8 \times 10^{-11}$ .

- Determine the pH, the concentration of all carbon-containing species, and the percent dissociation, first and second stages, in a solution of  $\text{H}_2\text{CO}_3$ , concentration 0.100 M.
- Rainwater has a pH of about 5.6 resulting from the  $\text{CO}_2$  dissolved from the atmosphere. What is the total concentration of all carbon containing species ( $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ), dissociated and undissociated, in rainwater?
- What volume of  $\text{CO}_2(\text{g})$  has dissolved in each litre of rainwater to produce this acidity? (Take the molar volume as 22.4 L mol<sup>-1</sup>.)

- d. What is the pH of an 0.100 M solution of sodium carbonate,  $\text{Na}_2\text{CO}_3$  (washing soda)?
19. Vitamin C is a diprotic acid with  $K_{\text{a}1} = 7.9 \times 10^{-5}$  and  $K_{\text{a}2} = 1.6 \times 10^{-12}$ .



- a. What is the pH of a solution prepared by dissolving 10.0 g of ascorbic acid to make one litre of solution?
- b. What is the concentration of the doubly charged ascorbate anion in this solution?

20. A solution of sulfuric acid (diprotic) is prepared by dissolving 0.100 mol of  $\text{SO}_2$  gas in 1.00 L of water, the reaction being:



- a. Write an equation for the first dissociation of  $\text{H}_2\text{SO}_3$ .
- b. If the solution has  $\text{pH} = 1.47$ , what is the percent dissociation of the  $\text{H}_2\text{SO}_3^2-$ ?
- c. Determine  $K_{\text{a}1}$  for  $\text{H}_2\text{SO}_3$ .
- d. If  $K_{\text{a}2}$  for this acid is  $6.2 \times 10^{-8}$ , what is the concentration of sulfite ion,  $[\text{SO}_3^{2-}]$ ?
21. Determine the equilibrium concentrations of all species present for the equilibrium of a 0.150 M solution of the diprotic acid  $\text{H}_2\text{SO}_3$ . What is the pH of the solution?

Data:  $K_{\text{a}1} = 1.2 \times 10^{-2}$ ,  $K_{\text{a}2} = 6.2 \times 10^{-8}$

## 3.4 Buffer Solutions

### OBJECTIVES

After studying this topic, you should be able to:

- Identify the components needed to prepare a buffer solution.
- Determine whether a given set of components will create a buffer solution.
- Find the pH of a buffer solution, both before and after adding a strong acid or base.
- Identify the titration curves for a strong acid-strong base, strong acid-weak base, and weak acid-strong base by their respective shapes.
- Identify the buffer regions on titration curves.

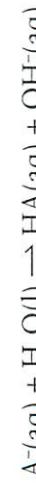
### INTRODUCTION

Consider the behaviour of a weak acid in aqueous solution:



This solution is acidic due to the presence of  $\text{H}_3\text{O}^+$  in the equilibrium mixture.

If a solution contains only  $\text{A}^-$  initially, the solution is basic due to hydrolysis. The conjugate base produces  $\text{OH}^-$  as follows:



What happens if both the weak acid, represented by HA, and its conjugate base (in the form of a salt), represented by  $\text{A}^-$ , are present in the same solution? This type of solution is called a buffer solution. The outstanding feature of a buffer solution is its ability to withstand (or “buffer”) changes in pH when small amounts of a strong acid or base are added to it. In order for a solution to perform in this manner, it must meet some specific requirements, such as:

1. A buffer solution must contain a weak acid that will react with any  $\text{OH}^-$  ions (from a strong base) that may be added to the solution.

2. A buffer solution must also contain a weak base that will react with any  $\text{H}_3\text{O}^+$  ions (from a strong acid) that may be added to the solution.
3. The acid and the base in the buffer solution must not react with each other; the only species that can possibly qualify are a weak acid or base and its own conjugate partner. In addition, the weak species and its conjugate partner must both be present in significant amounts. Buffers work best when there is about a 1:1 mixture of the weak species and its conjugate, but the solution will still perform its buffering function if the two concentrations are within a factor of 10.

If a solution contains *both* a weak acid and its conjugate base, they must be in equilibrium. Therefore, a buffer solution consists of a weak acid with its conjugate base behaving as a common ion, or a weak base with its conjugate acid behaving as a common ion.



#### PREPARING A BUFFER SOLUTION

The preparation of a buffer solution can be accomplished several ways, but the final solution must always contain a weak species and its conjugate partner. Note that if a buffer solution contains a weak acid and its conjugate base, the pH of that buffer will generally fall in the acidic range. Conversely, if the buffer solution contains a weak base and its conjugate acid, the pH of that solution will usually be basic.

### Acid Buffer

A buffer solution composed of a weak acid and its conjugate base is often termed an acid buffer. For an acid buffer to be effective, both the weak acid ( $\text{HA}$ ) and its conjugate base ( $\text{A}^-$ ) must be present in significant and similar quantities. The easiest way to prepare this solution is to start with a solution of weak acid and add a salt that contains the conjugate base. This is shown in Figure 3.4.1 below:

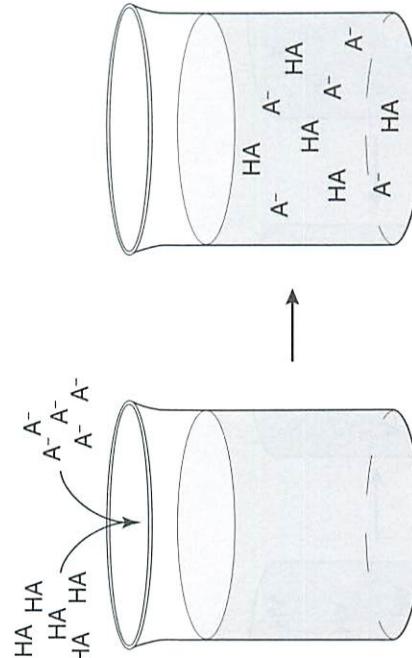
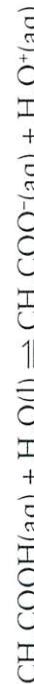


Figure 3.4.1

For example, 100 mL of a 0.150 M solution of acetic acid ( $\text{CH}_3\text{COOH}$ ) plus about 1.25 g (0.0152 mol) of sodium acetate ( $\text{CH}_3\text{COONa}$ ) is a buffer solution. The sodium acetate contains the acetate ion ( $\text{CH}_3\text{COO}^-$ ), which is the conjugate base of acetic acid. The resultant solution will contain approximately 0.015 moles of each species. The equilibrium reaction is:



While the simplest method of preparing a buffer is to mix the two required species together, there are two other ways to make the previously described buffer solution. These involve starting with one of the two ingredients, and using a strong acid or strong base to create the other *in situ*.

Using acetic acid as an example, this is done by the reaction of acetic acid with hydroxide, thereby creating the acetate ion in the beaker.



The key is to use the correct amount of strong base to convert roughly half of the weak acid to its conjugate base. In the case of acetic acid, the number of moles of acetate ion,  $\text{CH}_3\text{COO}^-$ , formed is equivalent to the number of moles of hydroxide ion,  $\text{OH}^-$ , added.

This is shown in Figure 3.4.2 below:

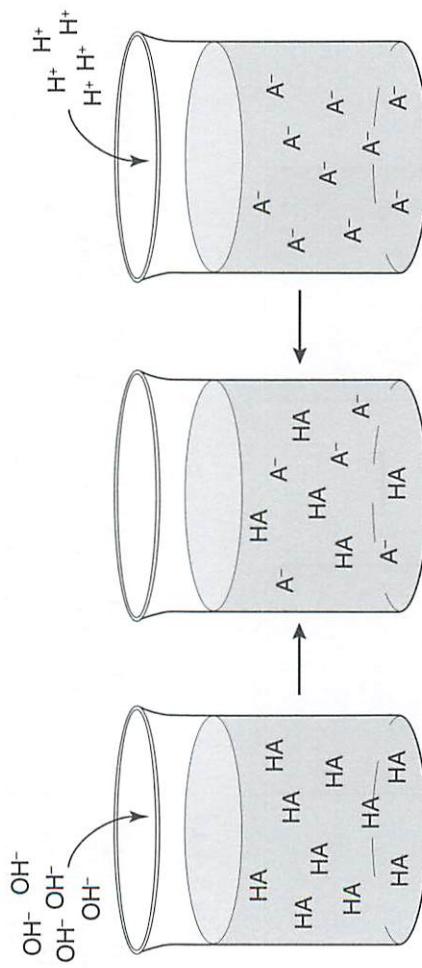


Figure 3.4.2

In a similar fashion, the same buffer can be created using strong acid to convert a conjugate base back to the weak acid. In the case of acetate ion and acetic acid, the strong acid HCl is added to sodium acetate,  $\text{CH}_3\text{COONa}$ , (a weak conjugate base) to form acetic acid,  $\text{CH}_3\text{COOH}$ , (the parent weak acid) in solution:



Again, it is important to convert approximately half of the acetate ions into acetic acid by reaction with HCl to form an effective buffer.

**Base Buffer**

Analogous combinations can be used for weak bases ( $B$ ) and their conjugate acids ( $BH^+$ ) to form base buffers. For example, suppose that 2.14 g (0.0400 mol) of ammonium chloride,  $NH_4Cl$ , are added to 250 mL of 0.160 M aqueous ammonia,  $NH_3$ . The ammonia is a weak base and the ammonium ion,  $NH_4^+$ , (from the  $NH_4Cl$ ) is its conjugate acid, so the resultant solution will be a buffer solution, as both species are present in significant and roughly equivalent amounts (0.040 mol). This is shown in Figure 3.4.3 below:

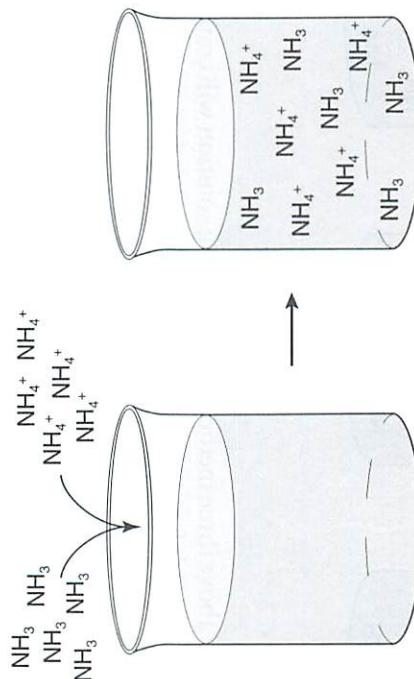


Figure 3.4.3

As was the case with weak acids, a reaction can also be used to produce the species required to form a buffer solution. That is, use a strong acid such as  $HNO_3$  to convert roughly half of the base ( $NH_3$ ) to its conjugate acid ( $NH_4^+$ ):



Similarly, a strong base such as  $NaOH$  can be added to convert approximately half of the conjugate acid ( $NH_4^+$ ) back to the parent base ( $NH_3$ ):



This is shown in Figure 3.4.4 below:

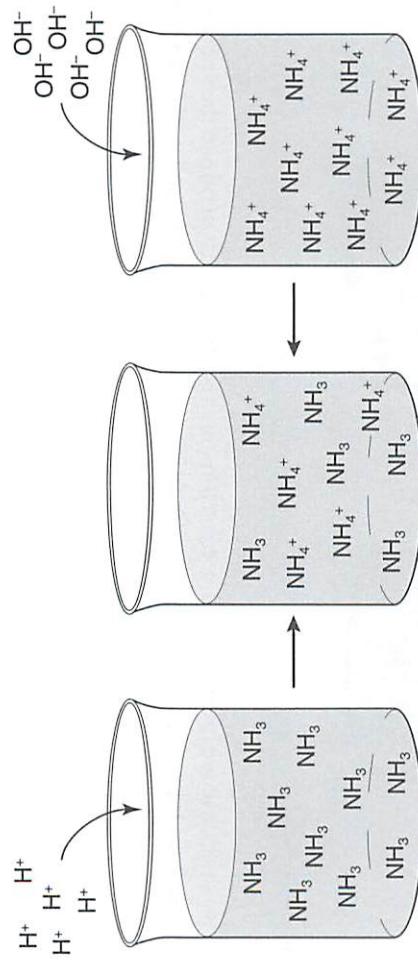


Figure 3.4.4

Using any of the above three methods, the resulting solution will consist of roughly equal amounts of weak base and its conjugate acid, producing a buffer solution.

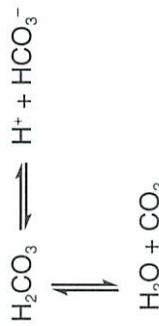
**Example 3.4.1. Preparing Buffer Solutions (In-Class Exercise)**

Determine which of the following combinations will produce a buffer solution.

- 0.15 mol  $\text{HCOOH}$  and 0.15 mol  $\text{HCOOK}$
- 0.20 mol  $\text{CH}_3\text{COOH}$  and 0.20 mol  $\text{KOH}$
- 0.10 mol  $\text{CH}_3\text{COONa}$  and 0.05 mol  $\text{HCl}$
- 0.25 mol  $\text{NH}_4\text{Cl}$  and 0.10 mol  $\text{NaOH}$
- 0.10 mol  $\text{NH}_3$  and 0.10 mol  $\text{HClO}_4$
- 0.35 mol  $\text{CH}_3\text{NH}_2$  and 0.25 mol  $\text{HNO}_3$

### pH OF A BUFFER SOLUTION

The outstanding feature of a buffer solution is its ability to resist changes in pH. If it is essential that the pH of a solution remain nearly constant, a buffer solution is employed to accomplish this task. Human blood, with a pH of about 7.4, is an example of a buffered system. If small amounts of either acid or base make their way into the bloodstream, the pH does not change much. This is a good thing, as a change in blood pH of only 0.1 of a pH unit in either direction can be disastrous for a person's health. If a solution is to be used for buffering purposes, it is useful to calculate the pH of that solution.



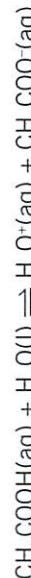
#### Example 3.4.2. pH of an Acetate Buffer

Calculate the pH of the resultant solution when 500 mL of 0.400 M  $\text{CH}_3\text{COOH}$  and 200 mL of 0.500 M  $\text{CH}_3\text{COONa}$  are mixed together.

**Data:**  $K_a$  for  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$

**Solution:** This solution contains both the weak acid,  $\text{CH}_3\text{COOH}$ , and its conjugate base,  $\text{CH}_3\text{COO}^-$ , in comparable quantities. It should be recognized that this is a buffer solution and an example of the *common ion effect*. (The *common ion effect* was introduced in the *Solubility of Ionic Compounds* section.)

The equilibrium containing these two species may use the weak acid as the “reactant” with the conjugate base as the product, or vice versa. Either concept is valid, but it is much simpler to use the parent species as the reactant.



Before setting up the equilibrium, the molarities of both the  $\text{CH}_3\text{COOH}$  and the  $\text{CH}_3\text{COO}^-$  (which comes from the  $\text{CH}_3\text{COONa}$ ) in solution after mixing must be found:

$$\text{Moles CH}_3\text{COOH} = 0.500 \text{ L} \times 0.400 \text{ M} = 0.200 \text{ mol}$$

$$\text{Moles CH}_3\text{COO}^- = 0.200 \text{ L} \times 0.500 \text{ M} = 0.100 \text{ mol}$$

$$\text{Molarity CH}_3\text{COOH} = \frac{0.200 \text{ mol}}{0.700 \text{ L}} = 0.286 \text{ M}$$

$$\text{Molarity CH}_3\text{COO}^- = \frac{0.100 \text{ mol}}{0.700 \text{ L}} = 0.143 \text{ M}$$

Now, set up the equilibrium as an example of a weak acid with the conjugate base acting as the common ion:

$\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^{\text{(aq)}} + \text{CH}_3\text{COO}^{\text{(aq)}}$
Initial:	0.286 M	0 0.143 M
Equilibrium:	$0.286 \text{ M} - x$	$x 0.143 \text{ M} + x$

Note that the amount of  $\text{CH}_3\text{COOH}$  ionized is expressed as the variable  $x$ . This amount is equal to  $[\text{H}_3\text{O}^+]$ .

The equilibrium constant expression is:

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(0.143+x)}{(0.286-x)}$$

In a buffer solution, the percent ionization is fairly small, often being just a percent or two. According to Le Châtelier's principle, if the acetate ion is added to the weak acid equilibrium, the reaction will proceed to the left. The value for  $x$  will be much smaller than in the weak acid solution alone. So, for a buffer solution, the value of  $x$  is *always negligible* when compared to the concentration of the parent or conjugate species.

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.143)}{(0.286)}$$

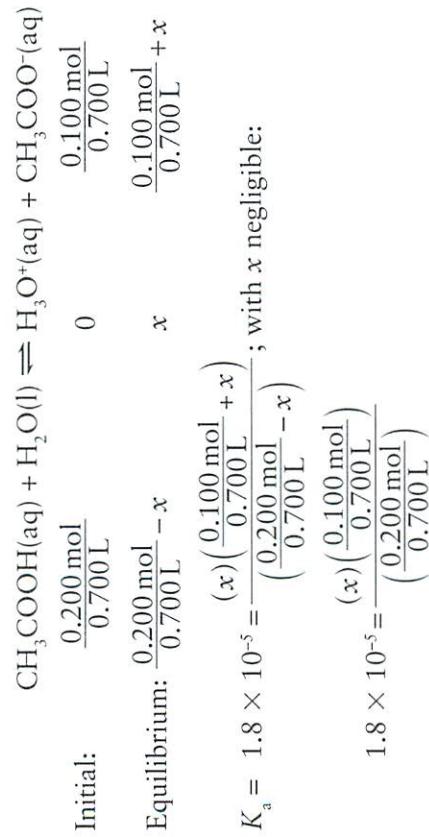
Therefore:  $x = 3.6 \times 10^{-5} = [\text{H}^+]$ , and the  $\text{pH} = 4.44$ .

Note that the volume used to calculate molarity is the same for both species (they are both in the same solution). For buffer calculations, it is usually possible and often preferable to use mole amounts of the parent and conjugate species instead of concentration units. The other species ( $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ ) must always be in concentration units (see example that follows).

There are two reasons why mole amounts work:

1. The parent and conjugate species are always in the same volume.
2. The value of  $x$  is always negligible when compared to the initial concentration of the parent and conjugate.

Revisiting the example:



The volumes cancel, thus:  $1.8 \times 10^{-5} = \frac{(x)(0.100 \text{ mol})}{(0.200 \text{ mol})}$

Solving:  $x = 3.6 \times 10^{-5} = [\text{H}^+]$ , and the pH = 4.44.

Calculations for buffer solutions may therefore be carried out using moles or concentration units for the parent and conjugate. However, the parent and conjugate must be in the same units and, as previously stated, the  $\text{H}_3\text{O}^+$  (for an acid buffer) and  $\text{OH}^-$  (for a base buffer) *must always be* in concentration units,  $M$ .

For a weak acid buffer, the equilibrium expression becomes:

$$K_a = \frac{[\text{H}_3\text{O}^+](\text{moles of conjugate base})}{(\text{moles of parent acid})}$$

This expression shows that the pH of a solution is dependent on the ratio of parent to conjugate species. Another outcome is that the volume of the solution is not a factor in determining pH. Thus, diluting a buffer solution does not change its pH.

### The Henderson-Hasselbalch Method

A second method that is often used in solving buffer problems is the Henderson-Hasselbalch equation. Starting from the general form of the equilibrium reaction for a weak acid, HA, with water, the  $K_a$  expression is simply:



Taking the negative log of both sides results in:

$$-\log(K_a) = -\log\left(\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}\right)$$

When terms are multiplied within a logarithm, they become added together when we separate the logarithm, resulting in:

$$-\log(K_a) = -\log[\text{H}_3\text{O}^+] - \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Then adding  $\log([\text{A}^-]/[\text{HA}])$  to both sides gives:

$$-\log(K_a) + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = -\log[\text{H}_3\text{O}^+]$$

$-\log[\text{H}_3\text{O}^+]$  is pH, and  $-\log[K_a]$  is  $pK_a$ , which gives the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

However, as above, because concentrations are moles/volume:

$$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{\left(\frac{n_{\text{A}^-}}{V_{\text{tot}}}\right)}{\left(\frac{n_{\text{HA}}}{V_{\text{tot}}}\right)}$$

and the Henderson-Hasselbalch equation can also be expressed as:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[n_{\text{A}^-}]}{[n_{\text{HA}}]}\right)$$

Using the Henderson-Hasselbalch equation, the  $K_a$  given in the question, and the moles found above, the solution to Example 3.4.2 becomes:

$$\text{pH} = 4.74 + \log\left(\frac{[0.100]}{[0.200]}\right)$$

or  $\text{pH} = 4.44$ .

As described in the *Preparing a Buffer Solution* section, there are many different ways to prepare a buffer solution. If the required pH of the solution is known, it is possible to work backward to determine the amount of reagents needed.

**Example 3.4.3. Preparing a Buffer with a Given pH (In-Class Exercise)**

What mass, in grams, of  $\text{NaNO}_2$  must be added to 700 mL of 0.165 M  $\text{HNO}_2$  to produce a solution with a pH of 3.50?

**Data:**  $K_a$  for  $\text{HNO}_2 = 4.5 \times 10^{-4}$

**Example 3.4.4. Base Buffers (In-Class Exercise)**

The same principles may also be applied to base buffers. These solutions consist of a weak base and its conjugate acid.

A solution was prepared by adding 21.5 g of  $\text{NH}_4\text{Cl}$  to 1.50 L of 0.250 M  $\text{NH}_3$ . Find the pH of this solution.

**Data:**  $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$

Buffer solutions can also be prepared using an acid–base reaction. Several examples of this type of reaction have already been discussed. An excess amount of some weak species (acid or base, parent or conjugate) is reacted with a strong acid or base. The reaction produces the second weak component necessary to produce a buffer solution.

**Example 3.4.5. Buffers via an Acid–Base Reaction**

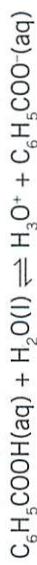
100 mL of 0.500 M benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ ,  $K_a = 6.3 \times 10^{-5}$ , is mixed with 100 mL of 0.200 M NaOH. Find the pH of the resultant solution.

**Solution:** The species initially present are the weak acid,  $C_6H_5COOH$ , and the strong base,  $NaOH$ . These will react.

First, write the equation for the reaction. The strong base is the limiting reagent and, because it is strong, it is simply written as  $OH^-$ .

	$C_6H_5COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + C_6H_5COO^-(aq)$
Initial:	0.0500                    0
After:	0.0300                    0.0200

When the reaction is complete, both the weak acid,  $C_6H_5COOH$ , and the conjugate base,  $C_6H_5COO^-$ , are present in roughly equal amounts. Once the buffer solution is formed, it is treated as an equilibrium containing a common ion. A buffer solution may be calculated using moles for the parent and conjugate species.



Equilibrium:    0.0300 moles                     $x$                     0.0200 moles

$$K_a = 6.3 \times 10^{-5} = \frac{[H_3O][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{(x)(0.0200)}{(0.0300)}$$

$$\text{Solving: } x = 9.45 \times 10^{-5} M = [H_3O^+] \text{ and pH} = 4.02$$

The same principles can be applied to the reaction of excess weak base with a strong acid; this reaction will also result in the formation of a buffer solution.

#### Example 3.4.6. pH of an Ammonium Buffer (In-Class Exercise)

250 mL of 0.135  $M$  ammonia ( $NH_3$ ) are mixed with 150 mL of 0.110  $M$   $HNO_3$ . Calculate the pH of this solution.

Data:  $K_b$  for  $NH_3 = 1.8 \times 10^{-5}$

### HOW BUFFERS WORK

Buffer solutions resist changes in pH. If a small amount of strong acid is added to an acid buffer, it will react with the conjugate base component of the buffer to produce more of the weak acid. The ratio of these two components will change only slightly, which results in a small drop in pH. A similar reaction will take place if a small amount of strong base is added to the same buffer. The weak acid will react with the strong base, producing more conjugate base. Once again, the ratio of weak acid to conjugate base does not change very much. In this case, the pH of the solution will increase.

#### Example 3.4.7. Adding Strong Acid to a Buffer

A buffer solution consists of 0.200 moles of formic acid, HCOOH, and 0.150 moles of sodium formate, HCOONa, in 2.0 L of solution. The pH of the initial buffer solution is 3.60. What is the effect on the pH if 0.0300 moles of HCl are added to the buffer solution?

**Data:**  $K_a$  for HCOOH =  $1.9 \times 10^{-4}$

**Solution:** This buffer solution consists of a weak acid, HCOOH, and its conjugate base, HCOO<sup>-</sup> (which comes from HCOONa). HCl is a strong acid and it will react with the conjugate base to form more of the weak acid. The quantities used in the following reaction are moles:

$\text{HCOO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{HCOOH}(\text{aq})$			
Initial:	0.150	0.0300	0.200
After:	0.150 - 0.0300	0	0.200 + 0.0300
	= 0.120		0.230

Examination of the species present after the reaction shows both the weak acid and its conjugate base are still present. Only their quantities have changed a little. This solution is still a buffer so the moles of the acid and its conjugate base, after the reaction, can be used. It is not necessary to calculate the molarity of those species.

$\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$			
Initial:	0.230	0	0.120
Equilibrium:	0.230 - x	x	0.120 + x

Note that subtracting or adding concentration values from/to mole amounts would be unworkable if not for the fact that the value of  $x$  were negligible.

Since  $x$  is negligible:

$$K_a = 1.9 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(x)(0.120)}{(0.230)}$$

Solving:  $x = 3.64 \times 10^{-4}$  M =  $[\text{H}_3\text{O}^+]$  and pH = 3.44

The pH of the solution decreased by 0.16 pH units after adding the strong acid.

Examine the ratio of conjugate base to weak acid before and after the addition of the HCl:

$$\text{Before the HCl: } \frac{\text{HCOO}^-}{\text{HCOOH}} = \frac{0.150 \text{ mol}}{0.200 \text{ mol}} = 0.75$$

$$\text{After the HCl: } \frac{\text{HCOO}^-}{\text{HCOOH}} = \frac{0.120 \text{ mol}}{0.230 \text{ mol}} = 0.52$$

The small change in the ratio results in a small change in pH.

