CHEMISTRY 2



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Chemistry 2

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1.0: Phase Diagrams of Pure Substances

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure **1.0.1**). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure **1.0.1**) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

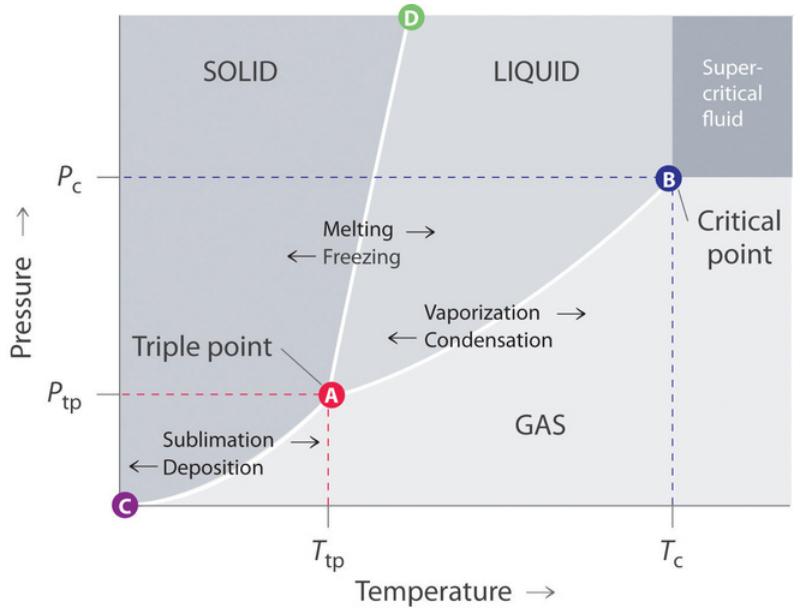


Figure **1.0.1**: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure **1.0.1**, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure **1.0.1**, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a

substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure **1.0.2** shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

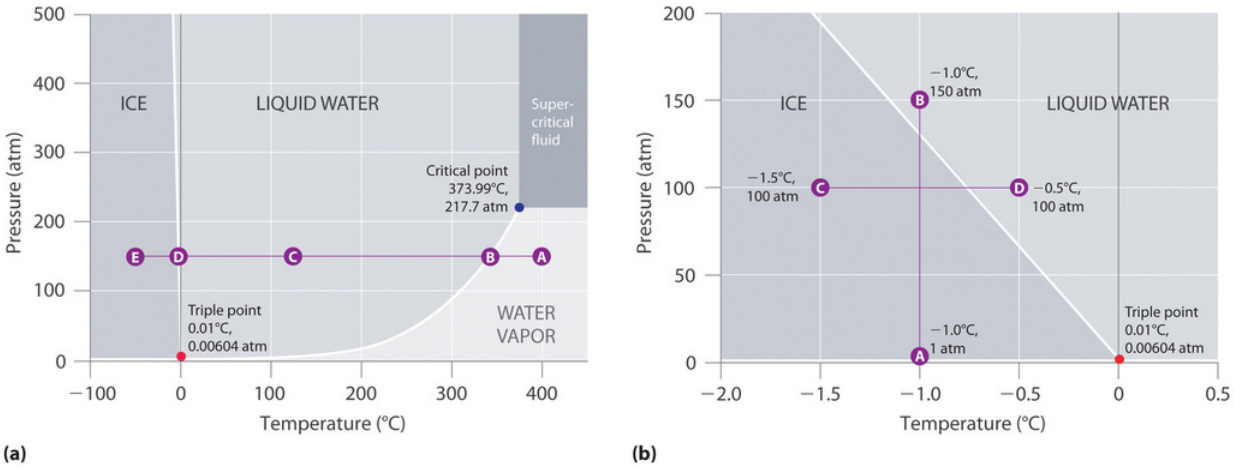


Figure **1.0.2**: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example **1.0.1**).

The phase diagram for water illustrated in Figure **1.0.2*b*** shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure **1.0.1**; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure **1.0.2*b*** point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.



Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (P) is the force (F) applied per unit area (A):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where m is the mass and g is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✔ Example 1.0.1: Water

Referring to the phase diagram of water in Figure 1.0.2:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure **1.0.2**. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.
b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure **1.0.2**. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

? Exercise 1.0.2

Referring to the phase diagram of water in Figure **1.0.2**, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure **1.0.3**) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