#### **Example 3.4.8. Adding Strong Base to a Buffer (In-Class Exercise)**

The buffer solution in the previous example consists of 0.200 moles of HCOOH and 0.150 moles of HCOONa in 2.0 L of solution. Calculate the change in pH if 1.60 g of NaOH are added to the solution.

**Data:**  $K_a$  for HCOOH =  $1.9 \times 10^{-4}$

#### **Comparing a Buffer Solution to Water**

The previous examples have shown how adding a small amount of a strong acid or base to a buffer solution results in a small change in pH. What happens when (a) 0.0300 moles of HCl or (b) 1.60 g of NaOH are added to 2.00 L of water?

- When 0.0300 moles of HCl are added to 2.00 L of water (pH = 7.0), the  $[\text{H}_3\text{O}^+] = 0.0150$  M. The pH of the solution is 1.82 (i.e., it decreases by 5.18 pH units). The same amount of HCl causes the pH of the buffer solution to decrease by only 0.17 pH units.

- b. When 1.60 g of NaOH (0.0400 moles) are added to 2.00 L of water ( $\text{pH} = 7.0$ ), the  $[\text{OH}^-] = 0.0200 \text{ M}$ . The pH of this solution is 12.3 (i.e., increases by 5.3 pH units). Compare this increase to the small increase observed when the same amount of NaOH is added to a buffer solution.

### ACID-BASE TITRATIONS

Acid-base titration is a method used to determine parameters such as the concentration of base (or acid) in a solution. There are two possibilities in a titration process: acid is added to neutralize a base, or a base is added to neutralize an acid. The *equivalence point* of a titration is reached when stoichiometrically equivalent amounts of acid and base have been combined. For example, the equivalence point is reached when mixing 0.1 mol HCl with 0.1 mol of NaOH; or 0.2 mol  $\text{CH}_3\text{COOH}$  with 0.1 mol  $\text{Ca}(\text{OH})_2$ . The pH at the equivalence point is not always 7.0, as shown in the examples below.

**Case 1:** Strong acid-strong base:



At the equivalence point, all of the HCl and NaOH have reacted with each other, resulting in a solution of NaCl. Since both  $\text{Na}^+$  and  $\text{Cl}^-$  are spectator ions, the solution is neutral (pH 7).

**Case 2:** Weak acid-strong base:



At the equivalence point, all of the  $\text{CH}_3\text{COOH}$  and NaOH have reacted with each other, resulting in a solution of  $\text{CH}_3\text{COONa}$ .  $\text{Na}^+$  is a spectator ion and the acetate ( $\text{CH}_3\text{COO}^-$ ) is a weak base, so the solution is basic.

**Case 3:** Strong acid-weak base:



At the equivalence point, all of the HCl and  $\text{NH}_3$  have reacted, resulting in a solution of  $\text{NH}_4\text{Cl}$ .  $\text{Cl}^-$  is a spectator ion and the ammonium ion ( $\text{NH}_4^+$ ) is a weak acid, so the solution is acidic.

The products of the ionization reaction of the salt determines whether the final solution is acidic or basic. Note that any reaction involving a strong species will go to completion and therefore, a unidirectional arrow ( $\rightarrow$ ) is used.

### pH at Equivalence Point

It is often useful to determine the pH at the equivalence point of a titration. As seen in the acid–base titration lab, a colour change of an indicator signals the arrival at the equivalence point if an appropriate indicator was used. Because different indicators change colours at different pHs, having an estimate of the equivalence point pH enables a chemist to select the appropriate indicator.

For any titration involving a weak species and a strong species (such as formic acid and NaOH, respectively), an equilibrium will be established between the excess weak species and the just-formed conjugate species. This is, of course, a buffer solution. At the equivalence point, the only species present is the conjugate, which will then react with water. It is this reaction of the conjugate species that is ultimately responsible for the pH of the solution at the equivalence point. Thus, when determining the pH at the equivalence point, the acid–base reaction must be used to accurately determine the amount of conjugate formed.

#### Example 3.4.9. pH at the Equivalence Point of a Weak Acid–Strong Base Titration

Find the pH at the equivalence point of the titration of 25.00 mL of 0.165 M formic acid, HCOOH ( $K_a = 1.9 \times 10^{-4}$ ), with 0.185 M KOH.

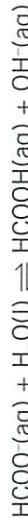
**Solution:** First, write the reaction between the acid and base, assuming the reaction goes to completion:



At the equivalence point of this titration, the number of moles of weak acid will be equal to the number of moles of strong base:

$$\# \text{ moles HCOOH} = 0.165 \text{ M} \times 0.02500 \text{ L} = 0.004125 \text{ moles} = \text{moles OH}^-$$

From the stoichiometry of the reaction, the number of moles of  $\text{HCOO}^-$  produced must be equal to the number of moles of  $\text{HCOOH}$  initially (0.004125 moles). To calculate the pH, the hydrolysis reaction of  $\text{HCOO}^-$  with water must be considered:



Initial:	$c$	0	0
Equilibrium:	$c - x$	$x$	$x$

$c$  is the initial  $[\text{HCOO}^-]$ . This can be calculated from the number of moles of  $\text{HCOO}^-$  produced in the reaction and the total volume of the solution. To determine the total volume of the solution, the volume of the strong base used must first be calculated.

$$\text{Volume OH}^- = \text{Volume KOH} = \frac{0.004125 \text{ moles}}{0.185 M} = 0.02230 \text{ L}$$

$$[\text{HCOO}^-] = \frac{0.004125 \text{ moles}}{(0.02500 + 0.02230) L} = 0.08721 \text{ M} = c$$

$$\text{The equilibrium constant expression is: } K_b = \frac{x^2}{c - x}$$

In order to solve for  $x$  in this expression,  $K_b$  for  $\text{HCOO}^-$  must be calculated using  $K_a$  for  $\text{HCOOH}$  and  $K_w$ .

$$K_b = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-4}} = 5.26 \times 10^{-11}; \text{ substituting: } 5.26 \times 10^{-11} = \frac{x^2}{0.08721 - x}$$

A comparison of  $c$  and  $K_b$  indicates that using the approximation  $0.08721 - x \approx 0.08721$  is valid.

$$\text{Therefore: } x = \sqrt{0.08721 \times 5.26 \times 10^{-11}} = 2.142 \times 10^{-6} = [\text{OH}^-]$$

To find pH, pOH must first be calculated using  $[\text{OH}^-]$ :

$$\text{pOH} = 5.67, \text{ so pH} = 14 - 5.67 = 8.33$$

**Example 3.4.10. pH at the Equivalence Point of a Weak Base–Strong Acid Titration (In-Class Exercise)**

Calculate the equivalence point pH for the titration of 0.175 M methylamine ( $\text{CH}_3\text{NH}_2$ ) with 0.250 M  $\text{HNO}_3$ .

**Data:**  $K_b$  for  $\text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}$

### Acid–Base Indicators

Acid–base indicators are used to detect the equivalence point in a titration. An indicator is a weak organic acid (represented by HIn) that has a different colour than its conjugate base. As a weak acid, it will set up the following equilibrium:



In an acidic solution, the indicator mostly exists in its acid form (colour 1). Conversely, under basic conditions it mostly exists in its base form (colour 2). The colour change takes place around the pH value where  $[\text{HIn}] = [\text{In}^-]$ . The equilibrium constant expression for the indicator is:

$$K_{\text{HIn}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

When  $[\text{HIn}] = [\text{In}^-]$ , then  $K_{\text{HIn}} = [\text{H}_3\text{O}^+]$  which gives  $\text{p}K_{\text{HIn}} = \text{pH}$ . Therefore, the  $\text{p}K_{\text{HIn}}$  of the indicator is equal to the pH at which the colour change occurs.

- At 1 pH unit below this pH or  $\text{p}K_a$  value (acidic) the indicator is about 90% in the HIn form.
- At 1 pH unit above this pH or  $\text{p}K_a$  value (basic) the indicator is about 90% in the  $\text{In}^-$  form.
- The point of the titration at which the indicator changes colour is called the endpoint.

Note that the indicator is present in a very low concentration. The value of  $[\text{H}_3\text{O}^+]$ , and hence the pH, is driven by the acid–base reaction and is NOT affected by the presence of the indicator.

When an indicator is being chosen for a titration, it is important that it changes colour at (or close to) the pH of the equivalence point. Therefore, the ability to predict the pH at the equivalence point (as shown in previous examples) enables one to choose the correct indicator. For the reasons described above, it is best to choose an indicator that has a  $\text{p}K_a$  value within one unit of the pH of the solution at the equivalence point.

Different types of titrations will have different equivalence-point pH values. For a strong acid–strong base titration, the pH at the equivalence point will be 7. In theory, an indicator chosen for this type of titration should have a  $pK_a$  between 5 and 9. In practice, however, almost any indicator may be used because the pH change is very large near the equivalence point.

More care must be used when choosing an indicator for titrations that involve a weak species. For a weak acid–strong base titration, the pH at the equivalence point will be above 7, usually in the range of pH 8 to pH 10. The indicator chosen must have a  $pK_a$  in this range. An example of this type of indicator is phenolphthalein, which has a  $pK_a$  of about 9.

The choice of indicator is also critical for weak base–strong acid titrations. In these titrations, the pH at the equivalence point will be below 7, usually in the range of pH 4 to pH 6. An example of a suitable indicator for this titration is methyl red, with a  $pK_a$  of about 5.

Table 3.4.1 shows some typical indicators, their  $pK_a$  values and applicable titrations.

TABLE 3.4.1 TYPICAL  $pK_a$  INDICATOR VALUES

TITRATION	EQUIVALENCE POINT pH	DESIRED INDICATOR $pK_a$	TYPICAL INDICATOR
Strong acid–strong base	neutral	around 7*	bromothymol blue
Strong acid–weak base	acidic	4–6	methyl red
Weak acid–strong base	basic	8–10	phenolphthalein

\* In practice, almost any indicator may be used for this type of titration because the pH change at equivalence is extremely large.

### TITRATION CURVES

In the previous topic, the equivalence point of a titration was introduced. In the case of either a weak acid-strong base or a weak base-strong acid titration, the only species present at the equivalence point (in addition to water and the spectator ions) is the conjugate species of the original weak acid or base. The conjugate species then undergoes a hydrolysis reaction with the water. It is this reaction that accounts for the fact that the pH at the equivalence point of a titration is not always 7.

There are other processes occurring both before and after the equivalence point in a titration, and those processes depend on the type of titration. A titration curve shows, in the form of a graph, the pH resulting from all the reactions occurring during a titration (see Figure 3.4.5).

#### Strong Acid–Strong Base Titration

An example of this type of titration is:



The titration curve plots the pH of the solution versus the volume of base added to the acid. At the beginning of the titration, the solution is strongly acidic due to the presence of excess or unreacted HCl. Even though NaOH is being added, the reaction between the HCl and the NaOH occurs virtually instantaneously, leaving slightly less HCl in solution. Keep in mind that the pH scale is logarithmic. Reacting 90% of the available acid will only increase the pH by one unit.

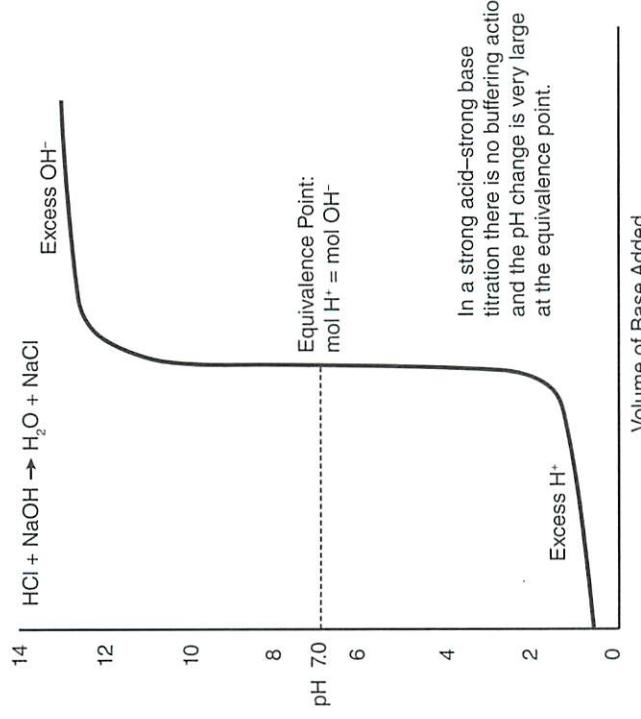


Figure 3.4.5 Titration curve for a strong acid-strong base.

As the equivalence point is approached, there is very little HCl left in the solution so the pH begins to increase, culminating in a very rapid increase just before and after the equivalence point. The equivalence point occurs at the inflection point of the curve.

At the equivalence point, the pH is 7 and the only species present in the solution are NaCl and water. If more NaOH is added after the equivalence point has been reached, a basic solution results. Just past the equivalence point, the pH will continue to increase rapidly. Once a basic solution is achieved, the pH will appear to almost level off, increasing only very slightly.

### Weak Acid–Strong Base Titration

A typical example of this type of titration is:



As the base is strong and therefore completely ionized, it is shown as OH<sup>-</sup> for increased clarity:



At the beginning of this titration, the solution is acidic due to the presence of CH<sub>3</sub>COOH. As this is a weak acid, the pH will be higher than it would be in the case of a strong acid with the same concentration. Once the addition of OH<sup>-</sup> begins, the conjugate base, CH<sub>3</sub>COO<sup>-</sup> will be formed. In the early stages of the titration, there will still be weak acid present, so the presence of both the weak acid and its conjugate base produces a buffer solution.

The pH will continue to increase (see Figure 3.4.6), but only gradually as the OH<sup>-</sup> is added. This is another illustration of the ability of a buffer solution to resist large changes in pH. At the midpoint of the titration (half of the volume needed to reach the equivalence point), the pH of the solution equals the pK<sub>a</sub> of the acid due to the 1:1 ratio of the acid and conjugate:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

At the midpoint, [A<sup>-</sup>] = [HA]

$$\therefore K_a = [\text{H}^+] \\ \text{and} \\ \text{p}K_a = \text{pH}$$

As the equivalence point is reached, there is so little weak acid left that the buffering capability of the solution is diminished. The pH will increase rapidly just before the equivalence point and continue the sharp increase after the equivalence point. Once again, the equivalence point is at the inflection point of the curve.

At the equivalence point, the only species present that may react are the conjugate base and water. The reaction of the conjugate base produces a basic solution. At the equivalence point of a weak acid–strong base titration, the solution is basic.

After the equivalence point, the pH will increase until the solution is strongly basic due to an excess of  $\text{OH}^-(\text{aq})$ . The pH will continue to increase only slightly as the excess amount of  $\text{OH}^-(\text{aq})$  increases.

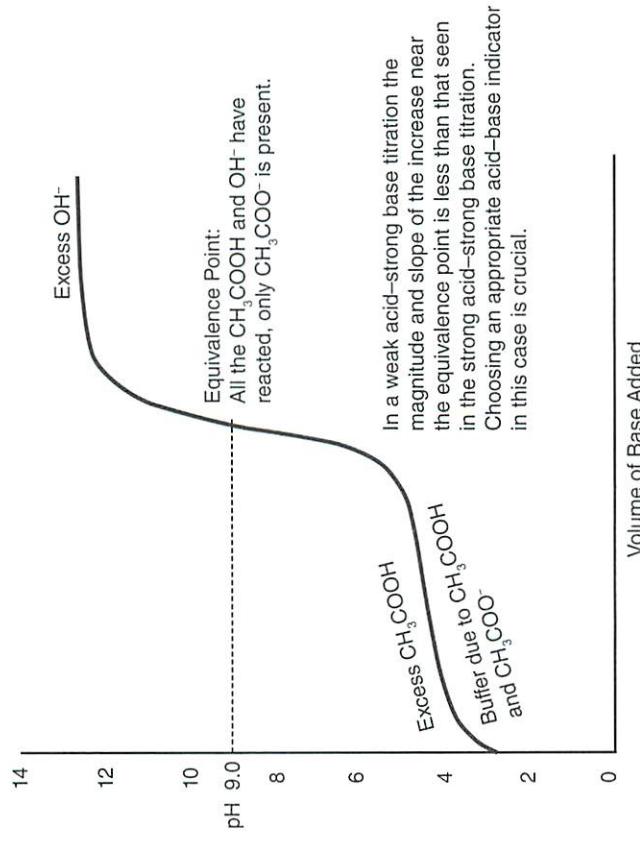
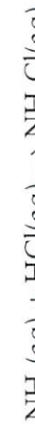


Figure 3.4.6 Titration curve for a weak acid–strong base.

#### Weak Base–Strong Acid Titration

Another familiar example helps illustrate a weak base–strong acid titration:



Because the acid is strong, it is shown as  $\text{H}_3\text{O}^+$ , the result of the complete ionization of HCl:



In this titration, the initial pH will be basic due to the presence of the weak base. As the strong acid is added, the reaction shown above occurs, producing the conjugate acid ( $\text{NH}_4^+$ ). Both the weak base and its conjugate acid are present. This region of the titration curve represents the “buffered” solution (see Figure 3.4.7).

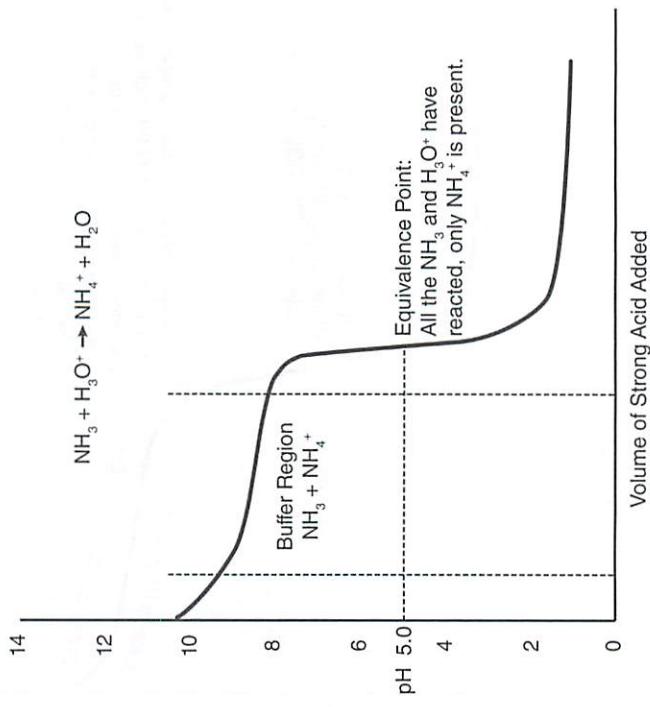


Figure 3.4.7 Titration curve for a weak base-strong acid.

As more of the strong acid is added, most and then all of the weak base will be consumed and the solution will no longer be a buffer.

At the midpoint of this titration, the pH of the solution =  $pK_b$  of the base:

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

At the midpoint,  $[HB^+] = [B]$

$$\therefore K_b = [OH^-]$$

and

$$pK_b = pOH$$

or

$$pH = 14 - pK_b$$

When the number of moles of HCl added is equal to the initial moles of  $NH_3$ , the solution is at the equivalence point and contains only the salt  $NH_4Cl$  (ammonium chloride). The pH is < 7.0 as the solution contains the ammonium ion, the conjugate acid of ammonia. When adding strong acid to weak conjugate acid, the pH will fall rapidly.

Consider what effect the presence of the strong acid HCl has on the percent hydrolysis of the weak acid  $NH_4^+$ . Note that the ammonium ion would normally undergo hydrolysis according to:



The strong acid, HCl, is fully ionized in solution, and if 0.10 moles of HCl are added beyond the equivalence point, there will be 0.10 moles of  $H_3O^+$  present in the solution. The  $H_3O^+$  suppresses the ionization of ammonium.

**Example 3.4.11. Weak Base–Strong Acid Titration (In-Class Exercise)**

Referring to the titration curve shown in Figure 3.4.7, suppose that 25.0 mL of 0.400 M  $\text{NH}_3$  is titrated with 0.200 M HCl.

1. Determine the pH:
  - a. After 20.0 mL of HCl are added.
  - b. At the equivalence point.
  - c. If 65.0 mL of HCl are added.
2. Find the percent ionization of the  $\text{NH}_4^+$  at points (b) and (c).

### Section 3.4 Review Problems

1. Determine whether the following combinations of species will produce a buffer solution.
  - a. 250 mL of 0.150 M  $\text{HNO}_2$  and 100 mL of 0.150 M NaOH
  - b. 7.20 g of  $\text{C}_6\text{H}_5\text{COONa}$  and 500 mL of 0.100 M  $\text{HClO}_4$
  - c. 500 mL of 0.250 M  $(\text{CH}_3)_2\text{NH}$  and 525 mL of 0.100 M  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$
  - d. 300 mL of 0.125 M  $\text{CH}_3\text{NH}_3^+$ Cl and 125 mL of 0.100 M KOH
  - e. 400 mL of 0.115 M  $\text{NH}_4^+\text{NO}_3$  and 200 mL of 0.110 M  $\text{HNO}_3$
2. Supply the missing words to complete the following three sentences:
  - a. A buffer solution contains two components, either a \_\_\_\_\_ acid and its \_\_\_\_\_, or a \_\_\_\_\_ base and its \_\_\_\_\_.
  - b. The pH of a buffer depends only on the \_\_\_\_\_ of the concentrations of the two components, so it is \_\_\_\_\_ by dilution.
  - c. If strong acid is added to a buffer mixture, it is removed by reaction with the \_\_\_\_\_ component, while added strong base is removed by reaction with the \_\_\_\_\_ component.
3. A solution is made from 0.200 mol formic acid,  $\text{HCOOH}$ , and 0.500 mol potassium formate,  $\text{HCOOK}$ , diluted to 750 mL volume. Formic acid has  $K_a = 1.9 \times 10^{-4}$ . Calculate:
  - a. The pH of this solution.
  - b. The change in pH if the total volume is diluted to 2.00 L with water.
  - c. The change in pH if 4.0 g of sodium hydroxide is added.
4. What mass, in grams, of  $\text{NaNO}_2$  must be added to 700 mL of 0.165 M  $\text{HNO}_2$  to produce a solution with a pH of 3.50?  
Data:  $K_a$  for  $\text{HNO}_2 = 4.5 \times 10^{-4}$

5. Answer the following:
- Calculate the pH of aqueous ammonia, concentration  $0.12\text{ M}$  ( $K_b = 1.8 \times 10^{-5}$ ).
  - 4.40 g of ammonium chloride,  $\text{NH}_4\text{Cl}$ , is added to a 500 mL portion of  $0.12\text{ M}$  aqueous ammonia. What is the change in pH?
  - How will the pH of the solution in (b) change if the solution is diluted to 1.0 L volume?
  - How will the pH of the solution in (b) change if 50 mL of  $1.0\text{ M}$  HCl is added?
6. Answer the following:
- What mass of sodium acetate should be dissolved in 1.00 L of acetic acid,  $0.150\text{ M}$  concentration, in order to produce a buffer with  $\text{pH} = 4.5$ ? ( $K_a$  for  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ )
  - What mass of  $\text{NH}_4\text{NO}_3$  must be added to 500 mL of  $0.85\text{ M}$   $\text{NH}_3\text{(aq)}$  in order to prepare a buffer solution with a pH of 9.70? ( $K_b$  for  $\text{NH}_3 = 1.8 \times 10^{-5}$ )
7. Answer the following:
- What mass of sodium acetate must be added to 500 mL of  $1.00\text{ M}$  acetic acid to provide a solution of  $\text{pH} = 5.00$ ? ( $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ )
  - What is the effect on the pH of the above solution of adding: (i) 50 mL of  $1.00\text{ M}$  HCl(aq) (ii) 50 mL of  $1.00\text{ M}$  NaOH(aq)?
8. Answer the following:
- In contrast to hydrides of the other halogens, HF is a weak acid, with  $K_a = 7.2 \times 10^{-4}$ . What would be the pH of a solution made by adding 1.00 g of solid NaOH to 50.0 mL of  $1.00\text{ M}$  HF?
  - 50 mL of a  $1.00\text{ M}$  solution of HF is titrated with  $1.00\text{ M}$  KOH solution. What would the pH be when 25 mL of the KOH solution has been added?
  - Suppose 25 mL of  $1.00\text{ M}$  HCl is added to 50 mL of  $1.00\text{ M}$  HF. What is the pH and the percent ionization of the HF in this solution?

9. Phosphate buffers are important in controlling the pH of physiological fluids, including blood. An important equilibrium is that for the second dissociation of phosphoric acid ( $\text{H}_3\text{PO}_4$ ):



If blood has a pH of 7.40, what is the ratio  $[\text{H}_2\text{PO}_4^-] / [\text{HPO}_4^{2-}]$ ?

10. Carbonic acid,  $\text{H}_2\text{CO}_3$ , has  $K_{a1} = 4.4 \times 10^{-7}$  and  $K_{a2} = 4.7 \times 10^{-11}$ . Calculate the pH of:

- 0.20 mol sodium carbonate,  $\text{Na}_2\text{CO}_3$ , and 0.40 mol sodium hydrogen carbonate,  $\text{NaHCO}_3$ , in solution in a 500 mL volume.
- 0.050 mol sodium hydrogen carbonate,  $\text{NaHCO}_3$ , and 0.010 mol of carbonic acid,  $\text{H}_2\text{CO}_3$ , in solution in a 100 mL volume.

11. When 35.0 mL of 0.200 M acetic acid ( $K_a = 1.8 \times 10^{-5}$ ) is titrated with 0.250 M NaOH solution, what is the pH at the equivalence point?

12. Calculate the pH in the following solutions.

- At the equivalence point when 0.500 M nitrous acid ( $\text{HNO}_2$ ) is titrated with 0.100 M NaOH.
- At the equivalence point when 0.800 M methylamine ( $\text{CH}_3\text{NH}_2$ ) is titrated with 0.400 M HCl.
- Joe Student is titrating two weak acids with KOH solution. They have the same original concentration, but acid A is 10% dissociated while acid B is stronger and is 20% dissociated. Joe therefore expects acid B to require twice the volume of KOH solution that acid A requires. However, it doesn't work out that way. What is wrong with Joe's reasoning?
- Three indicators are available: bromocresol purple,  $\text{p}K_a = 6.8$ ; bromophenol blue,  $\text{p}K_a = 3.9$ ; *o*-cresolphthalein,  $\text{p}K_a = 8.9$ . Without performing detailed pH calculations, which indicator should be used for each of the following titrations:
  - $\text{NH}_3(\text{aq})$  with  $\text{HNO}_3$
  - $\text{Ba}(\text{OH})_2$  with  $\text{HBr}$
  - $\text{LiOH}$  with  $\text{HCOOH}$



# Chapter 4

## Electrochemistry



### 4.1 Redox Reactions

#### OBJECTIVES

After studying this topic, you should be able to:

- Identify a redox reaction.
- Separate an overall redox reaction into two half-reactions.
- Describe the difference between an oxidation and reduction half-reaction.
- Assign oxidation states to all species in a reaction.
- Balance various types of redox reactions.

#### INTRODUCTION

Oxidation–reduction reactions, commonly referred to as “redox” reactions, are characterized by a change in the *oxidation state* of one or more elements in the reactants. In essence, in a redox reaction there is a net transfer of electrons from one reactant to another.

#### REDOX HALF-REACTIONS

The overall redox reaction consists of two half-reactions. In one half-reaction, electrons are lost (donated); this is called the *oxidation* half-reaction. In the other half-reaction, electrons are gained (received); this is called the *reduction* half-reaction. For example, in the reaction that occurs when iron is dissolved in hydrochloric acid:

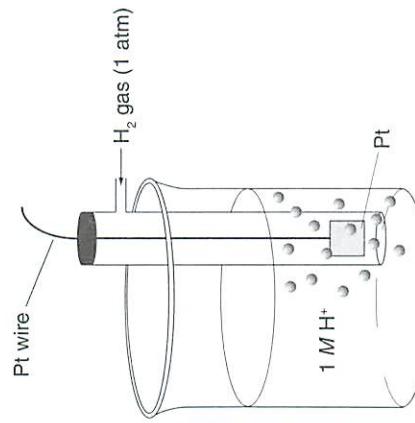


I have been so electrically occupied of late that I feel as if hungry for a little chemistry; but then the conviction crossed my mind that these things hang together under one law and that the more haste we make onwards, each in his own path, the sooner we shall arrive, and meet each other at that state of knowledge of natural causes from which all varieties of effects may be understood and enjoyed.

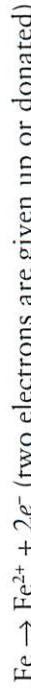
Michael Faraday (1791–1867)

#### Topics Covered:

- 4.1 Redox Reactions
- 4.2 Voltaic Cells
- 4.3 Electrolysis and Electrolytic Cells
- 4.4 Batteries



The two half-reactions are:



In this case, the iron gave up two electrons so this is the oxidation half-reaction. The hydrogen gained two electrons so this is the reduction half-reaction. A quick way to remember the process is to think of OIL RIG: Oxidation Is Loss; Reduction Is Gain.

In a redox reaction, the species that donates (or loses) electrons is called the *reducing agent*. After the reaction has taken place, the reducing agent has been *oxidized*.

Conversely, the species that accepts (or gains) electrons is called the *oxidizing agent*. After the reaction has taken place, the oxidizing agent has been *reduced*.

When the two half-reactions previously mentioned are combined:



it is easy to see that the metal, Fe, acts as the reducing agent by transferring two electrons to the H<sup>+</sup> ions, which results in hydrogen gas. Note that the chloride ions (Cl<sup>-</sup>) are spectator ions and neither gain nor lose electrons.

Oxidation and reduction always occur together. In the balanced reaction, the number of electrons lost in the oxidation half-reaction must equal those gained in the reduction half-reaction.

### OXIDATION STATES

*Oxidation states* are used to facilitate the electron accounting in redox reactions.

Note that because oxidation state refers to a number, the term *oxidation number* is often used synonymously. For an atom in a covalent molecule, the oxidation number is equal to the charge that the atom would have if both electrons of each covalent bond in the Lewis structure were assigned to the more electronegative atom. In general, however, oxidation states are determined by a set of rules.

The rules for assigning oxidation states to species are listed below:

1. The oxidation state is always zero in a pure element or elemental substance.
2. When assigning oxidation states to the elements in a compound, follow the rules below in the sequence provided:
  - a. Fluorine is always  $-1$
  - b. Group 1 metals (Na, K, etc.) are  $+1$
  - c. Group 2 metals (Ca, Mg, etc.) are  $+2$
  - d. Hydrogen is  $+1$  (except when it is bonded to a metal, where it is  $-1$ )
  - e. Oxygen is usually  $-2$
  - f. Other halogens (Group 17) are usually  $-1$ .
3. The oxidation state is equal to the charge on a monatomic ion.  
(e.g.,  $\text{Na}^+ = +1$ ;  $\text{Ba}^{2+} = +2$ ;  $\text{Cl}^- = -1$ ; etc.)
4. In a neutral species, the total must equal 0.  
[e.g.,  $\text{HBr} = (+1) + (-1) = 0$ ;  $\text{PBr}_3 = (+5) + 5(-1) = 0$ ]
5. In a complex ion, the total must equal the charge on the ion.  
[e.g.,  $\text{NH}_4^+ = (-3) + 4(+1) = +1$ ]

Oxidation states (numbers) are not to be confused with formal charges in Lewis structures, even though the two may occasionally coincide.

#### Example 4.1.1. Determination of Oxidation States (In-Class Exercise)

What is the oxidation state of phosphorus in sodium phosphate,  $\text{Na}_3\text{PO}_4$ , and chromium in  $\text{Cr}_2\text{O}_7^{2-}$ ?

In any redox reaction, there must be a change in the oxidation state of one or more of the elements. Since electrons have a negative charge, elements in a redox reaction are actually gaining or losing negative charges. When a species loses electrons (oxidizes), the oxidation state increases (e.g.,  $-3$  to  $-1$ ). When a species gains electrons (is reduced), the oxidation state decreases (e.g.,  $+3$  to  $+1$ ). For example, the equation:



is a redox reaction because aluminum increases in oxidation state from  $0$  to  $+3$ , and copper decreases from  $+2$  to  $0$ . The Al is oxidized; the Cu $^{2+}$  is reduced. Al is the reducing agent and Cu $^{2+}$  is the oxidizing agent.

#### Example 4.1.2. Oxidation and Reduction (In-Class Exercise)

In the following reaction, identify the oxidizing agents and the reducing agents:



#### Oxidation States of Carbon

When studying organic chemistry, it is often useful to assign oxidation states to carbon atoms in a molecule. The oxidation state of carbon may be determined by comparing the electronegativity of carbon to the electronegativity of each atom to which the carbon atom is bonded.

If the carbon atom is bonded to an atom more electronegative than itself, that bond contributes  $+1$  to the oxidation state of carbon. If the carbon atom is bonded to an atom less electronegative than itself, that bond contributes  $-1$  to the oxidation state of carbon.

For example, a C–H bond would contribute  $-1$  to the oxidation state of the carbon, because H is less electronegative than C.

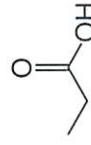
A C–O bond would contribute  $+1$  to the oxidation state of the carbon, because O is more electronegative than C.

A C=O bond would contribute  $+2$  to the oxidation state of the carbon,  $+1$  for each bond.

A C–C bond would contribute  $0$  to the oxidation state of each of the C atoms.

**Example 4.1.3. (In-Class Exercise)**

Determine the oxidation state of each Carbon atom in the following molecule.

**STEPS FOR BALANCING REDOX REACTIONS**

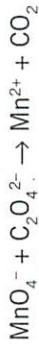
The following method works by splitting a redox reaction into two half-reactions, balancing first the stoichiometry and then the charges within each half-reaction, and finally by combining the two balanced half-reactions.

1. Recognize a redox reaction by noting the changes in oxidation numbers.
2. Write the reaction as two half-reactions.
3. In each half-reaction, balance the stoichiometric coefficients for all atoms except H and O.
4. Add  $\text{H}_2\text{O}$  to the side deficient in O to balance O.
5. Balance the H atoms as follows. Calculate the number of H atoms by which one side is deficient in H. Then
  - a. For acidic conditions: Add that number of  $\text{H}^+$  ions to the side deficient in H.
  - b. For basic conditions: Add that number of  $\text{H}_2\text{O}$  molecules to the side deficient in H *and* the same number of  $\text{OH}^-$  ions to the other side. (The addition of  $\text{OH}^-$  is necessary to compensate for the excess of H and O atoms arising through the addition of  $\text{H}_2\text{O}$ .)
6. Balance the charges in each half-reaction by adding electrons to the side deficient in negative charge. Make sure that the electrons are on opposite sides of the two half-reactions.
7. If the half-reactions have different numbers of electrons, multiply one or both half-reactions by coefficients that result in electron parity.

- Add the balanced half-reactions, cancel species if necessary, and check for the overall stoichiometric and charge balance.

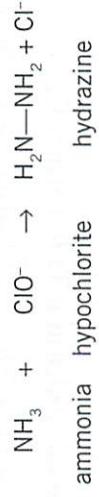
#### Example 4.14. Balancing an Acidic Redox Reaction (In-Class Exercise)

Balance the following redox reaction by the half-reaction method:



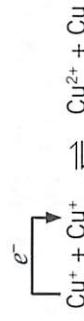
#### Example 4.15. Balancing a Basic Redox Reaction (In-Class Exercise)

Balance the following redox reaction using the half-reaction method:



### DISPROPORTIONATION REACTIONS

One other type of redox reaction is called a *disproportionation reaction*, where a substance in an intermediate oxidation state goes to higher and lower states by electron transfer. For example, the +1 oxidation state is unstable for Cu:

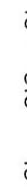


This type of redox reaction can be balanced as follows:

- Oxidation:  $\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^-$
- Reduction:  $\text{Cu}^+ + e^- \rightarrow \text{Cu}$
- Add the two equations:  $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$ .

#### Example 4.16. Balancing a Disproportionation Reaction (In-Class Exercise)

When  $\text{Cl}_2(\text{g})$  dissolves in a base, it disproportionates. Balance the redox equation:



## Section 4.1 Review Problems

1. In the following balanced redox reactions, identify the species (ion or molecule) that has been oxidized and the species that has been reduced. If the species contains more than one element, indicate which element (or elements) has undergone a change in oxidation state, and the magnitude of the change.
  - a.  $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{C}_2\text{O}_4^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{CO}_2(\text{g}) + 7\text{H}_2\text{O}$
  - b.  $\text{Cu}_2\text{S}(\text{s}) + 8\text{HNO}_3(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow 2\text{Cu}^{2+}(\text{aq}) + \text{SO}_2(\text{g}) + 8\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}$
  - c.  $2\text{F}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{OF}_2(\text{aq}) + 2\text{F}^-(\text{aq}) + \text{H}_2\text{O}$
2. Balance the following reactions.
  - a. Acidic:  $\text{MnO}_4^-(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{Sn}^{4+}(\text{aq})$
  - b. Basic:  $\text{Zn}(\text{s}) + \text{MnO}_2(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Mn}(\text{OH})_3(\text{s})$
3. The thiosulfate ion reacts with iodine according to the unbalanced equation:
$$\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$$
  - a. Balance this equation. The reaction occurs in neutral solution.
  - b. A 50.0 mL sample of a solution of iodine reacted with exactly 16.00 mL of a solution of 0.0240 M sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). What was the molar concentration of iodine in the solution?
4. In acidic aqueous solution, the permanganate ion ( $\text{MnO}_4^-$ ) reacts with the oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ ) to give  $\text{Mn}^{2+}$  ions and  $\text{CO}_2$ .
  - a. Write a balanced equation for this reaction.
  - b. When a sample containing 0.1608 g sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) was titrated with a solution of potassium permanganate ( $\text{KMnO}_4$ ) under acidic conditions, 24.00 mL of  $\text{KMnO}_4$  was required to reach the endpoint. What was the concentration of the  $\text{KMnO}_4$  solution?

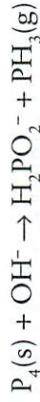
5. The following reaction occurs in acidic solution:



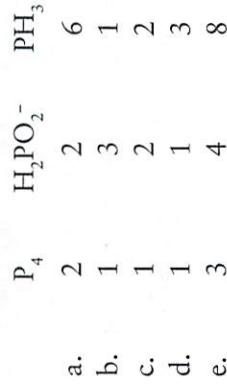
Which one of (a) through (e) below represents a correct set of coefficients for the balanced reaction?



6. Phosphine,  $\text{PH}_3$ , is prepared by the reaction:



Which one of (a) through (e) below represents a correct set of coefficients for the balanced reaction?



## 4.2 Voltaic Cells

### OBJECTIVES

After studying this topic, you should be able to:

- Write a cell diagram for a given spontaneous redox reaction.
- Use standard reduction potentials to determine the cell potential of an electrochemical cell, and the associated free energy change, under standard and nonstandard conditions.
- Predict the direction of a reversible redox reaction.
- Use the Nernst equation to determine the concentration of an ion in solution.

### INTRODUCTION

Electrons transferred in redox reactions are the same charged particles that move in a metal wire as an electric current. This suggests that there should be a way to harness the chemical energy of a spontaneous redox reaction to generate an electric current. Conversely, there should be a way to use an electric current to cause a nonspontaneous redox reaction to occur. The branch of chemistry that studies this interconversion of chemical and electrical energy is called *electrochemistry*.

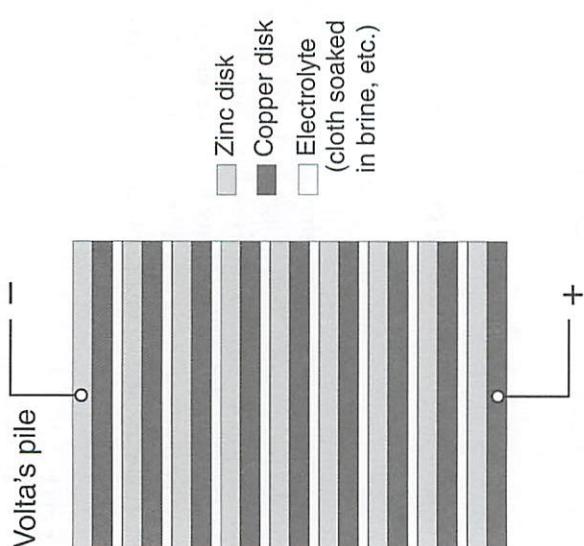
### ELECTROCHEMICAL CELLS

The experimental setup that produces an electric current and does electrical work through the use of a redox reaction is called an *electrochemical cell*. Electrochemical cells are also known as *galvanic cells*, after the 18th century Italian physiologist Luigi Galvani, who discovered the principle of chemically generated electricity while experimenting with dissected frogs. Another term used is *voltaic cell*, after the Italian physicist Alessandro Volta, who built the first working electrical battery.

If a chemical reaction is forced to occur in an electrochemical cell by introducing an electric current from an external source (e.g., recharging the cell), the process is called *electrolysis* and the cell nomenclature changes from voltaic cell to *electrolytic cell*. Electrolytic cells are examined in more detail in the next topic.

**The Daniell Cell**

The battery built by Volta was a stacked pile of alternating zinc and copper disks separated by cloth soaked in brine and sulfuric acid (see the image below). Volta's battery could only sustain a current for a short time, however. In 1836, British chemist John Daniell added the same two metals in oxidized form (cations) to the battery in comparable amounts and greatly improved Volta's original design.



The Daniell cell is based on the overall redox reaction:



which consists of the two half-reactions:



The overall reaction can be carried out by placing a bar of zinc metal in an aqueous solution of copper sulfate (see Figure 4.2.1). In this instance, the electrons will migrate from the reducing agent ( $\text{Zn}$ ) to the oxidizing agent ( $\text{Cu}^{2+}$ ) at

the solid–liquid boundary. The zinc bar will gradually dissolve to form aqueous  $\text{ZnSO}_4$ , while metallic copper will appear in the form of a precipitate. No useful electrical work is obtained in this experimental arrangement, however, because the apparatus does not harvest the energy of the electron transfer.

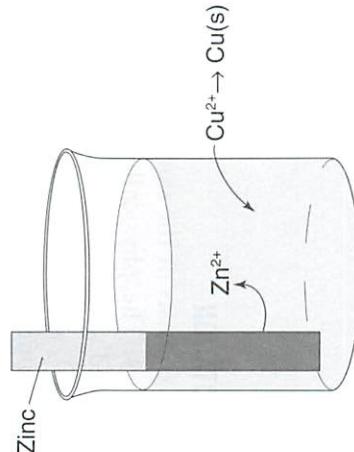


Figure 4.2.1 Oxidation of Zn by  $\text{Cu}^{2+}$  solution.

In constructing a Daniell cell, Zn and Cu bars are first immersed in separate beakers filled with aqueous  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  solutions respectively, and then connected with a wire. At this stage nothing will happen because the flow of electrons from Zn to Cu would upset the charge balance of the beakers. Therefore, the next step is to compensate for the negative charge loss in the Zn beaker and negative charge gain in the Cu beaker by allowing the negatively charged  $\text{SO}_4^{2-}$  ions in the Cu beaker to migrate to the Zn beaker. This is achieved by connecting the two sulfate solutions with a *salt bridge*, which is an inverted U-tube filled with an aqueous solution of an electrochemically inert salt (e.g.,  $\text{K}_2\text{SO}_4$ ). The salt bridge has a glass wool plug at each end to limit unnecessary mixing of  $\text{K}_2\text{SO}_4$  with the reactants.

Once the electric circuit is completed, the Zn bar will start dissolving, Cu metal will be deposited on the Cu bar, and a light bulb connected to the wire will glow. The complete experimental setup of this voltaic cell is shown in Figure 4.2.2.

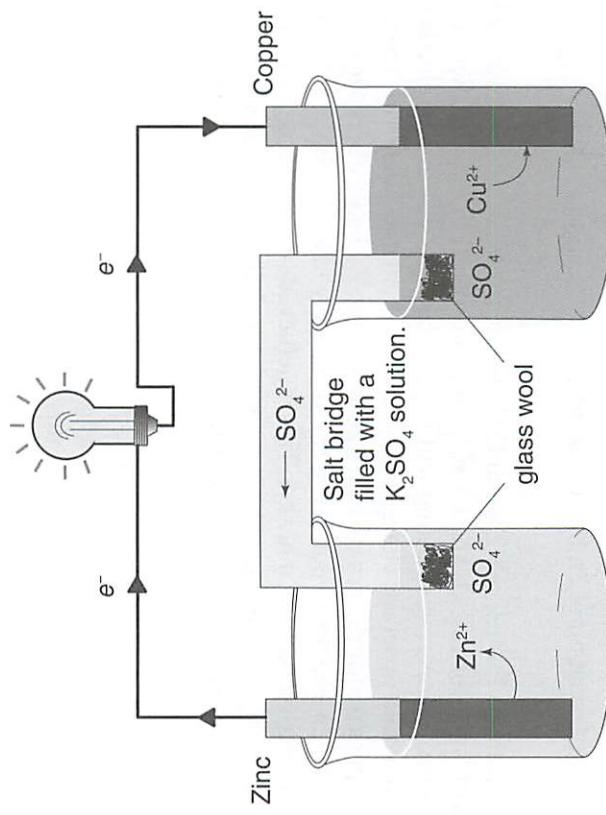


Figure 4.2.2 Daniell cell.

#### ELECTROCHEMICAL CELL NOTATION

Every electrochemical cell consists of the same components, commonly referred to by their technical names. The physically separated subsystem where each half-reaction occurs is called a *half-cell*. In the Daniell cell, one half-cell is the beaker containing the  $ZnSO_4$  solution with the immersed Zn bar, and the other half-cell is the beaker containing the  $CuSO_4$  solution with the immersed Cu bar.

The half-reaction in each half-cell takes place on the surfaces of an *electrode*. An electrode is an electronic conductor (usually a metal or graphite bar) that is in contact with an *electrolyte* (a solution or a molten salt). Often, the electrode is also one of the reactants (as are the Zn and Cu bars in the Daniell cell). However, when none of the reactants in a half-cell is a solid conductor, a nonreactive metal is used as the electrode instead. Each of the two electrodes has its own name. By convention, the electrode where the reduction occurs is called the *cathode*, and the electrode where the oxidation occurs is called the *anode*. In the Daniell cell, Zn is the anode and Cu is the cathode.

**Cell Diagram**

There is a convenient shorthand notation for representing a voltaic cell called the *cell diagram*. For example, the diagram for the Daniell cell is:



The following conventions are used when writing a cell diagram:

1. The anode is written first on the left, followed by the other species in the order in which they occur in the cell from the anode to the cathode.
2. A phase boundary is represented by a single vertical bar.
3. The salt bridge (or equivalent) is indicated by a double vertical bar.
4. If two or more reactants are in the same phase, separate them by a comma.
5. If inert electrodes such as graphite or platinum are involved, they are placed on the anode or cathode end of the diagram as applicable, and separated by a single vertical bar.
6. Stoichiometric coefficients and species that are neither reduced nor oxidized are not shown.

A simple method to help remember the first (least intuitive) convention is that the anode and cathode appear in a cell diagram in alphabetical order.

**Example 4.2.1. Writing Cell Diagrams (In-Class Exercise)**

Write cell diagrams for voltaic cells based on the following reactions:

- a.  $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{Br}_2(\text{l})$  [inert graphite electrodes]
- b.  $\text{Co(s)} + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Co}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$  [Co and inert Pt electrodes]
- c.  $10\text{I}^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 5\text{I}_2(\text{s}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O(l)}$  [inert graphite electrodes]

### CELL POTENTIAL

The electrical energy difference between any two electrodes in an electrochemical cell, which is also known as the cell potential or cell voltage, can be experimentally measured using a voltmeter. The voltage measured depends not only on the nature of the reactants in the cell, but also on their concentrations (or pressures for gaseous reactants) and on the surrounding temperature.

For example, if the concentrations of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions in the Daniell cell are both 1.0 M and the temperature is 25 °C, the voltmeter will show that  $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$ . As we have seen previously, the superscript "°" denotes standard conditions, which are defined below. (Note that 1.0 M and 25 °C are the standard conditions for electrochemical cells.)

### Standard Hydrogen Electrode

Although the potential difference for a complete cell can be measured with a voltmeter, it is not possible to measure the potential for a half-cell. So, the potential for a half-cell can only be measured relative to a commonly accepted reference half-cell. The electrode chosen for this purpose is typically the *standard hydrogen electrode*. It consists of  $\text{H}_2$  gas (1 atm) surrounding a platinum electrode immersed in 1 M strong acid,  $\text{H}^+(\text{aq})$ , at 25 °C (see Figure 4.2.3). The net ionic equation describing the equilibrium at the surface of this electrode is:



$$E^{\circ} = 0 \text{ volts}$$

Standard electrode potentials of all other electrodes are relative to the standard hydrogen electrode. (The  $E^{\circ} = 0$  volts of the standard hydrogen electrode is an arbitrary assignment.) By convention, the standard electrode potential ( $E^{\circ}$ ) measures the tendency for a reduction process to occur at an electrode.

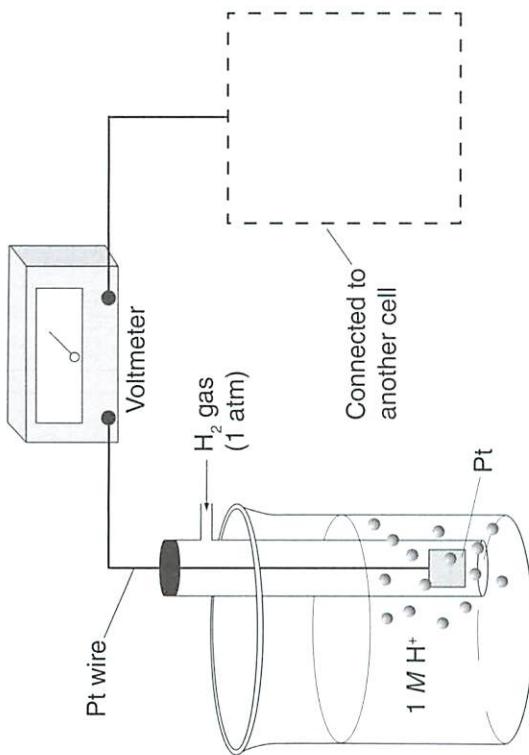


Figure 4.2.3 Standard hydrogen electrode.

Table 4.2.1 and Table 4.2.2 list standard reduction potentials that have been measured experimentally for many half-reactions (electrodes). Stronger oxidizing agents are more easily reduced and have more positive  $E^\circ_{\text{red}}$  values.



Stronger oxidizing agents form products that are more difficult to oxidize, so if a species has a more positive reduction potential, then the product is a weaker reducing agent. Reversing the two reactions above:



TABLE 4.2.1 STANDARD REDUCTION POTENTIALS (V) AT 25 °C\*

HALF-REACTION	$E^\circ_{\text{red}}$	HALF-REACTION	$E^\circ_{\text{red}}$
$\text{Li}^+(\text{aq}) + e^- \rightarrow \text{Li(s)}$	-3.05	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{K}^+(\text{aq}) + e^- \rightarrow \text{K(s)}$	-2.93	$\text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{Ba}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ba(s)}$	-2.90	$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.59
$\text{Sr}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Sr(s)}$	-2.89	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ca(s)}$	-2.87	$\text{Fe}^{2+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na(s)}$	-2.71	$\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)}$	+0.80
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mg(s)}$	-2.37		
$\text{Be}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Be(s)}$	-1.85	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow 2\text{H}_2\text{O}$	+0.82 (pH = 7)
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Al(s)}$	-1.66	$\text{Hg}_{2+}(\text{aq}) + 2e^- \rightarrow 2\text{Hg(l)}$	+0.85
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mn(s)}$	-1.18	$2\text{Hg}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Hg}_{2+}(\text{aq})$	+0.92
$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83	$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \rightarrow \text{NO(g)} + 2\text{H}_2\text{O}$	+0.96
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn(s)}$	-0.76	$\text{Br}_2(\text{l}) + 2e^- \rightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{Cr}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Cr(s)}$	-0.74	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Fe(s)}$	-0.44		
$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.41 (pH = 7)	$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{Cr}^{3+}(\text{aq}) + e^- \rightarrow \text{Cr}^{2+}(\text{aq})$	-0.41	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{Cd}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cd(s)}$	-0.40	$\text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{PbSO}_4(\text{s}) + 2e^- \rightarrow \text{Pb(s)} + \text{SO}_4^{2-}$	-0.31	$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6e^- \rightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}$	+1.45
$\text{Co}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Co(s)}$	-0.28	$\text{Au}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Au(s)}$	+1.50
$\text{Ni}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Ni(s)}$	-0.25	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51
$\text{Sn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Sn(s)}$	-0.14	$\text{Ce}^{4+}(\text{aq}) + e^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb(s)}$	-0.13		
$2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$	0.00		

HALF-REACTION	$E^\circ_{\text{red}}$	HALF-REACTION	$E^\circ_{\text{red}}$
$\text{Sn}^{4+}(\text{aq}) + 2e^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.13	$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2e^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{Cu}^{2+}(\text{aq}) + e^- \rightarrow \text{Cu}^+(\text{aq})$	+0.15	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow 2\text{H}_2\text{O}$	+1.77
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	+0.20	$\text{Co}^{3+}(\text{aq}) + e^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{AgCl}(\text{s}) + e^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22	$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s})$	+0.34	$\text{F}_2(\text{g}) + 2e^- \rightarrow 2\text{F}^-(\text{aq})$	+2.87

\* The concentration is 1 M for dissolved species and the pressure is 1 atm for gases.

TABLE 4.2.2 STANDARD REDUCTION POTENTIALS (BASIC) (V) AT 25 °C\*

OXIDIZED SPECIES	EQUATION	REDUCED SPECIES	$E^\circ_{\text{red}}$
Aluminum(III)	$[\text{Al}(\text{OH})_4]^- + 3e^- \rightarrow \text{Al}(\text{s}) + 4\text{OH}^-$		-2.35
Manganese(II)	$\text{Mn}(\text{OH})_2(\text{s}) + 2e^- \rightarrow \text{Mn}(\text{s}) + 2\text{OH}^-$		-1.55
N <sub>2</sub> (to hydrazine)	$\text{N}_2(\text{g}) + 4\text{H}_2\text{O} + 4e^- \rightarrow \text{N}_2\text{H}_4 + 4\text{OH}^-$		-1.16
Water	$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$		-0.83
Nitrate (to nitrite)	$\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$		0.00
Oxygen	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$		+0.40
Hypochlorite (to Cl <sub>2</sub> )	$\text{ClO}^- + \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{Cl}_2 + 2\text{OH}^-$		+0.40
Iodine	$\text{I}_2(\text{s}) + 2e^- \rightarrow 2\text{I}^-$		+0.53
Permanganate	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$		+0.59
Chlorate	$\text{ClO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Cl}^- + 6\text{OH}^-$		+0.61
Hypochlorite (to Cl <sup>-</sup> )	$\text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^-$		+0.89
Bromine	$\text{Br}_2(\text{l}) + 2e^- \rightarrow 2\text{Br}^-$		+1.08
Chlorine	$\text{Cl}_2(\text{g}) + 2e^- \rightarrow 2\text{Cl}^-$		+1.36

\* The concentration is 1 M for dissolved species and the pressure is 1 atm for gases.

**STANDARD CELL POTENTIAL**

One of the most common uses of standard electrode potentials is the determination of standard cell potential or  $E_{\text{cell}}^{\circ}$  for an electrochemical cell. To find the  $E_{\text{cell}}^{\circ}$  for a given redox reaction, follow these steps:

1. Based on the chemical equation for the overall reaction as written, identify the reduction half-reaction and look up its standard potential  $E_{\text{red}}^{\circ}$ .
2. Identify the oxidation half-reaction, look up the standard potential for the reduction half-reaction, and take that value with an opposite sign. This is the standard oxidation potential  $E_{\text{ox}}^{\circ}$ . Note that half-reactions often must be multiplied by a coefficient to make the number of  $e^-$  cancel. The  $E$  value is NOT multiplied when this occurs (unlike the  $\Delta H$  in thermodynamics).
3. The cell potential as the sum of  $E_{\text{ox}}^{\circ}$  and  $E_{\text{red}}^{\circ}$ :

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} \quad (4.2.1)$$

**Example 4.2.2. Standard Cell Potential of an  $\text{Fe}^{3+}$  and  $\text{I}^-$  Reaction (In-Class Exercise)**

Determine  $E_{\text{cell}}^{\circ}$  for a galvanic cell based on the reaction:

**Example 4.2.3. Standard Cell Potential of a Cd and  $\text{Cu}^{2+}$  Reaction (In-Class Exercise)**

Given the cell diagram below, determine the standard cell potential.

**Example 4.2.4. Determining the Standard Electrode Potential of  $\text{Al}^{3+}$  (In-Class Exercise)**

Consider a voltaic cell based on the reaction:



The concentrations of the ions are  $[\text{Al}^{3+}] = [\text{H}^+] = 1\text{ M}$ , the temperature is at  $25^\circ\text{C}$  and the voltmeter reads 1.66 V. Without using Table 4.2.1, predict the standard electrode (half-cell) potential of  $\text{Al}^{3+}$  relative to  $\text{H}^+$ .

### SPONTANEITY OF REDOX REACTIONS

In this section, the relationship between the standard Gibbs free energy change ( $\Delta G^\circ$ ) and standard cell potentials is examined.

The standard cell potential of a redox reaction is quantitatively related to that reaction's standard free energy change by the equation:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad (4.2.2)$$

In the equation:

$n$  is the number of *moles of electrons* transferred between the electrodes.

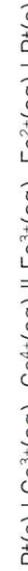
$F$  is a proportionality constant (called the Faraday constant), which is equal to 96,485 coulombs (C) per mole of electrons. (The Faraday constant will be explained in more detail in the next topic.)

In order for a reaction to occur spontaneously under standard conditions, the change of the standard free energy over the course of this reaction has to be negative, i.e.,  $\Delta G^\circ < 0$ . But according to Equation 4.2.2, a negative  $\Delta G^\circ$  means a positive  $E_{\text{cell}}^\circ$  and vice versa. Thus, one can tell whether a given redox reaction will occur spontaneously under standard conditions based on the sign of the corresponding standard cell potential:

- If  $E_{\text{cell}}^\circ + 0$ , then the reaction is spontaneous from left to right as written.
- If  $E_{\text{cell}}^\circ < 0$ , then the reverse reaction (from right to left) is spontaneous.
- If  $E_{\text{cell}}^\circ = 0$ , then the cell reaction is at equilibrium.

### Example 4.2.5. Spontaneity of a Ce<sup>3+</sup> and Fe<sup>3+</sup> Reaction (In-Class Exercise)

Consider the cell diagram below:



Will the resulting reaction proceed spontaneously as written?

**Example 4.2.6. Identifying the Anode and Cathode (In-Class Exercise)**

A galvanic cell was constructed from two half-cells:  $\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq})$  and  $\text{Ni}(\text{s}) \mid \text{Ni}^{2+}(\text{aq})$ . For the reaction to proceed spontaneously, which electrode is the cathode and which is the anode? What is the standard cell potential?

**Example 4.2.7. Which Metals Dissolve in HCl? (In-Class Exercise)**

Which of the metals Ag, Cu, Au, Sn, and Fe will dissolve in 1 M HCl?

**GIBBS FREE ENERGY AND THE NERNST EQUATION**

For standard concentrations (1 M) and temperature, the cell potential can be obtained using the standard reduction potentials collected in Tables 4.2.1 and 4.2.2.

To determine the cell potential for a cell in which the reactants are products in concentrations other than 1 M, the so-called Nernst equation is used. This equation can be derived as follows. Recall that the free energy of a reaction varies with concentrations of the reactants according to the equation:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (4.2.3)$$

where  $Q$  is the reaction quotient,  $R$  is the gas constant =  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $T$  is the absolute temperature in Kelvin. The free energies  $\Delta G$  and  $\Delta G^\circ$  are related to the cell potentials by the equations:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \text{ and } \Delta G = -nFE_{\text{cell}}$$

Substituting these expressions for  $\Delta G$  and  $\Delta G^\circ$  in Equation 4.2.3 we obtain:

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q$$

which can be rewritten as:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \left( \frac{RT}{nF} \right) \ln Q \quad (4.2.4)$$

Equation 4.2.4 was proposed in the early 20th century by German chemist Walter Nernst and is known as the Nernst equation.

The combination  $RT/F$  appears frequently in electrochemistry. Its value at  $T = 298.15\text{ K}$  is:

$$\frac{RT}{F} = \frac{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}}{96,485\text{ C mol}^{-1}} = 0.0257\text{ V}$$

When  $T = 298.15\text{ K}$ , the Nernst equation may be written as:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left( \frac{0.0257\text{ V}}{n} \right) \ln Q \quad (4.2.5)$$

The reaction quotient,  $Q$ , involves concentrations of the ions (products in the numerator, reactant ions in the denominator) raised to the powers given by the corresponding stoichiometric coefficients. For example, for the reaction



the reaction quotient is given by

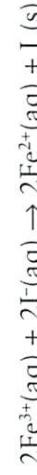
$$Q = \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2 [\text{I}^-]^2}$$

The Nernst equation can also be used to predict the spontaneity of a redox reaction under nonstandard conditions and to calculate the unknown concentration of a reactant if a cell voltage is known.

#### Example 4.2.8. Cell Potential of a Nonstandard Zn and Cu<sup>2+</sup> Reaction (In-Class Exercise)

Find the cell potential of the Daniell cell at 25 °C if the concentration of Zn<sup>2+</sup> ions is 0.50 mol L<sup>-1</sup> and that of Cu<sup>2+</sup> ions is 0.050 mol L<sup>-1</sup>.

In the example above, one mole of Zn reacts with one mole of Cu<sup>2+</sup> and two moles of electrons are involved, so  $n = 2$ . In general, to determine the value of  $n$  it is necessary to use the balanced equation for the redox reaction. For example, in the reaction:



each species changes oxidation state by one unit and there are two moles of each species involved. Thus,  $n = 2$ .

**Example 4.2.9. Concentration of an Ion in a Cell (In-Class Exercise)**

A voltmeter connected to the cell:



shows  $E_{\text{cell}} = 1.15 \text{ V}$  at  $25^\circ\text{C}$ . What is the concentration of  $\text{Cd}^{2+}$ ?

**Example 4.2.10. Concentration Cell (In-Class Exercise)**

Calculate the voltage of the following cell at  $25^\circ\text{C}$ :



## Section 4.2 Review Problems

1. Which one of the following correctly defines the terms anode and cathode?
  - a. The anode is the negative electrode, the cathode is the positive electrode.
  - b. The anode is the positive electrode, the cathode is the negative electrode.
  - c. Oxidation occurs at the anode, reduction occurs at the cathode.
  - d. Reduction occurs at the anode, oxidation occurs at the cathode.
  - e. Current flows from the cathode to the anode.
2. Separate the following redox reactions into two half-reactions and write conventional cell abbreviations for each:
  - a.  $2\text{Al(s)} + 3\text{Cd}^{2+}\text{(aq)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 3\text{Cd(s)}$  [acidic solution]
  - b.  $\text{Cl}_2\text{(g)} + 2\text{Fe}^{2+}\text{(aq)} \rightarrow 2\text{Cl}^-\text{(aq)} + 2\text{Fe}^{3+}\text{(aq)}$  [acidic solution]
  - c.  $2\text{Mn(s)} + \text{O}_2\text{(g)} + 2\text{H}_2\text{O} \rightarrow 2\text{Mn(OH)}_2\text{(s)}$  [basic solution]
3. For the following cell:
$$\text{Al(s)} \mid \text{Al}^{3+}\text{(aq)} \parallel \text{Br}_2\text{(l)} \mid \text{Br}^-\text{(aq)} \mid \text{Pt(s)}$$
write out the equations for each half-reaction, as reductions, give the  $E^\circ$  value for each, and evaluate  $E_{\text{cell}}^\circ$ . Combine the two half-reactions to make a balanced redox reaction, written in the direction in which the reaction would spontaneously proceed.
4. Evaluate  $E_{\text{cell}}^\circ$  for the following voltaic cells. In each case, state the direction in which the reaction would spontaneously proceed.
  - a.  $\text{Pt(s)} \mid \text{Mn}^{2+}\text{(aq)}, \text{MnO}_4^-\text{(aq)} \parallel \text{I}_2\text{(s)} \mid \text{I}^-\text{(aq)} \mid \text{Pt(s)}$  [acidic solution]
  - b.  $\text{Ni(s)} \mid \text{Ni}^{2+}\text{(aq)} \parallel \text{Ag}^+\text{(aq)} \mid \text{Ag(s)}$  [acidic solution]
  - c.  $\text{Pt(s)} \mid \text{NO}_2^-\text{(aq)}, \text{NO}_3^-\text{(aq)} \parallel \text{Mn(OH)}_2\text{(s)} \mid \text{Mn(s)}$  [basic solution]

5. Determine  $E_{\text{cell}}^{\circ}$  for the following reactions taking place in voltaic cells. In each case, state the direction in which the reaction would spontaneously proceed.

Acid solutions:

- a.  $6\text{Cr}^{2+}(\text{aq}) + \text{ClO}_3^{-}(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 6\text{Cr}^{3+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) + 3\text{H}_2\text{O}$
- b.  $2\text{Cr}^{3+}(\text{aq}) + 3\text{I}^{-}(\text{s}) + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{I}^{-}(\text{aq}) + 14\text{H}^+(\text{aq})$

Basic solutions:

- c.  $3\text{O}_2(\text{g}) + 2\text{Cl}^{-}(\text{aq}) \rightarrow 2\text{ClO}_3^{-}(\text{aq})$
- d.  $2\text{Al}(\text{s}) + 2\text{OH}^{-}(\text{aq}) + 6\text{H}_2\text{O} \rightarrow 2[\text{Al}(\text{OH})_4]^{-}(\text{aq}) + 3\text{H}_2(\text{g})$

6. Translate the following abbreviated voltaic cells into balanced redox reactions. Work out  $E_{\text{cell}}^{\circ}$  for each and indicate the direction in which reaction would spontaneously proceed.



7.  $E_{\text{cell}}^{\circ}$  is +0.33 V for the following cell:



- a. Write a balanced equation for the cell reaction as it occurs spontaneously.
- b. Evaluate  $E^{\circ}$  for the cathode half-reaction.
8. Use  $E^{\circ}$  values to explain why copper metal will dissolve in nitric acid, but not in hydrochloric acid.
9. The Daniell cell consists of a Zn/Zn<sup>2+</sup> half-cell and a Cu/Cu<sup>2+</sup> half-cell. What is  $E_{\text{cell}}^{\circ}$  when  $[\text{Zn}^{2+}] = 0.35 \text{ M}$  and  $[\text{Cu}^{2+}] = 1.20 \text{ M}$ ?
10. A galvanic cell consists of a Ni/Ni<sup>2+</sup> half-cell and an Mn/Mn<sup>2+</sup> half-cell.
- a. What is  $E_{\text{cell}}^{\circ}$  for this cell?
- b. What is  $E_{\text{cell}}^{\circ}$  when  $[\text{Ni}^{2+}] = 0.650 \text{ M}$  and  $[\text{Mn}^{2+}] = 0.150 \text{ M}$ ?
- c. Explain what happens to the concentrations of the ionic species as the cell is used.
- d. What are the concentrations of the ionic species when  $E_{\text{cell}}^{\circ} = 0$ ?

## 4.3 Electrolysis and Electrolytic Cells

### OBJECTIVES

After studying this topic, you should be able to:

- Explain the following terms: electrolysis, electrolytic cell, electrolyte, molten salt, overpotential, and electropolating.
- Predict the products of electrolysis.
- Relate the amount of reactant or product consumed or produced during electrolysis to the amount and duration of the current generated.

### INTRODUCTION

The process by which a nonspontaneous chemical reaction is forced to occur by the application of electrical energy is called *electrolysis*. In this topic, electrolysis and *electrolytic cells* are explained in detail, and important industrial applications of electrolytic processes such as electroplating and the chlor-alkali process are introduced.

### ELECTROLYSIS

A redox reaction that has a negative  $\Delta G$  (that is, a positive  $E_{\text{cell}}$ ) will occur spontaneously. The corresponding reverse reaction has a positive  $\Delta G$  (a negative  $E_{\text{cell}}$ ) and therefore will not occur spontaneously.

For example, when ignited at room temperature  $\text{H}_2$  and  $\text{O}_2$  combine to form  $\text{H}_2\text{O}$ , but water molecules do not break down into hydrogen and oxygen under the same conditions. Nevertheless, nonspontaneous reactions with  $E_{\text{cell}} < 0$  can be forced to occur electrochemically by using an electric current in a process called electrolysis. In electrolysis, electrical energy from an external source drives a nonspontaneous chemical reaction.

### Electrolytic Cells

The process of electrolysis is carried out in an *electrolytic cell*. In principle, an electrolytic cell can be readily constructed from the corresponding voltaic cell. Consider, for example, a voltaic cell based on the spontaneous reaction:



Under standard conditions, this cell generates a voltage of  $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$  and the Zn electrode produces electrons, while the Cu electrode consumes electrons. Thus, the spontaneous electron flow is from Zn to Cu. Now if a reverse voltage greater than 1.10 eV is applied to this cell from an external power source, then the direction of electron flow in the cell will be reversed and the overall reaction will change to:



as shown in Figure 4.3.1.

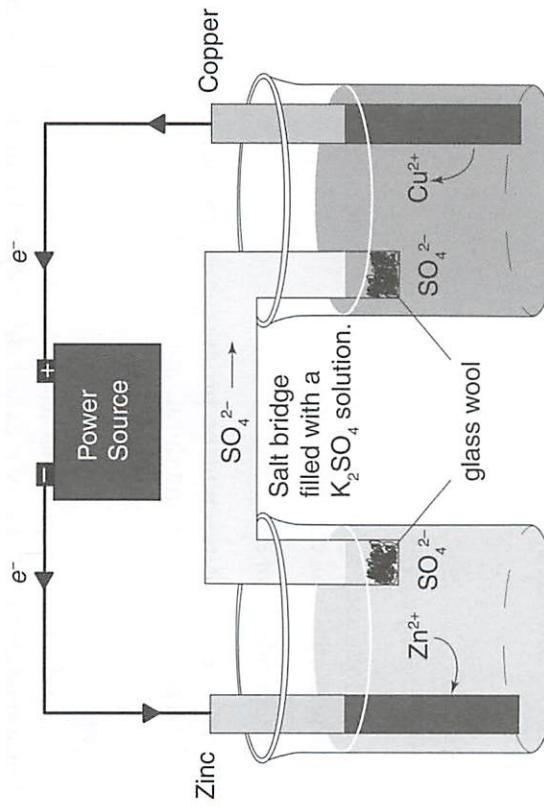


Figure 4.3.1 The Daniell cell in “recharging mode.”

In an electrolytic cell, as in any voltaic cell, the electrode at which reduction takes place is called the cathode, while the electrode at which oxidation takes place is called the anode. Since the roles of the Zn and Cu electrodes are reversed as the cell is changed from voltaic to electrolytic, so are their designations. In the voltaic cell, Zn is the anode and Cu is the cathode, whereas in the electrolytic cell, it is the other way around. Note, however, that in any electrochemical arrangement, the anode is always the electrode that supplies electrons, while the cathode is the electrode that consumes them.

The design of an electrolytic cell can be greatly simplified if the products of the reaction can be prevented from reacting with each other. In some cases, it is not necessary to place the electrolytes surrounding the cathode and anode in separate containers. A more typical electrolytic cell consists of two electrodes in a single vessel filled with an electrolyte solution. The electrolyte filling an electrolytic cell can be a pure compound, such as water or a *molten salt*, an aqueous solution of a salt, or a mixture of pure compounds or aqueous solutions. A solid ionic compound that is not melted or dissolved cannot be electrolyzed because its ions are immobilized and cannot travel to the electrodes.

Note that a molten salt (or fused salt) is a salt that has been melted into a liquid as opposed to a salt that has been dissolved in water. Liquid NaCl, for example, flows much like water and has a similar heat capacity. Unlike water, which is a liquid at temperatures between 0 °C and 100 °C, NaCl must be heated to over 800 °C before it liquifies.

### VOLTAGE NEEDED FOR ELECTROLYSIS

Theoretically, the minimum standard voltage required to force a nonspontaneous (i.e.,  $E_{\text{red}}^{\circ} < 0$ ) redox reaction to occur is:

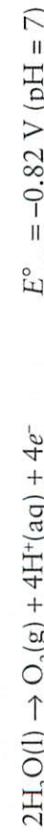
$$E_{\text{electrolysis}}^{\circ} = -E_{\text{cell}}^{\circ}$$

### Electrolysis of Neutral Water

Pure water contains no ions to conduct electricity and so is very difficult to electrolyze. The simplest way to increase water's conductivity is to add a nonreacting, readily ionizing salt such as  $\text{Na}_2\text{SO}_4$ . What makes electrolysis of water different from the electrolysis of salts is that individual  $\text{H}_2\text{O}$  molecules do not dissociate into cations and anions that migrate to the anode and to the cathode. Rather, some  $\text{H}_2\text{O}$  molecules are reduced at the cathode:



while others are oxidized at the anode:



The overall reaction is obtained by doubling the reduction half-reaction, adding it to the oxidation half-reaction, combining  $\text{H}^+$  and  $\text{OH}^-$  into  $\text{H}_2\text{O}$ , and removing  $4\text{H}_2\text{O}$  from each side to give:



Note that every time two moles of water react, four moles of electrons are involved.

The standard cell potential for the overall reaction:

$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ + E_{\text{ox}}^\circ = -0.41 \text{ V} - 0.82 \text{ V} = -1.23 \text{ V}$$

The theoretical minimum voltage required for the electrolysis:

$$E_{\text{electrolysis}}^\circ = -E_{\text{cell}}^\circ = -( -1.23 \text{ V}) = +1.23 \text{ V}$$

A simplified electrolytic cell where this reaction can be carried out consists of a single container filled with a dilute  $\text{Na}_2\text{SO}_4$  solution, two inert electrodes, and a battery, as shown in Figure 4.3.2.

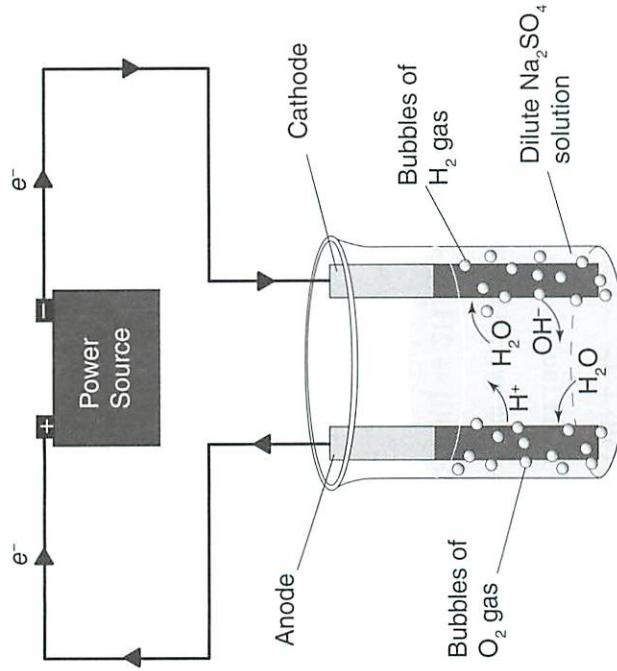
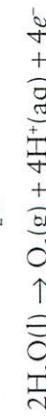
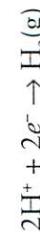


Figure 4.3.2 Electrolysis of neutral water.

In more practical designs, both electrolytic cell electrodes may be surrounded by glass compartments whose purpose is to collect the  $\text{H}_2$  and  $\text{O}_2$  gases and keep them from mixing. This is how  $\text{H}_2$  can be made from water, and this process requires electrical energy.

### Electrolysis of Water in Acidic Solution

Consider the electrolysis of water using platinum electrodes in the presence of 1 M HCl. Unlike in neutral water, there is an abundance of  $\text{H}^+$  ions in aqueous acid which can undergo reduction at the cathode. Therefore, the oxidation and reduction half-reactions are:



$$\begin{aligned} E^\circ_{\text{red}} &= 0.00 \text{ V} \\ E^\circ_{\text{ox}} &= -1.23 \text{ V} \end{aligned}$$

The standard cell potential for the overall reaction:



$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = 0.00 \text{ V} - 1.23 \text{ V} = -1.23 \text{ V}$$

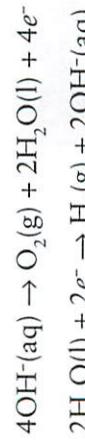
Thus, the theoretical minimum voltage needed to force this reaction to proceed is:

$$E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}} = -(-1.23) \text{ V} = +1.23 \text{ V}$$

### Electrolysis of Water in Basic Solution

Water may also be electrolyzed using platinum electrodes in the presence of 1 M NaOH. In this case, there is an abundance of OH<sup>-</sup> ions in the solution. These ions will undergo oxidation at the anode.

The half-reactions occurring are:



The standard cell potential for the overall reaction:



$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} = -0.40 \text{ V} - 0.83 \text{ V} = -1.23 \text{ V}$$

So, the theoretical minimum voltage needed to force this reaction to proceed is:

$$E^\circ_{\text{electrolysis}} = -E^\circ_{\text{cell}} = -(-1.23) \text{ V} = +1.23 \text{ V}$$

### Overpotential

In practice, however, the minimum applied voltage necessary to force a nonsimultaneous reaction has to be greater than the  $E^\circ_{\text{electrolysis}}$ . This additional voltage is called the *overpotential*. The overpotential arises from various kinetic factors such as the activation barrier for the chemical reactions taking place at the surface of the electrode (in our case, formation of H<sub>2</sub> and O<sub>2</sub> molecules from the hydrogen and oxygen atoms). This is why the voltage of a battery charger must be higher than the output voltage of the battery. The magnitude of the overpotential depends on several factors including the surface structure of the electrodes and the type of chemical reaction at the surface.

What is important to keep in mind is that the overpotential is not negligible. In the previous example, the overpotential of platinum electrodes for the electrolysis of water in an acidic solution is about 0.6 V. This means that the actual potential required to electrolyze water is close to  $1.23\text{ V} + 0.6\text{ V} = 1.83\text{ V}$ . The concept of overpotential has a major significance in industrial applications. In most cases, overpotential means higher consumption of electrical energy and higher production costs.

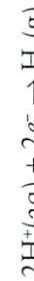
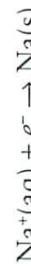
#### PREDICTING ELECTROLYSIS PRODUCTS OF AQUEOUS SOLUTIONS

If the electrolytic cell contains a mixture of compounds, then more than one reaction is possible at each electrode. Normally, one of these reactions will be favoured over the others. In such cases, it is often possible to predict the actual products of electrolysis based on the ability of reactants to give up or attract electrons.

When the electrolysis is carried out in an aqueous solution and all reactants are at or near their standard concentrations, the favoured products can be predicted by comparing standard reduction potentials for all possible half-reactions. The rules are as follows:

1. **For the reduction half-reaction at the cathode:** The higher (more positive or less negative) the value of the standard reduction potential  $E_{\text{red}}^{\circ}$ , the more favourable the reaction.
2. **For the oxidation half-reaction at the anode:** The higher (more positive or less negative) the value of the standard oxidation potential  $E_{\text{ox}}^{\circ}$ , the more favourable the reaction.

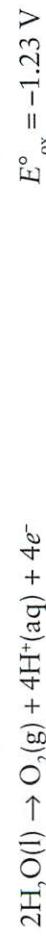
As an example of application of these rules, consider the electrolysis of an aqueous solution of NaBr where the  $[\text{H}^+] = 1.0\text{ M}$ . The possible reactions at the cathode are:



$$E_{\text{red}}^{\circ} = -2.71\text{ V}$$

$$E_{\text{red}}^{\circ} = 0.00\text{ V}$$

The reduction of  $\text{H}^+$  has a less negative  $E^\circ_{\text{red}}$  and so it will be favoured over the reduction of  $\text{Na}^+$  cations. For the same solution, the two competing reactions at the anode are:



Oxidation of  $\text{Br}^-$  has a higher (less negative) potential than of  $\text{H}_2\text{O}$ , so the  $\text{Br}^-$  ions will be oxidized in preference to  $\text{H}_2\text{O}$ .

It is important to realize, however, that these rules do not take into account the overpotentials that may differ considerably for competing half-reactions. For example, when a solution of NaCl is electrolyzed, the competing oxidation half-reactions are:



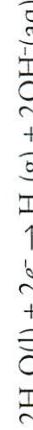
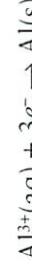
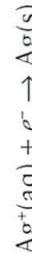
Based on the  $E^\circ_{\text{red}}$  values, the oxidation of water should be favoured over the oxidation of chloride ions. However, the overpotential for the oxidation of  $\text{H}_2\text{O}$  is higher than that of  $\text{Cl}^-$ . As a result, the  $\text{Cl}^-$  ions are oxidized in practice, not water. Note that overpotentials vary considerably from case to case and cannot be predicted as accurately as cell potentials. Do not take overpotential effects into account when solving exam questions unless explicitly told to do so.

#### Example 4.3.1. Predicting Products of the Electrolysis of HCl (In-Class Exercise)

Suppose a 1.0 M solution of HCl is electrolyzed using copper electrodes. What will be the favoured products of the electrolysis?

### QUANTITATIVE DETERMINATION OF ELECTROLYSIS PRODUCTS

There exists a simple quantitative relationship between the amount of electricity passed through an electrolytic cell and the amount of substances produced by reactions at the electrodes. For example, in the balanced half-equations below:



- 1 mole of electrons is required to produce 1 mole of Ag metal from 1 mole of  $\text{Ag}^+$  ions.
- 3 moles of electrons are required to produce 1 mole of Al metal from 1 mole of  $\text{Al}^{3+}$  ions.
- 2 moles of electrons are required to produce 1 mole of  $\text{H}_2$  gas by reduction of water.

This observation is summarized by Faraday's Law, formulated by famed English scientist Michael Faraday in the early 19th century:

*The number of moles of products reduced or oxidized by the passage of an electric current through an electrolytic cell is stoichiometrically equivalent to the number of moles of electrons supplied.*

To obtain a working formula for use in practical calculations, electric charge is measured in coulombs (C) and the charge of one electron is:

$$q_e = 1.60219 \times 10^{-19} \text{ C}$$

Therefore, 1 mole (Avogadro's number  $N_A$ ) of electrons carries a charge of:

$$F = N_A q_e = (6.02205 \times 10^{23} \text{ mol}^{-1}) \times (1.60219 \times 10^{-19} \text{ C}) = 96,485 \text{ C mol}^{-1}$$

where  $F$  is the Faraday constant, which was introduced in the previous topic. With the Faraday constant, the charge ( $Q$ ) of  $n$  moles of electrons can be written:

$$Q = n_e F \quad (4.3.1)$$

Since electric current ( $I$ ) is defined as the rate of flow of charge per unit time, the Faraday constant provides a link between the current, charge, and number of moles of electrons. The equation for electric charge is usually written:

$$Q = It \quad (4.3.2)$$

with  $I$  in amperes (A, where  $1\text{ A} = 1\text{ C s}^{-1}$ ) and time ( $t$ ) in seconds. Therefore, to determine the number of moles of electrons supplied by an electric current, the amount of current and the duration of time for which it flows must be known.

**Example 4.3.2. Relating Current and Time to Moles of Electrons (In-Class Exercise)**

A current of  $5.0\text{ A}$  flows through a metal wire. How many moles of electrons pass through a cross section of the wire in  $7.0\text{ seconds}$ ?

**Example 4.3.3. Amount of Ag Electroplated (In-Class Exercise)**

Electroplating is the deposition of a thin layer of metal on a conducting surface. In an electrolytic cell, the object to be electroplated is the cathode, and the electroplating metal is the anode. That being said, what mass in grams of silver (Ag) can be plated out from a solution of  $\text{AgNO}_3$ , if a current of  $0.75\text{ amperes}$  flows through an electrolytic cell for one hour?

**Example 4.3.4. Time Needed to Electroplate Cu (In-Class Exercise)**

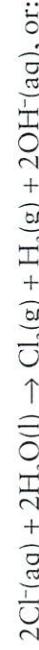
How long would it take to electroplate  $6.50\text{ grams}$  of copper (Cu) from a solution of  $\text{CuCl}_2$ , if the current used was  $3.5\text{ amperes}$ ?

### THE CHLOR-ALKALI PROCESS

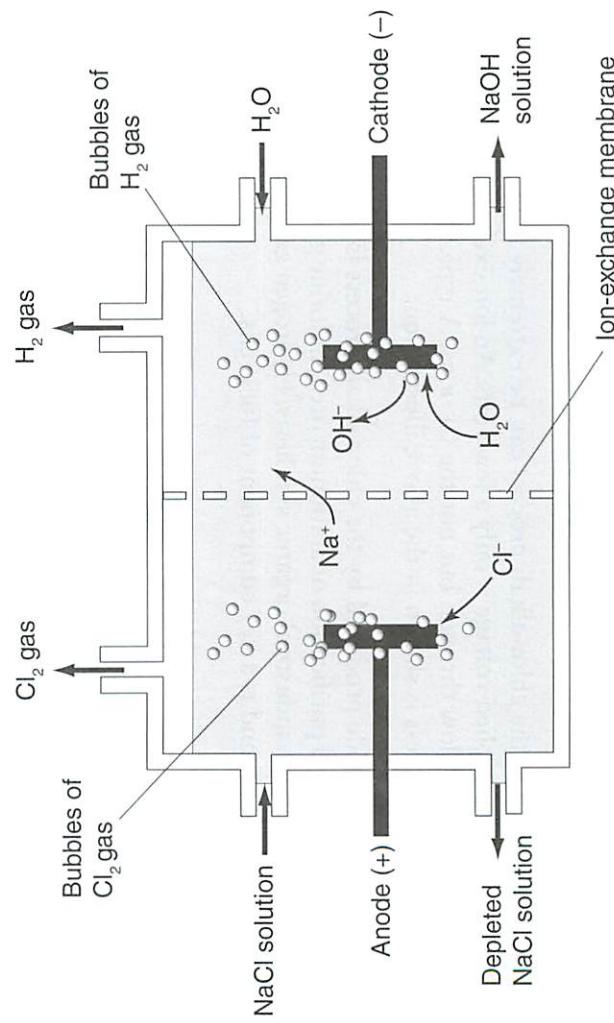
From a commercial standpoint, one of the most important applications of electrolysis is the chlor-alkali process in which an aqueous NaCl solution (brine) is electrolyzed to produce sodium hydroxide (NaOH), hydrogen gas ( $H_2$ ), and chlorine gas ( $Cl_2$ ). The half-reactions occurring at the electrodes in the chlor-alkali process are:



The overall reaction can be written as:



Note that water is not oxidized at the anode to produce  $O_2$  gas because of overpotential.



The current used in the chlor-alkali process can be extremely high, of the order of 105 A, but the applied voltage is only a few volts. An ion-exchange membrane allows  $\text{Na}^+$  ions to flow through but not the  $\text{Cl}^-$  ions. A typical reactor used in the chlor-alkali process is shown in the above illustration.

The sodium hydroxide produced by the chlor-alkali process is used in pulp and paper processing and purification of aluminum ores. Chlorine gas can be used for treating water and in industrial organic synthesis. Hydrogen gas is used in many industrial processes and is a key component of fuel cells.

### Section 4.3 Review Problems

1. What is the maximum mass, in grams, of Al(s) that can be produced from Al(OH)<sub>3</sub>(aq) using a current of 10.0 A for 5 hours?
  - a. 16.8
  - b. 151
  - c. 0.0140
  - d. 50.3
  - e. 0.0420
2. How much time, in minutes, will it take for an electric current of 3.64 A to deposit all the copper from 740 mL of solution containing 0.250 M Cu<sup>2+</sup>(aq)?
  - a. 163
  - b. 102
  - c. 82.0
  - d. 208
  - e. 326
3. A silver plating process requires the deposition of 10 g of silver. If a current of 0.50 A is passed, how long would this process take?
4. The reaction occurring in an alkaline battery is:



This battery provides a current of 0.40 amperes for 12.0 hours. What mass, in grams, of zinc was consumed?

- a. 5.86
  - b. 2.92
  - c. 14.6
  - d. 7.28
  - e. 11.70
5. Suppose one wants to coat both sides of a 1.0 m × 1.5 m metal sheet with a 0.05 mm layer of nickel by electrolytic deposition of Ni from a NiSO<sub>4</sub> solution. What constant current has to be supplied to the electrolytic cell in order to complete this process in one hour? The density of nickel is 8.90 g cm<sup>-3</sup>.
  6. It's not hard to figure out which two metals are used in the NiCd rechargeable battery. Under basic conditions, the cell reaction on discharge is approximately:
$$\text{Ni(OH)}_4(\text{s}) + \text{Cd(s)} \rightarrow \text{Ni(OH)}_2(\text{s}) + \text{Cd(OH)}_2(\text{s})$$
- a. What is the change in oxidation state for each metal on discharge?
  - b. What total mass of reactants is required to provide 96,485 C of electricity?
7. Water may easily be electrolyzed to H<sub>2</sub>(g) and O<sub>2</sub>(g) if a small amount of an unreactive electrolyte, such as Na<sub>2</sub>SO<sub>4</sub>, is added to lower the resistance.
    - a. Write equations for the reactions at each electrode and evaluate the minimum applied potential that would be needed for electrolysis to occur.
    - b. If a current of 0.100 A flows for 20 minutes, what volume of each gas would be evolved? Assume the molar volume of each gas is 22.4 L mol<sup>-1</sup>.

8. Consider the electrolysis of neutral water; i.e.,  $\text{pH} = 7$ .
- What are the  $[\text{H}^+]$  and  $[\text{OH}^-]$ ?
  - Use the Nernst equation to calculate the potential of each electrode under these nonstandard conditions.
  - Estimate the theoretical potential required to perform the electrolysis of “pure” water.

## 4.4 Batteries

### OBJECTIVES

After studying this topic, you should to be able to:

- Explain the difference between primary and secondary batteries.
- Explain the difference between recharging and discharging in terms of chemical processes involved.
- Write the half-cell and overall cell reactions for various batteries.
- Estimate the time required to charge a battery given applicable data.

### INTRODUCTION

A *battery* is a device that converts the chemical energy stored in its active materials into electrical energy, thus providing a source of power for countless devices ranging from wrist watches to hybrid cars. Batteries are classified as either *primary* or *secondary*. Primary batteries can be used only once because the chemical reactions that supply the electrical current are irreversible. Nonrechargeable flashlight batteries are primary batteries.

Secondary (or rechargeable) batteries can be used, recharged, and reused. In these batteries, the chemical reactions that supply electrical current are easily reversed so that the battery can regain its charge. For example, secondary batteries (e.g., lead-acid batteries) are the standard power source in cars. They are used to start a car's engine and are recharged by the alternator while the engine is running.

Rechargeable batteries are also commonly found in cell phones and laptop computers. In these devices, transformer-reduced voltages from household power outlets are used to recharge the batteries.

### DISCHARGING A BATTERY

In the discharge mode, a spontaneous redox reaction in the battery supplies an electric current. This spontaneous reaction continues until the battery becomes “dead.” A battery can die for either of the following reasons, whichever occurs first.

- The electrochemical cell reaches a state of equilibrium. This occurs when the concentrations of the reactants and products are such that  $E_{\text{cell}} = 0$  and hence  $\Delta G = -nFE_{\text{cell}} = 0$ .
- At least one of the reactants is completely used up. The reactant used up first is the limiting reagent.

Consider the following voltaic cell in the specified initial state:



The half-reactions are as follows:



The balanced overall reaction for the entire cell is



$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = 0.04 \text{ V}$

Because the concentrations of the reactants are nonstandard (not 1 M), the actual cell potential has to be calculated using the Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]}$$

At the initial concentrations,

$$E_{\text{cell}} = 0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.20}{0.95} = 0.06 \text{ V}$$

The initial amounts of the reactants are  $n(\text{Cd}^{2+}) = 0.95 \text{ mol}$  and  $n(\text{Fe}) = (100 \text{ g}) / (55.85 \text{ g mol}^{-1}) = 1.79 \text{ mol}$ , so  $\text{Cd}^{2+}$  is the limiting reagent (LR). As the reaction goes on,  $[\text{Fe}^{2+}]$  increases while  $[\text{Cd}^{2+}]$  decreases, and the cell potential decreases as well. After 0.90 mol of  $\text{Cd}^{2+}$  is reduced, the concentrations of  $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$  reach 1.10 M and 0.05 M, respectively. At that point, the cell potential becomes zero:

$$E_{\text{cell}} = 0.04 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{1.10}{0.05} = 0.00 \text{ V}$$

Therefore, at these concentrations, the cell reaches a state of equilibrium and the current stops, even though neither of the reactants is exhausted (Figure 4.4.1).

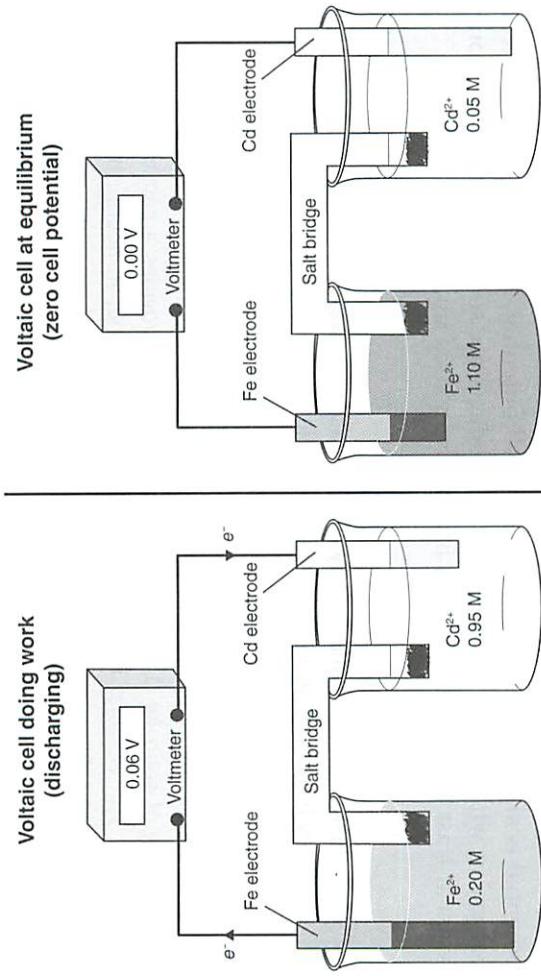


Figure 4.4.1 A voltaic cell discharging (left) and at equilibrium (right).

Next consider the same voltaic cell in the same initial state except that the initial mass of the iron electrode is only 24 g. We have  $n(\text{Fe}) = (24 \text{ g})/(55.85 \text{ g mol}^{-1}) = 0.23 \text{ mol}$ , so that now Fe is the L.R. With that setup, all of the iron metal will be oxidized before the equilibrium concentrations of  $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$  can be reached.

**Example 4.4.1. Concentrations at Zero Potential**

Consider the following cell:

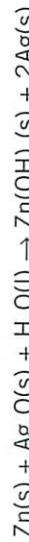


The initial concentrations of the  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  solutions are  $0.100\text{ M}$  and  $0.150\text{ M}$ , respectively, and each solution has a volume of  $1.00\text{ L}$ . The mass of each electrode is  $50.0\text{ g}$ . Find the initial overall cell potential and verify that this potential drops to zero when the concentrations of  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  reach  $0.175\text{ M}$  and  $7.05 \times 10^{-9}\text{ M}$ , respectively. Can one say that this cell stops producing an electric current when the limiting reagent is used up?

Consider also a voltaic cell in which all of the reactants and products are either solids or liquids. Such a cell remains in a standard state at all times, so its cell potential is always equal to the standard cell potential,  $E_{\text{cell}} = E^\circ_{\text{cell}}$ . Therefore, a battery in which all of the reactants or products are solids or liquids dies only when at least one of the reactants is completely used up.

**Example 4.4.2. Determining Battery Life (In-Class Exercise)**

A battery based on the following redox reaction:



generates  $1.5\text{ V}$ . Suppose that a battery of this type contains  $0.100\text{ g}$  of Zn metal,  $0.100\text{ g}$  of solid  $\text{Ag}_2\text{O}$ , and  $0.100\text{ g}$  of water, and provides a constant current of  $1.00 \times 10^{-3}\text{ A}$ . What is the maximum theoretical time, in hours, that the battery could deliver this current?

**ELECTROLYtic CELLS**

If the exhausted cell shown in Figure 4.4.1 can be recharged by an external source of electrical energy, it becomes an electrolytic cell, where  $\text{Fe}^{2+}$  is reduced to Fe and Cd is oxidized to  $\text{Cd}^{2+}$  (Figure 4.4.2).

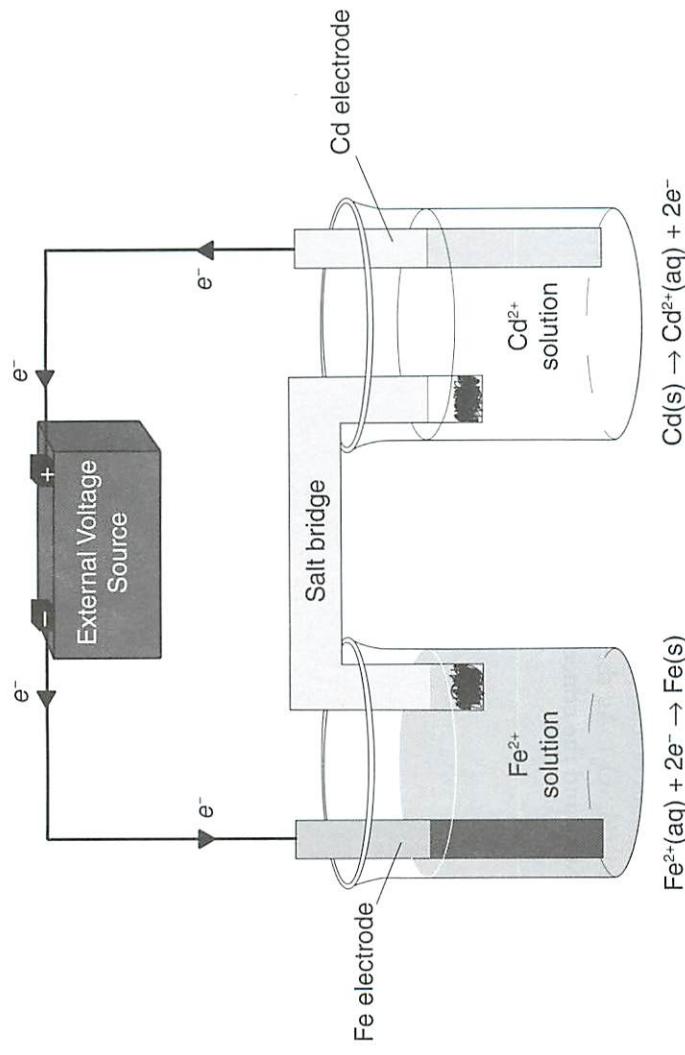


Figure 4.4.2 Recharging a battery (electrolytic cell).

Note that the direction of the current is the reverse of that in the voltaic cell shown in Figure 4.4.1, and the electrochemical reactions at the two electrodes are reversed as well. The Cd electrode is forced to become the anode, while the Fe electrode is forced to become the cathode.

The forced redox reaction that occurs when a voltage higher than the voltaic cell voltage is applied is the opposite (or reverse) of the spontaneous cell reaction is:



becomes:



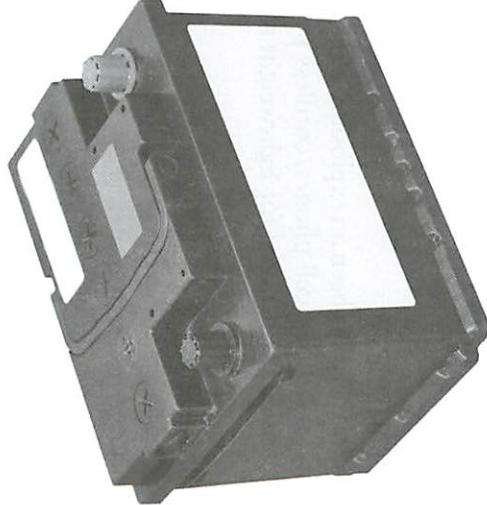
Reversible cells are essential components in rechargeable batteries.

**LEAD-ACID BATTERY**

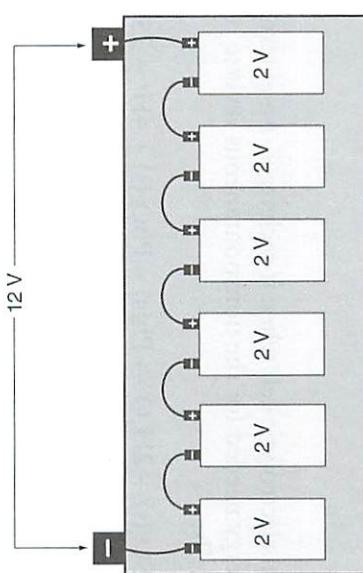
The lead-acid cell was the world's first rechargeable battery. Invented by French physicist Gaston Planté in 1859, the first lead-acid battery consisted of a spiral roll of two sheets of pure lead, separated by a linen cloth and immersed in a sulfuric acid solution. The following year Planté unveiled a nine-cell version, and by 1881 a more reliable model proved a success for use in early electric cars.

When a lead-acid car battery is used to operate the ignition, headlights, radio, or other accessories, its cells are in voltaic mode and are discharging. When the same battery is being charged by the alternator while driving, or by an external battery charger, its cells are electrolytic.

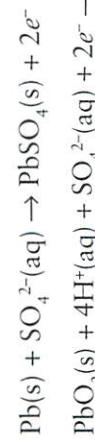
The lead-acid battery used in today's cars is comprised of six 2 V cells connected in series (see images that follow). In a series connection, the overall voltage is the sum of the voltages produced by the individual cells. In the charged state, each cell contains electrodes of lead ( $\text{Pb}$ ) and lead dioxide ( $\text{PbO}_2$ ) in an electrolyte of 6.0 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ). As the battery is discharged, both electrodes form lead sulfate ( $\text{PbSO}_4$ ) and the concentration of  $\text{H}_2\text{SO}_4$  is reduced.



Ensigma/Shutterstock.com



The anode (Pb) in a car battery is comprised of lead plates filled with “spongy” lead, and the cathode ( $\text{PbO}_2$ ) is comprised of lead plates (grills) filled with  $\text{PbO}_2$ . The large surface area supplied by the plates allows high currents to be generated for short periods of time (e.g., more “cranking amps” delivered to the car starter). When the battery is operating as a voltaic cell, the half-cell reactions at the anode and cathode are, respectively:



$$\begin{aligned}E_{\text{ox}}^\circ &= +0.31 \text{ V} \\ E_{\text{red}}^\circ &= +1.70 \text{ V}\end{aligned}$$

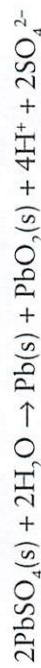
Overall:



Since each of the cells produce a voltage of 2.01 V, the overall battery voltage is approximately 12 V. The actual voltage is a little higher since the concentration of  $\text{H}_2\text{SO}_4$  is at 6 M instead of 1 M.

### Charging

A car battery is an electrolytic cell when it recharges. An external current is used to provide the energy needed for the nonspontaneous reverse reaction in each of the battery's six cells:



When a car's engine is running, this current is provided by the alternator. The alternator's job is to convert the mechanical energy supplied to it by the engine to the electrical energy required to recharge the battery. If the engine is off, or the battery is not in the vehicle, an external battery charger is required. A typical recharge period depends on the charger amperage and takes six to eight hours with recharge voltages of 14.2 V to 14.5 V.

### OTHER RECHARGEABLE BATTERIES

Over the past few decades there has been an explosion in the demand for "portable power." The popularity of laptops, cell phones, cordless power tools, and media players has greatly increased the demand for lightweight rechargeable batteries.

### Nickel-Cadmium (NiCd) Batteries

NiCd or "nye-cad" batteries were extremely popular in the recent past and were typically found in portable power tools, emergency lighting, and wireless telephones. NiCd batteries have a nominal cell potential of 1.2 V, which is lower than the 1.5 V of many primary cells (e.g., flashlight batteries), so they are not usable in all applications. As the name suggests, these batteries use nickel and cadmium in the redox reaction to generate electrical energy.

The reaction at the anode (oxidation) is:



The reaction at the cathode (reduction) is:



The overall redox reaction is:



#### Example 4.4.3. Recharging a NiCd Battery (In-Class Exercise)

A NiCd battery that initially contained 1.00 g of Cd and 0.900 g of  $\text{NiO}_2$  operated until it “died.” Assuming a full recharge is necessary, how long, in hours, would it take if a recharge current of 1.50 amperes is used.

One of the drawbacks of NiCd batteries is the so-called “memory effect,” where they gradually lose their maximum energy capacity after repeated recharging when they are not fully discharged. In effect, the NiCd “remembers” the smaller capacity and only charges to that level. This condition is the result of chemical changes to the cell’s underused active materials. It is simply a function of battery age. Other drawbacks include a low energy-to-weight ratio and the extreme toxicity of cadmium. For these reasons, nickel-metal hydride (NiMH) batteries have virtually replaced NiCd batteries in most applications.

#### Nickel-Metal Hydride (NiMH) Batteries

NiMH batteries, which are the most popular rechargeable batteries available today, address most of the problems associated with NiCd batteries. First, there is no toxic cadmium in a NiMH battery. Second, they are subject to much less of a memory effect. Finally, on a weight-by-weight basis, NiMH batteries are able to store more energy than NiCds. For these reasons, NiCds have been virtually phased out.

At the anode in an NiMH battery, a metal alloy (M) consisting of a proprietary mixture of metals is in the form of a metal hydride (MH). In the discharge mode, the oxidation reaction at the anode in the discharge mode is:



The cathode (reduction reaction) uses a nickel oxyhydroxide material:

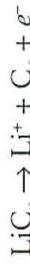


NiMH batteries are also relatively cheap to manufacture. All factors considered, they are reliable, relatively safe and, for the amount of energy they store, relatively light. For these reasons they are widely used, even in hybrid-electric vehicles.

### Lithium-Ion (Li-Ion) Batteries

Due to its high energy-to-weight ratio, the Li-ion battery is currently one of the most popular rechargeable batteries in consumer electronics and is supplanting the NiMH battery in many applications. The discharge reactions in a typical Li-ion cell are:

Anode (graphite):



Cathode ( $\text{CoO}_2$ ):



Overall:



Note that  $\text{Li}^+$  ions are not oxidized or reduced to generate a voltage in the Li-ion battery. The  $\text{Li}^+$  ions actually migrate to and from the anode and cathode in a process called *intercalation*. The layered structure of the electrodes allows intercalation to occur (see Figure 4.4.3). When  $\text{Li}^+$  ions exit the layers, the process is called *deintercalation*.

In a fully charged Li-ion battery,  $\text{Li}^+$  ions are interspersed between the sheets of graphite to form a solid material with the formula  $\text{LiC}_6$ . Because mobile  $\text{Li}^+$  ions are present in the layers, the valence electrons from this alkali metal are housed in the delocalized pi system of the graphite anode.

When discharging, the  $\text{Li}^+$  ions move out of the graphite anode across an electrolyte (usually a salt material such as dissolved  $\text{LiPF}_6$ ) to the cathode. In the discharge process, the Co in the  $\text{CoO}_2$  is reduced from  $\text{Co}^{4+}$  to  $\text{Co}^{3+}$ . When the battery is being charged,  $\text{Co}^{3+}$  is oxidized to  $\text{Co}^{4+}$ .

With graphite used as the standard anode material, the average voltage delivered from a Li-ion cell depends on the choice of cathode material as follows:

- $\text{LiMnO}_2$       4.0 V
- $\text{LiCoO}_2$       3.7 V
- $\text{Li}_2\text{FePO}_4$       3.6 V
- $\text{LiFePO}_4$       3.3 V

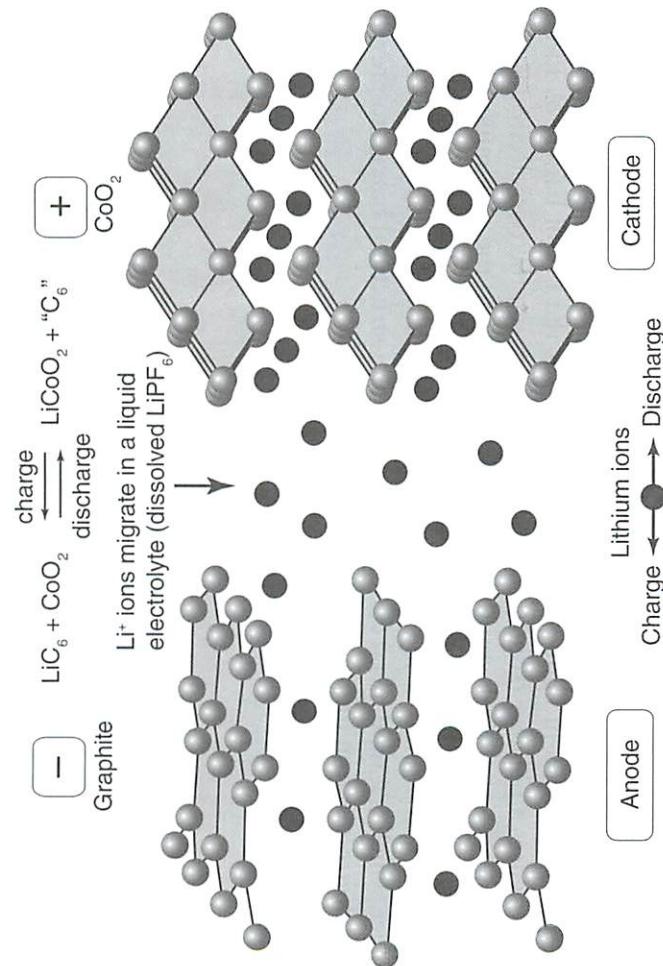


Figure 4.4.3 Intercalation and migration of  $\text{Li}^+$  ions in the Li-ion battery.

Although currently much more expensive than NiMH batteries, Li-ion batteries are lighter, deliver more power, and do not suffer from memory effect. These reasons alone make Li-ion cells the preferred power source for laptop computers.

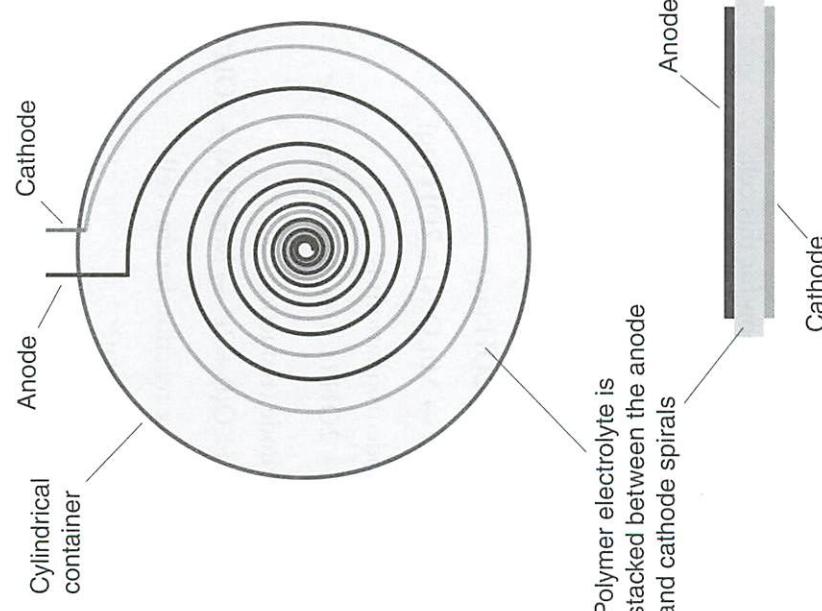
A key drawback of Li-ion cells is that they can rupture, ignite, and/or explode when subjected to high temperature or overcharging. Over the past several years there has also been a problem with contaminants in cells from certain manufacturers. This has resulted in short circuits and severe overheating, leading to massive recalls (over 45 million Li-ion batteries in 2007).

Another disadvantage of current Li-ion batteries is that, unlike their lead-acid counterparts which can deliver 1000+ amps, they are not designed to deliver high amperages (currents). This restricts Li-ion batteries to “moderate drain” applications.

On a positive note, Li-ion cell hazards are being mitigated by the application of stricter manufacturing standards, and by safety features built into the cells and the devices that use them. Chemists are continuously researching new materials to improve the safety, life cycle, and capacity of these and other rechargeable batteries.

#### LITHIUM-POLYMER (LI-POL) BATTERIES

A newer variation in lithium battery technology is the Li-Pol battery. A Li-Pol battery uses a polymer (solid phase) electrolyte between the two electrodes and, as a result, a cylindrical container is usually used to hold the maximum amount of reagents. The sheets of electrode material are usually situated, without touching each other, in a spiral inside the cylinder (see the following schematic). The cylinder, which is a rigid metal container, also acts as a structural barrier to prevent the electrodes from touching.



The advantage of a polymer electrolyte over a liquid electrolyte is that it allows the materials in the Li-Pol battery to be stacked, with little chance of the two electrodes coming into contact. This means that a Li-Pol battery can be manufactured in virtually any shape, since the stacked layers can be folded.

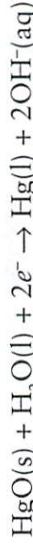
## Section 4.4 Review Problems

1. A mercury cell is a very small primary cell used in watches, hearing aids, cameras and some calculators. The anode is a zinc–mercury amalgam, with zinc as the reacting species, and the cathode is mercury (II) oxide,  $\text{HgO}$ .

The reaction at the anode (oxidation) is:

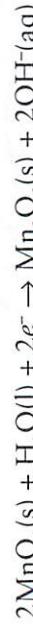


The reaction at the cathode (reduction) is:



- Write the overall redox reaction for this cell.
- Suppose the cell contained 0.030 g of Zn and 0.150 g of  $\text{HgO}$ . If it can deliver a current of 0.00100 millamps, how long (in hours) will it take for it to completely discharge?

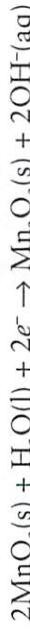
2. An alkaline battery uses  $\text{NaOH}$  or  $\text{KOH}$  as its electrolyte and is another common primary cell.



The reaction at the anode (oxidation) is:



The reaction at the cathode (reduction) is:



- Write the overall redox reaction for this cell.
- What is  $E_{\text{cell}}^\circ$  for the reaction?

$$E^\circ = -1.246\text{V}$$

$$E^\circ = +0.118\text{V}$$

3. Which of the following statements is/are correct?
  - a. The NiCd cell was the world's first rechargeable battery.
  - b. The lead-acid battery contains electrodes made of lead and lithium.
  - c. If the redox reactions in a cell can be reversed by applying external power to the cell electrodes, the cell is electrolytic.
  - d. Li<sup>+</sup> ions are reduced to Li atoms when a Li-ion battery is discharged.
  - e. A secondary cell is rechargeable, a primary cell is not.
4. Explain why NiMH batteries have virtually replaced NiCds as the most popular rechargeable batteries available today.
5. If battery compartment shape (not size) was the only factor to consider in the installation of batteries in a hybrid-electric vehicle, which lithium battery would you chose, a Li-ion or a Li-Pol, and why?



# Chapter 5

## Chemical Kinetics



Martin Tarey/age fotostock/Schüttphoto.com

It was obvious — to me at any rate — what the answer was to why an enzyme is able to speed up a chemical reaction as much as 10 million times. It had to do this by lowering the energy of activation — the energy of forming the activated complex. It could do this by forming strong bonds with the activated complex, but only weak bonds with the reactants or products.

### 5.1 Reaction Rates and Rate Laws

#### OBJECTIVES

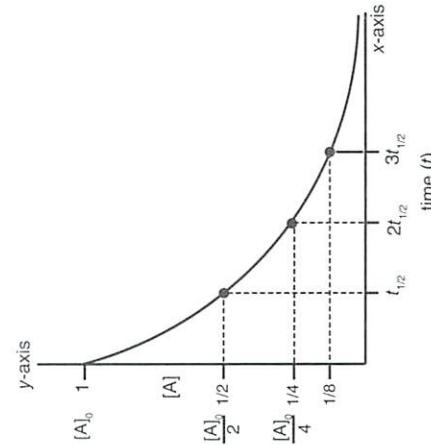
After studying this topic, you should to be able to:

- Explain the following terms: rate law; specific rate constant; integrated rate law; zero-, first-, and second-order reaction; exponential decay; and half-life.
- From given experimental data, determine the reaction order for the reactants in a reaction.
- Write a complete rate law for a reaction.
- From a rate law, deduce the value of the specific rate constant, and its units.
- Using the data provided, find the reaction rates, half-lives, and final concentrations of species in zero-, first-, and second-order reactions.

Linus Carl Pauling (1901–1994)

#### Topics Covered:

- 5.1 Reaction Rates and Rate Laws
- 5.2 Reaction Mechanisms and the Arrhenius Equation



#### INTRODUCTION

Chemical kinetics is the study of how fast chemical reactions proceed (ie, reaction rates) and the factors that affect those rates. In this topic, basic concepts of chemical kinetics are examined.

## REACTION RATES

The speed at which a reaction takes place is governed by several factors, including:

- What the reactants are, and their concentrations. For example:  
 $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{HF}(\text{g})$  is an explosively fast reaction.
- $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$  can take months (rusting of iron).
- $\text{C}(\text{diamond}) \rightarrow \text{C}(\text{graphite})$  is an undetectably slow reaction.
- The temperature: reactions tend to proceed faster at higher temperatures.
- Whether or not a catalyst is present.

The rate of a chemical reaction is a positive quantity usually defined by comparing the change in the product or reactant concentration over time. For example, in the production of ammonia from nitrogen:



one could measure the rate at which  $\text{N}_2$  and  $\text{H}_2$  are consumed or the rate at which  $\text{NH}_3$  is produced. Due to the stoichiometry of the reaction, the rate of  $\text{N}_2$  consumption will be  $\frac{1}{3}$  the rate of  $\text{H}_2$  consumption and  $\frac{1}{2}$  the rate of  $\text{NH}_3$  production. Thus, the reaction rate in this case can be defined as:

$$\text{Rate} = -\left(\frac{\Delta[\text{N}_2]}{\Delta t}\right) = -\frac{1}{3}\left(\frac{\Delta[\text{H}_2]}{\Delta t}\right) = +\frac{1}{2}\left(\frac{\Delta[\text{NH}_3]}{\Delta t}\right)$$

The negative signs in front of the  $\text{N}_2$  and  $\text{H}_2$  terms take into account that  $[\text{N}_2]$  and  $[\text{H}_2]$  decrease as the reaction takes place.

In summary, for any reaction:



the relationship between the rates for the various reactants and products can be expressed as:

$$\text{Rate} = -\frac{1}{a}\left(\frac{\Delta[\text{A}]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[\text{B}]}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta[\text{C}]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[\text{D}]}{\Delta t}\right)$$

### Concentration Effects and Rate Laws

The effect of concentration on a reaction is described using *rate laws*, which are mathematical expressions that link the rate of a reaction with reactant concentration. In the reaction:



The rate of the reaction (rate law) is given by the equation below:

$$\text{Rate} = k [A]^x [B]^y$$

where:

- $k$  is the *specific rate constant* for the reaction at a given temperature.
- $[A]$  and  $[B]$  are concentrations of components A and B in  $M$  ( $\text{mol L}^{-1}$ ).
- $x$  and  $y$  are the orders for each reactant and can only be found experimentally.

The “order” of a reaction defines how the rate of a reaction is affected by the concentration of the species involved in the reaction.

The exponent values are usually whole numbers (but not always). They determine the order of the reactant as follows:

- If  $x = 0$ , the reaction is zero order with respect to A. This means that the reaction rate is independent of  $[A]$ .
- If  $x = 1$ , the reaction is first order with respect to A.
- If  $x = 2$ , the reaction is second order with respect to A, and so on.
- If  $y = 0$ , the reaction is zero order with respect to B, and so on.
- The overall order of the reaction is  $x + y$ .

Remember, the exponents are experimentally measured and DO NOT correlate with the coefficients in the reaction equation. (This will be explained in more detail in the next topic.) Exponent values higher than 2 are seldom seen, but occasionally an order of  $\frac{1}{2}$  or  $-\frac{1}{2}$  is seen.

Determining the overall order of a reaction from the rate law is illustrated in the following example:

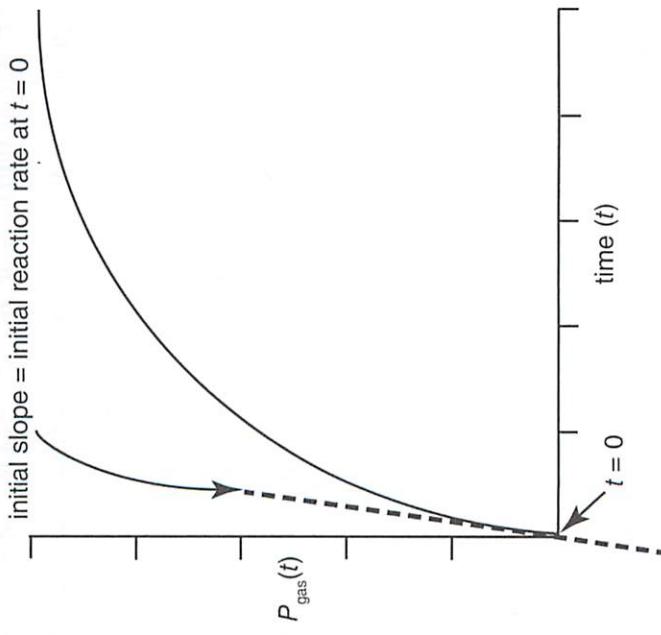


the rate law is:  $\text{Rate} = k [\text{H}_2]^1 [\text{NO}]^2$

The reaction is first order with respect to  $[\text{H}_2]$  and second order with respect to  $[\text{NO}]$ . The overall order of this reaction is three (the sum of all the individual orders). Note that the products of a reaction do not normally appear in the rate law because the forward rate is the rate measured most often. If the reverse rate is measured, then the concentrations of products will appear.

#### Experimental Determination of the Exponents

How are the exponents in the rate law determined? First, by measuring initial reaction rates for different concentrations (pressures) of the reactants. For example, for a reaction where a gas is produced, the initial reaction rate can be determined as the slope of the plot of the gas pressure as a function of time,  $P_{\text{gas}}(t)$ , at  $t = 0$ .



The experimental reaction rates measured in this manner for various initial concentrations (pressures) of the reactants are then processed as shown in the following examples.

**Example 5.1.1. Rate Law Determination #1 (In-Class Exercise)**

For the following reaction, use the experimental data provided to determine the exponents and specific rate constant,  $k$ .



$$\text{Rate} = k [\text{H}_2]^x [\text{NO}]^y$$

RUN	$[\text{H}_2]$ (mol L <sup>-1</sup> )	$[\text{NO}]$ (mol L <sup>-1</sup> )	RATE (mol L <sup>-1</sup> s <sup>-1</sup> )
i	0.1	0.2	5
ii	0.2	0.2	10
iii	0.1	0.4	20

**Example 5.1.2. Rate Law Determination #2 (In-Class Exercise)**

For the reaction  $\text{A} \rightarrow \text{products}$ , the data below was collected. Determine the rate law and specific rate constant,  $k$ .

RUN	$[\text{A}]$ (mol L <sup>-1</sup> )	RATE (mol L <sup>-1</sup> s <sup>-1</sup> )
i	$1.78 \times 10^{-2}$	$6.00 \times 10^{-5}$
ii	$2.85 \times 10^{-2}$	$7.59 \times 10^{-5}$

### FIRST-ORDER REACTIONS

Suppose  $A \rightarrow$  products is a first-order reaction. The rate law would be:

$$\text{Rate} = k[A] = -\left(\frac{\Delta[A]}{\Delta t}\right)$$

As the reaction proceeds,  $[A]$  decreases. Thus the rate can be integrated with respect to time to obtain the *integrated rate law* for a first-order reaction:

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad [A]_t = [A]_0 e^{-kt}$$

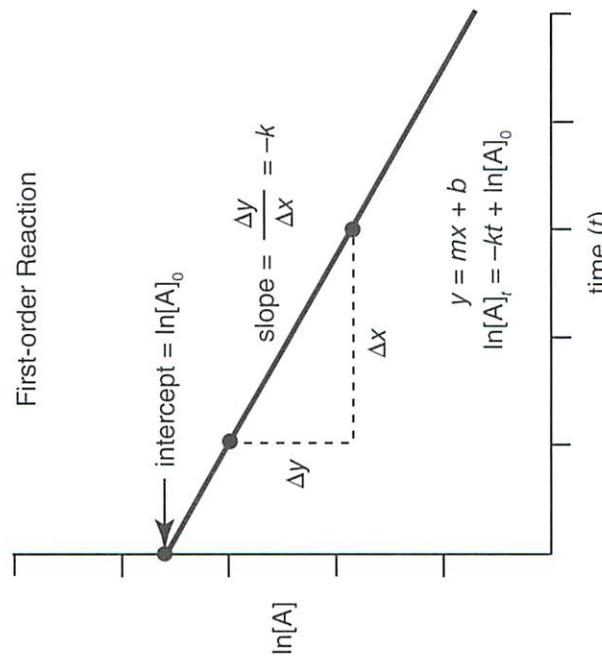
In the equation on the previous page:

- $[A]_t$  = concentration of A after time  $t$  has elapsed.
- $[A]_0$  = initial concentration.

The integrated rate law equation can be rearranged into an equation for a straight line (i.e.,  $y = mx + b$ ) as follows:

$$\ln[A]_t - \ln[A]_0 = -kt \quad \ln[A]_t = -kt + \ln[A]_0$$

Thus, if a reaction is first order, a plot of  $\ln[A]_t$  as a function of time should yield a straight line with a slope equal to  $-k$  and a  $y$ -intercept equal to  $\ln[A]_0$  (see graph that follows). This is a useful “test” to see if a reaction is first order or not.

**Example 5.1.3. Integrated First-order Rate Law (In-Class Exercise)**

For the decomposition reaction  $B \rightarrow$  products, a plot of  $\ln[B]$  versus time yielded a straight line with slope  $-0.35 \text{ min}^{-1}$ .

- If  $[B]_0 = 0.160 \text{ M}$ , find  $[B]$  at  $t = 4.00 \text{ minutes}$ .
- Find the time required for  $[B]$  to drop to  $0.100 \text{ M}$ .
- Find the time required for half of B to decompose.

**Exponential Decay and Half-Life**

Solution (c) of the “First-order Rate Law” In-Class Exercise example illustrates the concept of *half-life* ( $t_{1/2}$ ), which is the amount of time it takes to use up half of the reactant. The half-life for a first-order reaction is related to the rate constant as follows:

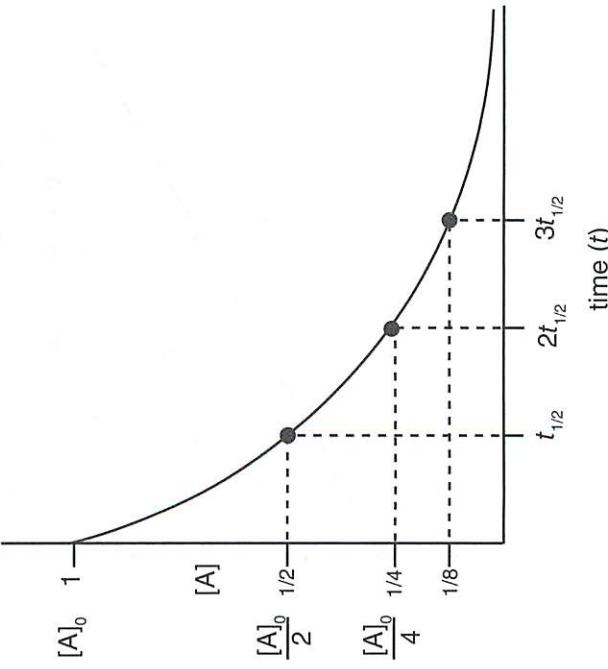
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = \ln \frac{1}{2} = -\ln 2 = -kt_{1/2}$$

Therefore,

$$t_{1/2} = \frac{\ln 2}{k} \qquad \ln 2 \approx 0.693$$

The half-life of a first-order reaction follows an *exponential decay* and is illustrated in the graph that follows. Note that the exponential decay plot is not a straight line. To get a straight line,  $\ln[A]$  versus time must be plotted as was previously shown.



For a first-order reaction, the half-life is a constant length of time; it only depends on the rate constant,  $k$ , and not the concentration or initial amount of the reactant. As shown by the graph, after one half-life ( $t_{\frac{1}{2}}$ ), half of the original reactant remains. After two half-lives ( $2t_{\frac{1}{2}}$ ), a quarter remains. After three half-lives ( $3t_{\frac{1}{2}}$ ), an eighth remains, etc. Therefore, the fraction of reactant remaining after  $n$  half-lives can be expressed as:

$$\text{Fraction remaining} = \frac{[A]_t}{[A]_0} = (0.5)^n$$

In order to use this expression effectively, the number of half-lives elapsed at any given time in a reaction must be known. Note that the symbol  $n$  used here does not refer to the number of moles. Also note that  $n$  need not be a whole number.

$$\text{Number of elapsed half-lives } (n) = \frac{\text{time elapsed}}{\text{length of half-life}}$$

**Example 5.1.4. First-order Half-Life #1 (In-Class Exercise)**

Radioactive decay proceeds according to first-order kinetics. The radioactive isotope  $^{210}\text{Po}$  has a half-life of 138.4 days. What fraction of  $^{210}\text{Po}$  remains after 1 year (365 days)?

**Example 5.1.5. First-order Half-Life #2 (In-Class Exercise)**

The first-order decomposition of  $\text{N}_2\text{O}_5$  into  $\text{NO}_2$  and  $\text{O}_2$  has a half-life of 120 seconds. If the initial concentration of  $\text{N}_2\text{O}_5$  is 0.850 M, what is its concentration after five minutes?

**ZERO-ORDER REACTIONS**

Suppose the process  $A \rightarrow$  products is zero order. That is, the rate of the reaction does not depend on  $[A]$ , only on  $k$ .

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0 = k$$

From the equation above, the integrated zero-order rate law can be obtained:

$$[A]_t - [A]_0 = -kt$$

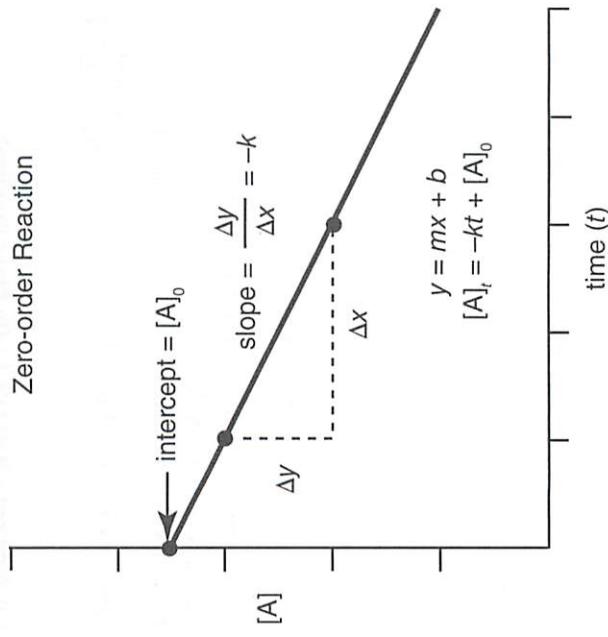
This equation can be rearranged into the form of a straight line equation (note that there are no logarithmic relationships):

$$[A]_t = -kt + [A]_0$$

$$(y = mx + b)$$

Thus a plot of  $[A]$  as a function of time yields a straight line with a slope of  $-k$  and a  $y$ -intercept of  $[A]_0$  (see graph that follows).

Zero-order Reaction



### SECOND-ORDER REACTIONS

Suppose the process  $A \rightarrow$  products is second order. The rate depends on  $k$  and the square of  $[A]$ .

$$\text{Rate} = -\left(\frac{\Delta[A]}{\Delta t}\right) = k[A]^2$$

From the equation above, the integrated second-order rate law can be obtained:

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

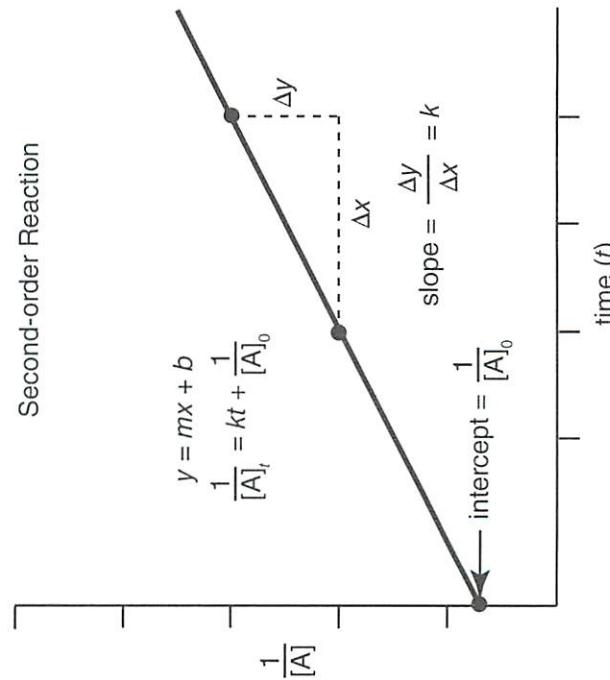
Like the integrated first-order and zero-order rate laws, the second-order rate law equation can be rearranged into the form of the equation for a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$(y = mx + b)$$

Remember, to determine if a reaction is zero, first or second order, plot  $[A]$ ,  $\ln[A]$ , or  $1/[A]$ , respectively, as a function of time. A straight line in one of the plots indicates the reaction order.

Second-order Reaction



While the half-life of a second-order reaction can be determined, it has little practical value. This is because the half-life of a second-order reaction depends on the concentration of the reactant. As the concentration changes, the length of the half-life also changes.

**Example 5.1.6. Rate of a Second-Order Reaction (In-Class Exercise)**

For the reaction  $\text{AB} \rightarrow \text{products}$ , a plot of  $[\text{AB}]^{-1}$  versus time (in seconds) results in a straight line with a slope of  $0.165 \text{ mol}^{-1} \text{ L s}^{-1}$ . What is the rate (in  $\text{mol L}^{-1} \text{ s}^{-1}$ ) of this reaction when  $[\text{AB}] = 0.750 \text{ M}$ ?

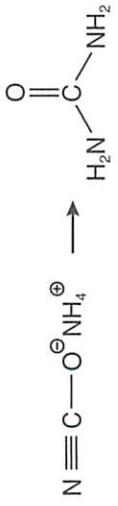
**Example 5.1.7. Second-Order Reaction Parameters (In-Class Exercise)**

In water, ammonium cyanate ( $\text{NH}_4\text{NCO}$ ) rearranges to produce urea,  $(\text{NH}_2)_2\text{CO}$ , a common fertilizer. (The discovery of this reaction in the early 19th century is considered to be the birth of organic chemistry.)



The rearrangement is a second-order reaction. If it takes 11.6 hours for the  $\text{NH}_4\text{NCO}$  concentration to go from  $0.250 \text{ M}$  to  $0.0841 \text{ M}$ :

- What is  $k$  for the reaction?
- At what rate is a  $0.839 \text{ M}$  solution of  $\text{NH}_4\text{NCO}$  changed to urea?



**Summary**

The chart below provides a summary of rate laws, integrated rate laws, half-lives, and units of  $k$  for zero-, first- and second-order reactions.

ORDER	RATE LAW	INTEGRATED RATE LAW	STRAIGHT LINE PLOT	SLOPE OF PLOT	UNITS OF $k$	HALF-LIFE
0	Rate = $k$	$[A]_t = -kt + [A]_0$	$[A]$ versus time ( $t$ )	negative	$\text{mol L}^{-1} \text{s}^{-1}$	$\frac{[A]_0}{2k}$
1	Rate = $k[A]$	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]$ versus time ( $t$ )	negative	$\text{s}^{-1}$	$\frac{\ln 2}{k}$
2	Rate = $k[A]^2$	$\frac{1}{[A]}_t = kt + \frac{1}{[A]}_0$	$\frac{1}{[A]}$ versus time ( $t$ )	positive	$\text{L mol}^{-1} \text{s}^{-1}$	$\frac{1}{k[A]_0}$

## Section 5.1 Review Problems

1. For each of the following reactions, express the rate in terms of each reactant and product concentration, ensuring that, whichever is used, “rate” has the same value in mol L<sup>-1</sup> s<sup>-1</sup>.



2. The following data were collected for the reaction A + B → products:

RUN	INITIAL [A] (mol L <sup>-1</sup> )	INITIAL [B] (mol L <sup>-1</sup> )	INITIAL RATE (mol L <sup>-1</sup> s <sup>-1</sup> )
i	0.10	0.20	$2.0 \times 10^{-3}$
ii	0.10	0.10	$5.0 \times 10^{-4}$
iii	0.30	0.10	$1.5 \times 10^{-3}$

- a. Evaluate the order of reaction in A and B and write the complete rate law.  
 b. Evaluate the specific rate constant, including its units.  
 c. What would the rate of reaction be when [A] = [B] = 0.20 M?  
 d. If [A] = 0.30 M, what value of [B] would give a rate of  $6.0 \times 10^{-3}$  mol L<sup>-1</sup> s<sup>-1</sup>?

3. The reaction A + B → products gave the following initial rate data as the concentrations were varied:

RUN	[A] (mol L <sup>-1</sup> )	[B] (mol L <sup>-1</sup> )	INITIAL RATE (mol L <sup>-1</sup> s <sup>-1</sup> )
i	0.75	0.25	$1.46 \times 10^{-3}$
ii	2.25	0.25	$1.32 \times 10^{-2}$
iii	0.75	1.00	$1.46 \times 10^{-3}$

- a. What is the order of the reaction in [A], in [B], and the overall order?  
 b. What is the value of the specific rate constant *k*, with units?

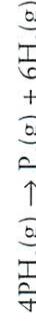
4. It sometimes happens that concentration of a product of a reaction can influence the rate. The following data were found in a study of the decomposition of carbonyl chloride (also known as phosgene, a chemical weapon):



EXPERIMENT	1	2	3	4
Initial $[\text{COCl}_2] \text{ M}$	0.16	0.16	0.040	0.16
Initial $[\text{CO}] \text{ M}$	0.10	0.10	0.10	0.50
Initial $[\text{Cl}_2] \text{ M}$	0.16	0.040	0.16	0.040
Initial Rate $\text{M s}^{-1}$	$1.9 \times 10^{-2}$	$9.6 \times 10^{-3}$	$4.8 \times 10^{-3}$	$9.6 \times 10^{-3}$

From these data, work out the complete rate law and the value of the rate constant.

5. For the decomposition of phosphine:



the rate equation is rate =  $k [\text{PH}_3]$ . Under the conditions of the experiment, the half-life for the decomposition was found to be 37.9 seconds.

- How much time must elapse until  $\frac{3}{4}$  of the sample has decomposed?
  - What is the specific rate constant for this reaction?
  - What fraction of the phosphine would remain after 5.0 minutes?
6. In a first-order process, it was found that  $\frac{1}{7}$  of a sample had been consumed in 20 minutes. What is the half-life of this reaction, in minutes?
7. Workers with radioactive isotopes use the generalization that the activity from any radioisotope will be negligible after 10 half-lives have elapsed. What fraction of the original sample of the isotope remains after this period?

8. Although hypochlorous acid, HOCl, has been known since the early 1800s, the fluorine analogue HOF was not synthesized until 1971. It is very unstable, decomposing according to:



with a first-order half-life of 30 minutes at 25 °C. If an experiment is started with a pressure of 100 kPa of HOF in a flask, what will be the total pressure and the partial pressure of HOF after (a) 30 min., (b) 45 min.?

9. It was found experimentally that the rate of the reaction

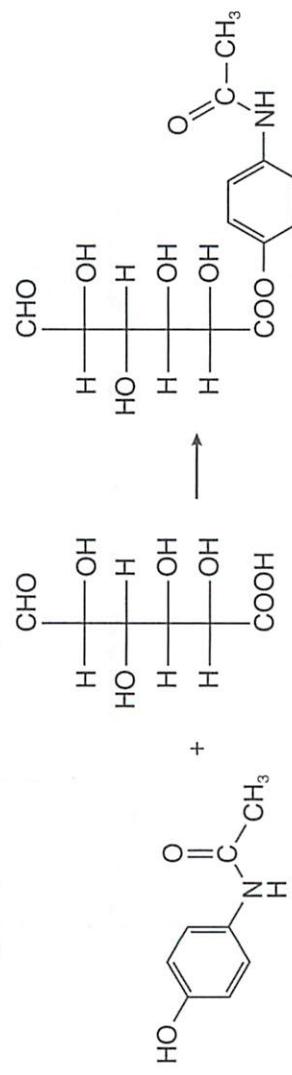


could be expressed by the equation:

$$\log(\text{rate}) = \log[\text{H}_2] + 5.697$$

when  $[\text{Br}_2] = 0.10 \text{ mol L}^{-1}$ . Another experiment showed that the reaction was first-order in  $\text{Br}_2$ . Determine the complete rate law and the value of the specific rate constant.

10. Drugs are typically metabolized via first-order kinetics. In healthy adults, the metabolic half-life ( $t_{1/2}$ ) of acetaminophen is two hours. The liver reacts acetaminophen with glucuronic acid (a derivative of glucose) so that it becomes more  $\text{H}_2\text{O}$ -soluble and can be excreted in the urine as conjugated acetaminophen (see reactions below).



**acetaminophen**      **glucuronic acid**      **conjugated acetaminophen**

If 1000 mg of acetaminophen (two extra-strength tablets) are consumed, how many mg of acetaminophen will have been metabolized after 3.25 hours? How many mg of conjugated acetaminophen would be found in the urine?

## 5.2 Reaction Mechanisms and the Arrhenius Equation

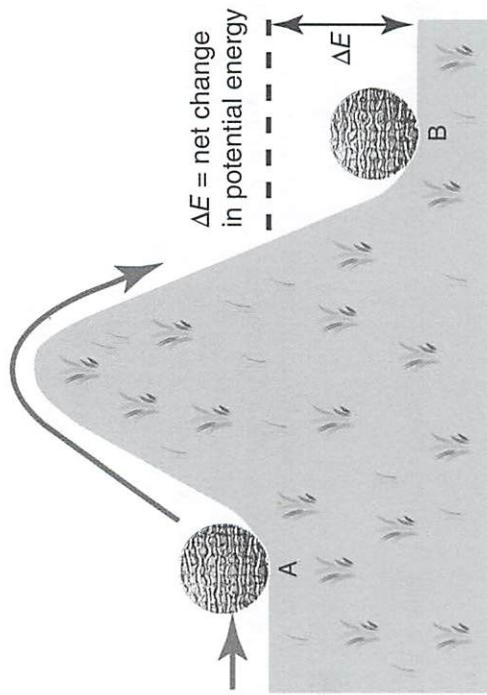
### OBJECTIVES

After studying this topic, you should be able to:

- Explain the following terms:
  - a. activation energy and activation barrier
  - b. catalyst and rate enhancement factor
  - c. reaction mechanism and rate determining step
  - d. molecularity
  - e. nucleophilic substitution
- Using data provided, calculate the activation energy and rate of a reaction.
- Using data provided, calculate the change of rate of a reaction after the introduction of a catalyst and/or modification of temperature, and the subsequent impact on  $E_a$ .
- Determine the rate law of various reactions given their reaction mechanisms.

### INTRODUCTION

Suppose one of several rocks, rumbling along the terrain after an earthquake, reaches the base of a hill (see position A in the figure that follows) and has enough momentum to clear the hill and roll down to position B. At position B, the rock will have less potential energy than it had at position A due to its net reduction in height (altitude). Even though the traverse from A to B reduces the rock's energy and thus would be favourable in a thermodynamic sense, the height of the hill more than anything else determines whether the rock gets to position B. This hill "barrier" would have to be overcome by any of the other post-earthquake rocks trying to roll from position A to B.



The hill-climbing exercise helps illustrate two separate concepts:

- Thermodynamics:  $A \rightarrow B$ , which results in a net energy difference ( $\Delta E$ ).
- Kinetics: the speed of  $A \rightarrow B$  conversion, which depends on the size of the barrier (hill).

### THERMODYNAMICS AND KINETICS

The rock and hill example was used to help emphasize that thermodynamics and kinetics are distinct. The former is a science concerned with the difference in energy between the reactants and the products in a reaction. The latter refers to the study of the rate at which the reaction occurs. For example, in thermodynamic terms the combustion reaction of methane ( $\text{CH}_4$ ) and oxygen ( $\text{O}_2$ ) is highly exothermic. Since the number of gaseous molecules on each side of the reaction are equal, no PV work is done and therefore  $\Delta E = \Delta H$ .



$$\Delta E = \Delta H = -802 \text{ kJ mol}^{-1}$$

Kinetically, however, the reaction has a rate near zero at room temperature. The *reaction coordinate* diagram shown in Figure 5.2.1 illustrates the energy changes that occur on the route from reactants to products. (A reaction coordinate is an abstract one-dimensional coordinate that represents progress along a reaction pathway.)

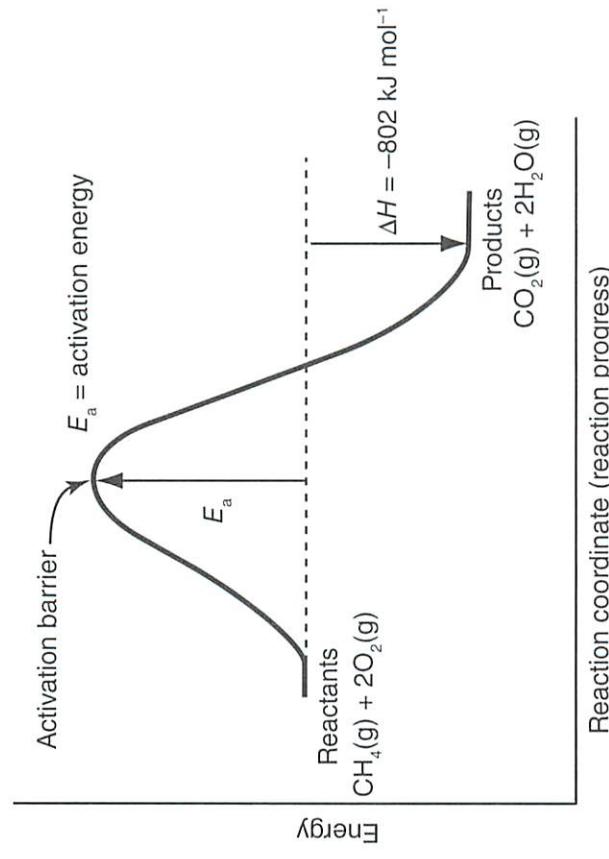


Figure 5.2.1 Reaction coordinate diagram for methane combustion.

### COLLISION THEORY

*Collision theory* is used to explain the various factors that influence reaction rates. In the previous topic, the effect of concentration on reaction rates was examined. What other factors affect whether a collision results in products?

### Activation Energy

In order for a chemical reaction to occur, the reactants (in this case CH<sub>4</sub> and O<sub>2</sub>) must first overcome an *activation barrier*. (Overcoming the hilltop shown on the second page is analogous to overcoming the activation barrier in the reaction

coordinate diagram.) The energy required to overcome this barrier is called the *activation energy* ( $E_a$ ). If the reaction proceeds, it releases a net energy of 802 kJ mol<sup>-1</sup>. However, the reaction does not occur, unless the reactants have sufficient combined energy to pass over the barrier. The energy needed to overcome the activation barrier comes from heat, which is measured by temperature. The heat-temperature relationship can be described as follows:

1. Heat has a direct impact on the kinetic energy of molecules.
2. Temperature is a measure of the average kinetic energy of a collection of molecules.
3. At any given temperature, there is a distribution of kinetic energies for molecules as shown in Figure 5.2.2.

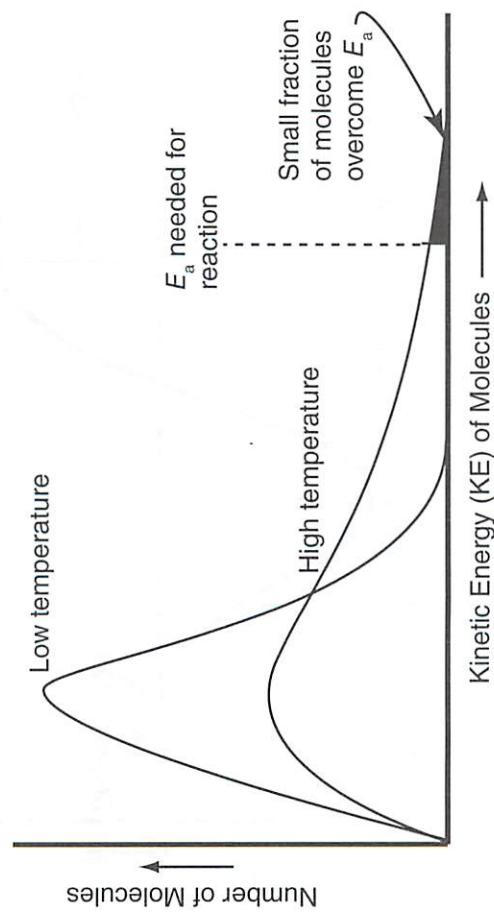
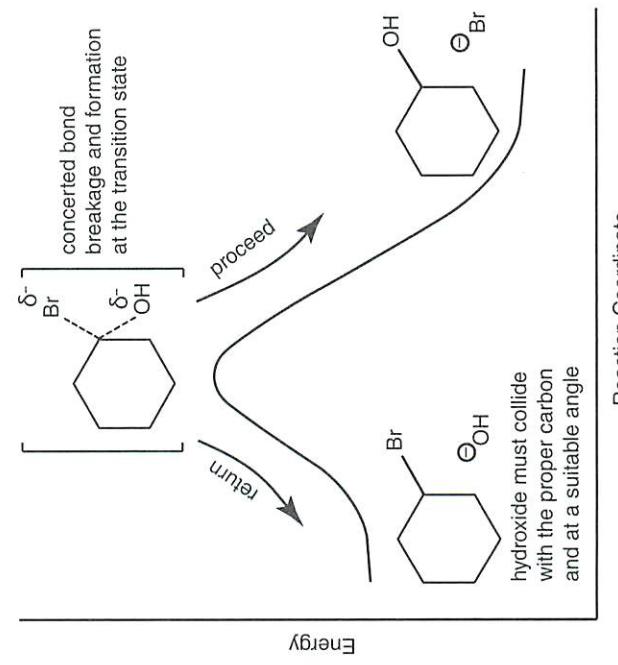


Figure 5.2.2 Boltzmann distribution of molecular kinetic energies.

With respect to the reaction of CH<sub>4</sub> with O<sub>2</sub>, at low temperature, none of the reactants have enough energy to overcome the activation barrier. When the temperature is increased by supplying heat, some of the reactant molecules gain enough energy to overcome  $E_a$ . The energy can be supplied by heating the entire mixture, by lighting the mixture with a match, or by introducing a spark. (Anyone who has ever taken a fire safety course should know the combustion triangle: fuel,

oxygen, and HEAT.) Once combustion has started, the heat released from the exothermic reaction is enough to propagate the reaction and allow it to continue until the limiting reagent is consumed.

Activation energy is just one aspect of collision theory. For a chemical reaction to occur, reactants must collide with sufficient energy to overcome the activation barrier, they must collide in a proper orientation, and even then the collision may not be successful because, at the moment of transition, the affected species can proceed to products or return to the reactants. An example is the conversion of bromocyclohexane to cyclohexanol (see reaction coordinate diagram below).



The rate of a reaction is affected by these factors:

- Reactant concentration (higher concentration = more collisions).
- Some probability factor based on the probabilities of colliding in a particular geometry (steric factor) and continuing to the products at the transition state.
- $E_a$  and temperature (higher temperature means more reactants have sufficient energy to overcome  $E_a$ ).

In equation form:

$$\text{Rate} = \frac{\text{number of collisions}}{\text{probability factor}} \times \frac{\text{probability factor}}{\text{(steric factor)}} \times \frac{\text{fraction of collisions with enough energy to overcome } E_a}{\text{enough energy to overcome } E_a}$$

### The Arrhenius Equation

In 1889, Swedish scientist Svante Arrhenius developed an equation that describes how temperature,  $E_a$ , and the probability factor affect the rate constant,  $k$ :

$$k = Ae^{-E_a/RT} \quad (5.2.1)$$

In the Arrhenius equation:

$A$  = Arrhenius probability factor for a specific reaction

$E_a$  = activation energy for a specific reaction

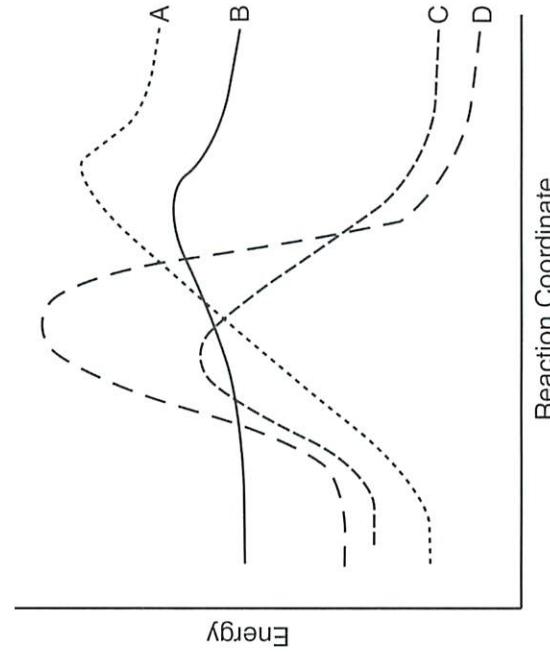
$R$  = gas constant  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$T$  = temperature (Kelvin)

The Arrhenius equation shows that when the value of  $E_a$  increases (the “hill” becomes higher), the value of  $k$  decreases.

**Example 5.2.1. Thermodynamics Versus Kinetics (In-Class Exercise)**

Four different reactions are shown in the reaction coordinate diagram below. Rank them in order of (a) increasing rate constant and (b) increasing thermodynamic favourability. Assume the same temperature and Arrhenius probability factor for all four.

**Effect of Temperature on Rate**

For a given reaction,  $E_a$  is a constant and can be determined without knowing the probability factor by performing two experiments at different temperatures while maintaining the same reactant concentrations.

$$\text{Rate}_1 = k_1 [A][B] \text{ at Temperature 1}$$

$$\text{Rate}_2 = k_2 [A][B] \text{ at Temperature 2}$$

If [A] and [B] are the same in both experiments:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k_2 [\text{A}][\text{B}]}{k_1 [\text{A}][\text{B}]} = \frac{k_2}{k_1} = \frac{Ae^{-E_a/RT_2}}{Ae^{-E_a/RT_1}} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}}$$

Taking natural logs:

$$\ln \frac{\text{Rate}_2}{\text{Rate}_1} = \ln \frac{k_2}{k_1} = \ln \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = \ln(e^{-E_a/RT_2}) - \ln(e^{-E_a/RT_1})$$

$$= -\frac{E_a}{RT_2} - \left( -\frac{E_a}{RT_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Thus,

$$\ln \frac{\text{Rate}_2}{\text{Rate}_1} = \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5.2.3)$$

Thus, using two rates or two rate constants obtained at different temperatures allows one to determine the activation energy for a reaction. Note that activation energies are often large. They are typically expressed in units of kJ mol<sup>-1</sup> while R, the gas constant, has units of J mol<sup>-1</sup> K<sup>-1</sup>. Care must be taken to ensure that all units in the equations are compatible.

#### Example 5.2.2. Activation Energy and Rate (In-Class Exercise)

When the temperature was increased from 20 to 30 °C, the rate of a reaction increased from 1.5 to 2.4 mol L<sup>-1</sup> s<sup>-1</sup>. Determine (a) the activation energy for this reaction and (b) the rate expected at 100 °C.

#### Example 5.2.3. Effect of Temperature on Reaction Rate (In-Class Exercise)

A reaction has an  $E_a$  of 41.6 kJ mol<sup>-1</sup> at 298 K. At what temperature will the reaction be thirty times faster?

### Determining Activation Energy Graphically

Using natural logarithms and then rearranging the Arrhenius equation results in an equation in the format of a straight line ( $y = mx + b$ ) as follows:

$$k = Ae^{-E_a/RT}$$

Using natural logarithms:

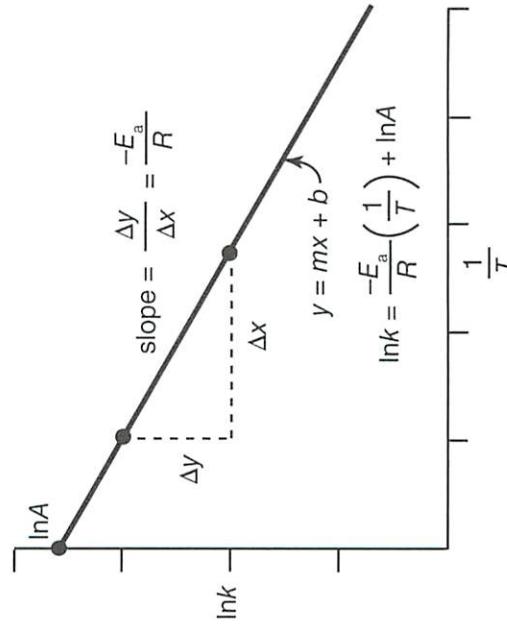
$$\ln k = \ln A - \frac{E_a}{RT}$$

or:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

Therefore,  $E_a$  can be determined experimentally by measuring a reaction rate at different temperatures, then plotting the graph of  $\ln k$  (calculated from the rate) versus  $1/T$ . The straight line has a slope of  $-E_a/R$  and a y-intercept of  $\ln A$  as shown in the graph that follows.



**Effect of a Catalyst on Activation Energy**

A catalyst is a species that increases the rate of a reaction but is not consumed in the reaction. It provides an alternate pathway with a lower  $E_a$  than, in turn, increases  $k$  (see Figure 5.2.3).

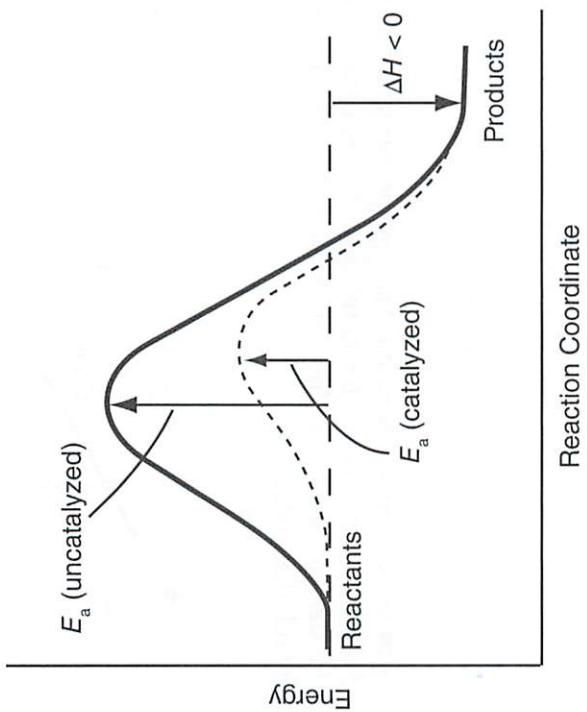
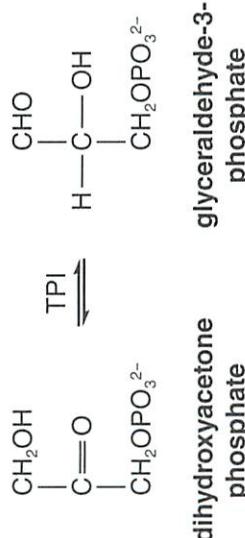


Figure 5.2.3 Effect of a catalyst on activation energy ( $E_a$ ).

A catalyst has no effect on the net enthalpy change ( $\Delta H$ ) of a reaction. It does not affect the equilibrium constant, but it does allow a system to attain equilibrium faster.

Enzymes, for example, are biological catalysts. One important enzyme is triose phosphate isomerase (TPI), which plays a crucial role in metabolizing glucose (glycolysis). It is thus an essential “energy” enzyme in humans, animals, and other organisms. During glycolysis, TPI interconverts two sugars, dihydroxyacetone phosphate and glyceraldehyde-3-phosphate, as shown in the reaction that follows.



The effect on the rate constant with and without the TPI enzyme (the catalyst) in the reaction is shown below:

- Rate constant (catalyzed):  $k_{\text{cat}} = 4.4 \times 10^3 \text{ s}^{-1}$
- Rate constant (uncatalyzed):  $k_{\text{uncat}} = 4.3 \times 10^{-6} \text{ s}^{-1}$

A term commonly used in the study of catalysts is the *rate enhancement factor*, which is simply the ratio of  $k$  values for the catalyzed and uncatalyzed reaction.

In this case, the rate enhancement factor is:  $\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{4.4 \times 10^3 \text{ s}^{-1}}{4.3 \times 10^{-6} \text{ s}^{-1}} = 1.0 \times 10^9$

Note that a deficiency of triose phosphate isomerase in humans is associated with a serious neurological disorder aptly called triose phosphate isomerase deficiency.

To determine the magnitude of the  $E_a$  reduction ( $\Delta E_a$ ) resulting from the introduction of a catalyst, keep all variables the same except for the absence or presence of the catalyst (i.e., both uncatalyzed and catalyzed reactions are taking place at the same temperature and with the same reactant concentration).

$$\frac{\text{Rate}_{\text{cat}}}{\text{Rate}_{\text{uncat}}} = \frac{k_{\text{cat}} [\text{reactants}]}{k_{\text{uncat}} [\text{reactants}]} = \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{Ae^{-E_{a(\text{cat})}/RT}}{Ae^{-E_{a(\text{uncat})}/RT}} = \frac{e^{-E_{a(\text{cat})}/RT}}{e^{-E_{a(\text{uncat})}/RT}} = \frac{\Delta E_a}{RT}$$

After taking the logarithm,

$$\ln \frac{\text{Rate}_{\text{cat}}}{\text{Rate}_{\text{uncat}}} = \ln \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \ln \frac{e^{-E_{a(\text{cat})}/RT}}{e^{-E_{a(\text{uncat})}/RT}} = \ln e^{-E_{a(\text{cat})}/RT} - \ln e^{-E_{a(\text{uncat})}/RT} = \frac{E_{a(\text{uncat})} - E_{a(\text{cat})}}{RT} = \frac{\Delta E_a}{RT}$$

Thus,

$$\ln \frac{\text{Rate}_{\text{cat}}}{\text{Rate}_{\text{uncat}}} = \ln \frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{\Delta E_a}{RT}$$

where  $\Delta E_a = E_{a(\text{uncat})} - E_{a(\text{cat})}$  is the activation barrier reduction brought about by the catalyst.

**Example 5.2.4. Reduction of  $E_a$  by an Enzyme (In-Class Exercise)**

If the triose phosphate isomerase reaction mentioned earlier takes place at 298 K, by how much does the enzyme reduce the  $E_a$ ?

**Example 5.2.5. Rate Enhancement Factor of an Enzyme (In-Class Exercise)**

A catalyst lowers  $E_a$  for a reaction from 100 to 70 kJ mol<sup>-1</sup> at 300 K. By what factor does the rate of the catalyzed reaction increase?

**REACTION MECHANISMS**

What actually happens at the molecular level when a reaction occurs? Which atoms collide to produce the reaction? Consider the reaction of NO with Cl<sub>2</sub>:



Although the balanced reaction shows three molecules on the reactant side, it is unlikely that all three molecules collide in the proper orientation and react together. Rather, chemical reactions often occur in multiple steps. A *reaction mechanism* describes the sequence of steps that occur. Each step in a reaction mechanism is called an *elementary step*. Experimentally, it has been determined that NO and Cl<sub>2</sub> actually react in a two-step mechanism:

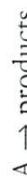


Note that NOCl<sub>2</sub> was formed in Step 1 and consumed in Step 2, so it is called a *reaction intermediate*.

Each of the two elementary steps listed above has an  $E_a$  and a rate constant. Elementary steps cannot be broken down further, as they are the simplest molecular events that occur. How was this particular mechanism determined? As with other reactions, chemists proposed possible mechanisms, derived their corresponding rate laws, and then noted which one matched the data obtained experimentally.

### Molecularity

To understand the use of kinetic data for determining a mechanism, the concept of *molecularity* is needed. Molecularity refers to how many species react together in an elementary step. If a process involves only one reactant species, it is termed a *unimolecular process* and must exhibit first-order kinetics.



A *bimolecular process* involves two species, either identical or different, and is second order. For example:



$$\text{Rate} = k[\text{A}]^2$$



$$\text{Rate} = k[\text{A}][\text{B}]$$

When reactions occur in two or more elementary steps, the steps can be of different molecularity. For example, in the decomposition of  $\text{O}_3$ :



$$\text{Rate} = k_1[\text{O}_3] \text{ (unimolecular)}$$



$$\text{Rate} = k_2[\text{O}_3][\text{O}] \text{ (bimolecular)}$$



There are two important consequences here:

1. In an elementary step, and ONLY in an elementary step, the coefficients of the reactants become the exponents in the rate law for that step.
2. The overall rate of a reaction is determined by the rate of the slowest or *rate-determining step* (RDS).

### Determining Reaction Mechanisms

Consider a reaction of alkyl halides known as a *nucleophilic substitution*. The electron-bearing nucleophile<sup>1</sup> ( $\text{Cl}^-$ ) replaces the bromide on the *electrophilic* (electron-deficient) carbon atom:

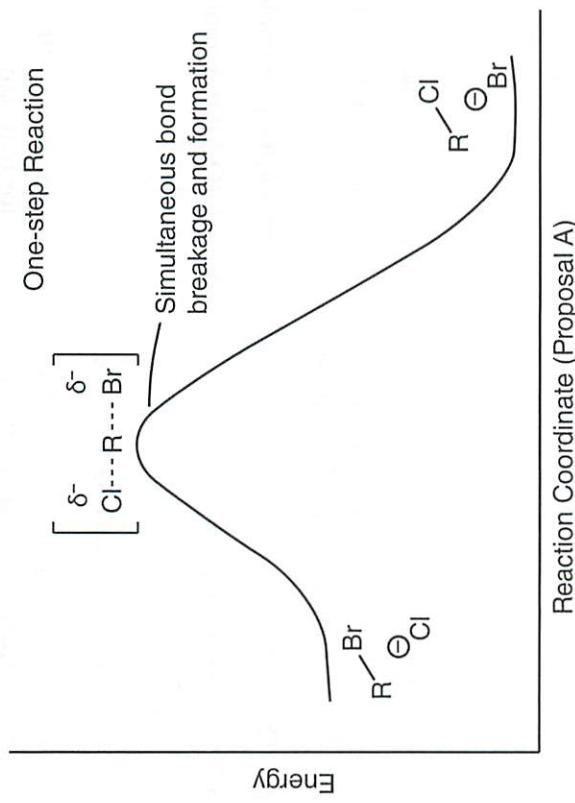


<sup>1</sup> A nucleophile (literally “nucleus lover”) is a reactant that seeks the centers of positive charge in a molecule and forms a chemical bond with its partner (the electrophile or “electron lover”) by donating both bonding electrons. By donating electrons, nucleophiles are, by definition, Lewis bases.

To determine the mechanism, a chemist normally proposes the possible mechanisms. The experimental data are then compared to overall rate laws of the possible mechanisms.

**Proposal A**

Suppose the reaction occurs in one step. Therefore, the overall reaction equation is the only elementary step. Breakage of the R-Br bond is concomitant with R-Cl bond formation (see diagram that follows).



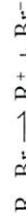
Since the elementary step is the overall reaction (i.e., the only step):

- The reaction is bimolecular.
- The rate law for the reaction is overall second order, as two reactants are involved in the RDS.
- $\text{Rate} = k [\text{R-Br}] [\text{Cl}^-]$ .

**Proposal B**

In this case, the reaction occurs in two steps:

- Step 1 involves a slow cleavage of the alkyl halide ( $\text{R}-\text{Br}$ ) to generate a carbocation intermediate in a reversible reaction. Rate =  $k[\text{R}-\text{Br}]$



- Step 2 is a fast reaction between the carbocation ( $\text{R}^+$ ) and  $\text{Cl}^-$ .

$$\text{Rate} = k_2[\text{R}^+][\text{Cl}^-]$$

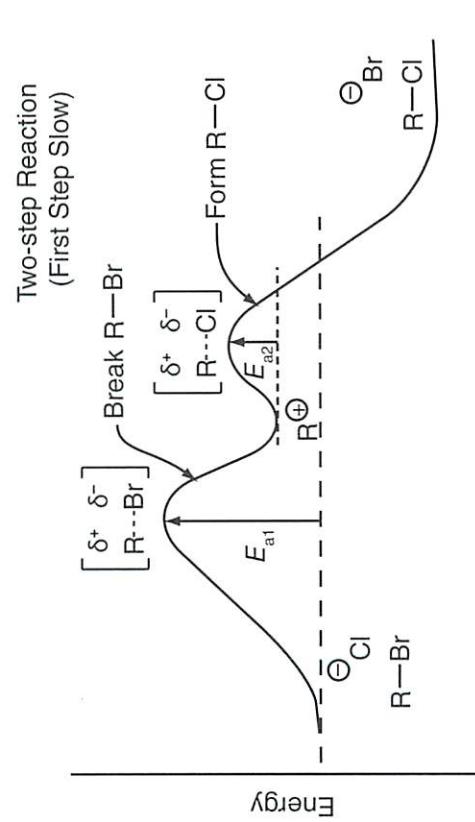


What would the rate law be for the overall reaction in Proposal B?



Based on the RDS (Step 1): Rate =  $k[\text{R}-\text{Br}]$

Since there are two steps, the reaction coordinate diagram that follows shows an intermediate and two transition states.



Reaction Coordinate (Proposal B)

The difference between an intermediate and a transition state is:

- An intermediate is a real species that can be found in the reaction mixture as the reaction progresses. Here, the intermediate is a carbocation,  $R^+$ .
- A transition state, also known as an activated complex, is a postulated high-energy structure that is very short-lived. It cannot be found in the reaction mixture.

### Proposal C

Suppose Proposal C is like Proposal B except the slow/fast assignments have been swapped. Again, the reaction occurs in two steps:

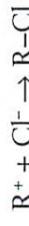
- Step 1 involves a fast cleavage of the alkyl halide to generate a carbocation intermediate in an equilibrium reaction.



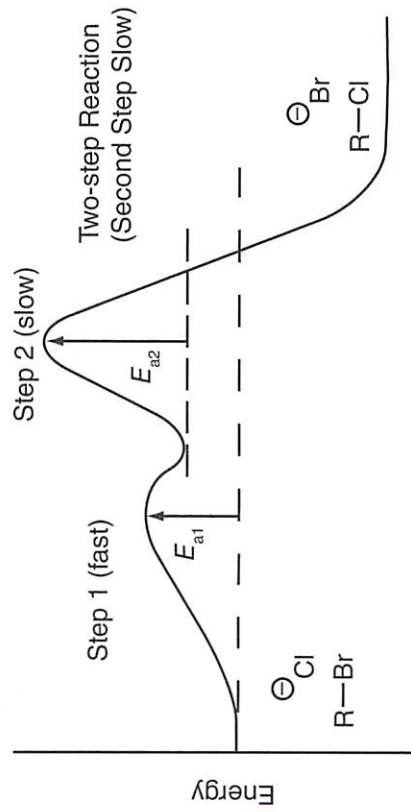
In an equilibrium reaction, the forward and reverse rates are equal.

$$\text{Therefore: rate} = k_1 [R-Br] = k_1[R^+] [Br^-]$$

- Step 2 is a slow reaction between the carbocation and the nucleophile.



$$\text{Therefore: rate} = k_2[R^+] [Cl^-]$$



Reaction Coordinate (Proposal C)

The overall rate law for the Proposal C reaction mechanism is based on the slow step (Step 2), so is it: rate =  $k_2[R^+][Cl^-]$ ? Well, yes. But since intermediates (i.e.,  $R^+$ ) cannot appear in the overall rate law, the rate expression from Step 1 must be rearranged and a substitute for  $R^+$  must be used in the Step 2 (RDS) rate expression.

Remember, the overall reaction is:



- From Step 1:  $k_{1F}[R-Br] = k_{1R}[R^+][Br^-]$

Therefore:

- From Step 2: rate =  $k_2[R^+][Cl^-]$

Therefore, substituting for  $[R^+]$  results in the overall rate law:

$$\text{Rate} = k_2 \left( \frac{k_{1F}[R-Br]}{k_{1R}[Br^-]} \right) [Cl^-] = k'[R-Br][Cl^-][Br^-]$$

( $k'$  is used to represent the ratio of constants.)

Note that Proposal C is an example where  $Br^-$  (a product) slows the reaction and therefore shows up in the rate law. High  $[Br^-]$  reduces  $[R^+]$ , which in turn slows down Step 2, the RDS. (This is Le Châtelier's principle at work. The equilibrium shifts to the left to minimize the disturbance caused by the high  $[Br^-]$ .)

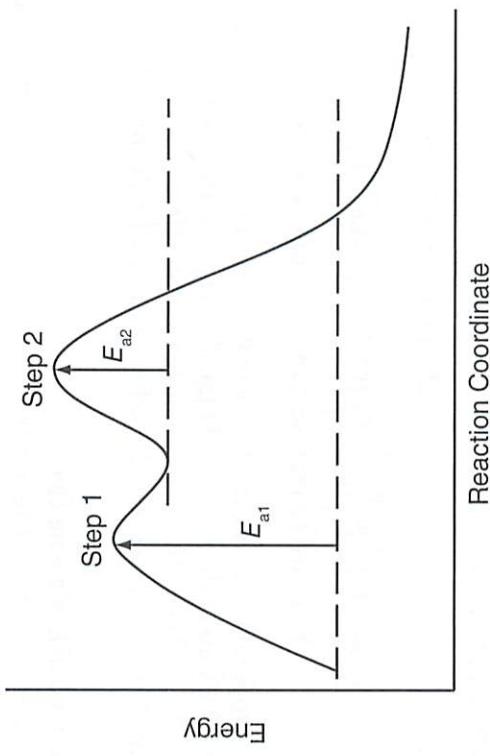
#### Guidelines for Deriving a Rate Law

The actions required to derive a rate law from a proposed reaction mechanism are summarized below:

1. Look for the slow or rate-determining step (RDS).
2. Write a rate law in terms of concentrations of reactants in the RDS. A maximum of two species should appear in the rate law at this stage.
3. If there are intermediates in the rate law, express their concentrations in terms of stable reactants appearing in the overall reaction equation. This may be done by writing equilibrium constant expressions for steps preceding the RDS.
4. Substitute concentrations of stable reactants for concentrations of intermediates in the rate law.
5. Fast steps following the RDS in the mechanistic sequence may be ignored.

6. The rate-determining step is not necessarily the one with the largest value of  $E_a$  for the step, as measured according to these figures. The rate-determining step is the step whose transition state has the highest overall energy in the reaction coordinate diagram. Completion of the reaction depends on getting to that highest energy point, since it is the overall peak of energy.

Consider the diagram below:



While Step 1 has the larger activation energy, it is more likely that step 2 will be the RDS due to its higher peak energy.

Even so, this analysis does not include a discussion of the pre-exponential term in the rate constant expression:

$$k = A e^{-E_a/RT}$$

As we have seen, the parameter  $A$  contains terms related to geometrical factors, which may also influence the rate of the step.

In general however, the highest point on the reaction coordinate diagram will indicate the RDS.

**Example 5.2.6. Mechanism of Substitution for *Tert*-butyl Bromide (In-Class Exercise)**

Using *tert*-butyl bromide, which is a tertiary alkyl halide (the carbon bearing the Br is connected to three carbons), the experimental data below were obtained. By which one of the proposed A, B, or C mechanisms does the reaction proceed?



RUN #	$[t\text{-BuBr}]^x$	$[\text{Cl}^-]^y$	$[\text{Br}^\ominus]^z$	RATE (mol L <sup>-1</sup> min <sup>-1</sup> )
i	0.1	0.1	0.1	5
ii	0.1	0.2	0.1	5
iii	0.2	0.2	0.1	10
iv	0.2	0.4	0.2	10

**Example 5.2.7. Mechanism of Substitution for Ethyl Bromide (In-Class Exercise)**

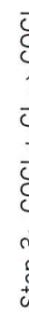
Using ethyl bromide, a primary alkyl halide, the experimental data below was obtained. By which proposed mechanism (A, B, or C) does the reaction proceed?



RUN #	$[\text{EtBr}]^x$	$[\text{Cl}^-]^y$	$[\text{Br}^\ominus]^z$	RATE (mol L <sup>-1</sup> min <sup>-1</sup> )
i	0.1	0.1	0.1	5
ii	0.1	0.2	0.1	10
iii	0.2	0.2	0.1	20
iv	0.4	0.4	0.2	80

**Example 5.2.8. Proposing Mechanisms for the Reaction of  $\text{Cl}_2$  with CO (In-Class Exercise)**

The following reaction occurs in three steps:



- What would be the overall rate law expected if Step 1 is slow and Steps 2 and 3 are fast?
- What if Step 2 is slow, Step 3 is fast, but Step 1 is a fast equilibrium?
- What if Step 3 is slow, but Steps 1 and 2 are fast equilibria?

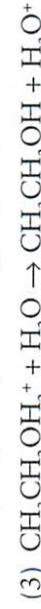
## Section 5.2 Review Problems

1. Which of the following statements is/are correct?
  - a. A rate law can be deduced from the balanced equation for an overall reaction.
  - b. If a reaction takes place in a series of steps, each step must proceed at the same rate.
  - c. A catalyst must be in the same phase as the reactants in order to be effective.
  - d. The difference between  $E_a$  for the forward reaction and  $E_a$  for the reverse reaction is equal to  $\Delta H$  for the overall reaction.
2. A certain reaction has an activation energy of 45 kJ mol<sup>-1</sup>. If the rate of reaction is  $1.2 \times 10^{-3}$  mol L<sup>-1</sup> s<sup>-1</sup> at 25 °C, calculate
  - a. The rate at 80 °C, other things being kept equal.
  - b. The temperature at which the rate has increased to  $7.2 \times 10^{-2}$  mol L<sup>-1</sup> s<sup>-1</sup>.
3. Keeping reactant concentrations constant, it was found that the rate of a certain reaction increased by a factor of 4.0 when the temperature was raised from 100 °C to 125 °C. What is the activation energy for this reaction?
4. The rate of a certain reaction increases from  $2.5 \times 10^{-2}$  to  $6.0 \times 10^{-2}$  mol L<sup>-1</sup> s<sup>-1</sup> when the temperature is raised from 0 °C to 15 °C.
  - a. What is the activation energy for this reaction?
  - b. What would be the rate of reaction at 40 °C with the same reactant concentrations?
5. A reaction has an activation energy of 60 kJ mol<sup>-1</sup>.
  - a. By what factor would the rate increase if the temperature were to be increased from 100 °C to 125 °C?
  - b. At what temperature would the rate be three times the rate at 60 °C?

6. An uncatalyzed reaction proceeds at a rate of  $7.5 \times 10^{-5}$  mol L<sup>-1</sup> s<sup>-1</sup> at 25 °C. If a catalyst lowers  $E_a$  by 25 kJ mol<sup>-1</sup>, what will be the rate of the catalyzed reaction at this temperature?
7. A reaction has specific rate constant  $k = 1.2 \times 10^{-3}$  L mol<sup>-1</sup> s<sup>-1</sup> at 25 °C. Introduction of a catalyst increases the rate constant to 1.0 L mol<sup>-1</sup> s<sup>-1</sup> at the same temperature. Calculate the change in activation energy, in kJ mol<sup>-1</sup>, made by the catalyst.
8. The addition of water to ethylene is catalyzed by an acid, such as H<sub>2</sub>SO<sub>4</sub>:



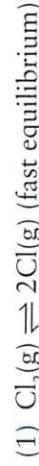
The following mechanism is suggested:



- What species appear in the reaction scheme as intermediates?
- What species is acting as a catalyst? Why is the term “catalyst” appropriate?
- What other species is present in the solution, but takes no part in the reaction?
- What rate law would be expected for the overall reaction:
  - If Step (1) is slow and the others are fast equilibria?
  - If Step (3) is slow and the others are fast equilibria?

Note that the catalyst *may* appear in the rate law because it is considered a reactant.

9. For the overall reaction:  $\text{CHCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{g}) + \text{HCl}(\text{g})$  the following step-wise mechanism is suggested:



- a. Which is the rate-determining step (RDS)?
- b. Which species are unstable intermediates in this scheme?
- c. What rate law would be expected for this reaction?