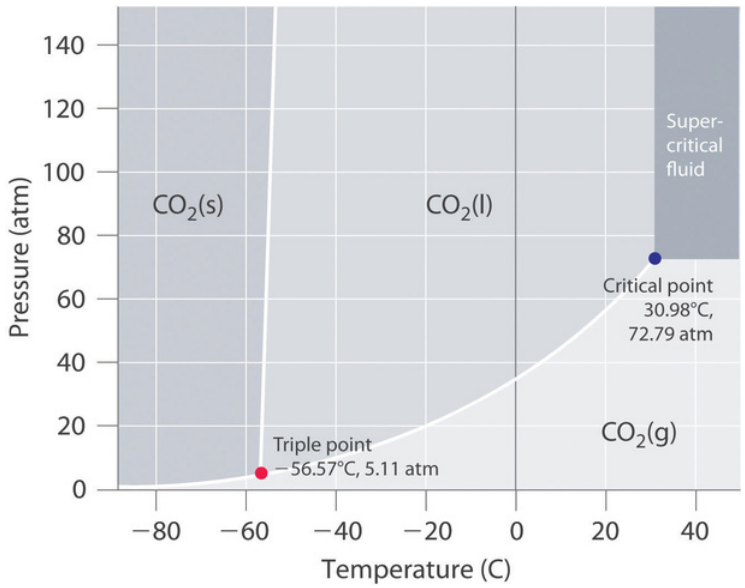


Figure **1.0.3**: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure **1.0.1**.

Figure **1.0.1**: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Supercritical Fluids

To understand what happens at the critical point, consider the effects of temperature and pressure on the densities of liquids and gases, respectively. As the temperature of a liquid increases, its density decreases. As the pressure of a gas increases, its density increases. At the critical point, the liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluid, which exhibits many of the properties of a gas but has a density more typical of a liquid. For example, the density of water at its critical point (T = 374°C, P = 217.7 atm) is 0.32 g/mL, about one-third that of liquid water at room temperature but much greater than that of water vapor under most conditions. The transition between a liquid/gas mixture and a supercritical phase is demonstrated for CO_2 in Figure **1.0.4**. At the critical temperature, the meniscus separating the liquid and gas phases disappears.



Figure **1.0.4**: Liquid CO_2 is heated in a pressure cell until it reaches the critical point were it changes into a supercritical fluid. Below the critical temperature the meniscus between the liquid and gas phases is apparent. At the critical temperature, the meniscus disappears because the density of the vapor is equal to the density of the liquid. Above T_c, a dense homogeneous fluid fills the tube.

In the last few years, supercritical fluids have evolved from laboratory curiosities to substances with important commercial applications. For example, carbon dioxide has a low critical temperature (31°C), a comparatively low critical pressure (73 atm), and low toxicity, making it easy to contain and relatively safe to manipulate. Because many substances are quite soluble in supercritical CO_2, commercial processes that use it as a solvent are now well established in the oil industry, the food industry, and others. Supercritical CO_2 is pumped into oil wells that are no longer producing much oil to dissolve the residual oil in the underground reservoirs. The less-viscous solution is then pumped to the surface, where the oil can be recovered by evaporation (and recycling) of the CO_2. In the food, flavor, and fragrance industry, supercritical CO_2 is used to extract components from natural substances for use in perfumes, remove objectionable organic acids from hops prior to making beer, and selectively extract caffeine from whole coffee beans without removing important flavor components. The latter process was patented in 1974, and now virtually all decaffeinated coffee is produced this way. The earlier method used volatile organic solvents such as methylene chloride (dichloromethane [CH_2Cl_2], boiling point = 40°C), which is difficult to remove completely from the beans and is known to cause cancer in laboratory animals at high doses.

Summary

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a **phase diagram**, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point. Within a given region, only a single phase is stable, but along the lines that separate the regions, two phases are in equilibrium at a given temperature and pressure. The lines separating the three phases intersect at a single point, the **triple point**, which is the only combination of temperature and pressure at which all three phases can coexist in equilibrium. Water has an unusual phase diagram: its melting point decreases with increasing pressure because ice is less dense than liquid water. The phase diagram of carbon dioxide shows that liquid carbon dioxide cannot exist at atmospheric pressure. Consequently, solid carbon dioxide sublimes directly to a gas.

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1.0.s: The Clapeyron Equation

The analysis in the two previous sections can be repeated for any phase change of a pure substance. Let α and β denote the two phases that are at equilibrium.

$$\alpha \rightleftharpoons \beta \tag{1.0.s.1}$$

Let $\overline{G}_\alpha$, $\overline{S}_\alpha$, and $\overline{V}_\alpha$ represent the Gibbs free energy, the entropy, and the volume of one mole of pure phase α at pressure P and temperature T. Let $\overline{G}_\beta$, $\overline{S}_\beta$, and $\overline{V}_\beta$ represent the corresponding properties of one mole of pure phase β. The equations

$$d\overline{G}\,(\alpha) = \overline{V}_\alpha dP - \overline{S}_\alpha dT \tag{1.0.s.2}$$

and

$$d\overline{G}\,(\beta) = \overline{V}_\beta dP - \overline{S}_\beta dT \tag{1.0.s.3}$$

describe the changes in the Gibbs free energy of a mole of α and a mole of β when they go from one $\alpha - \beta$-equilibrium state at P and T to a second $\alpha - \beta$-equilibrium state at $P + dP$ and $T + dT$. Since these Gibbs free energy changes must be equal, we have

$$\begin{aligned} d\overline{G}\,(\beta) - d\overline{G}\,(\alpha) &= \left(\overline{V}_\beta - \overline{V}_\alpha\right) dP - \left(\overline{S}_\beta - \overline{S}_\alpha\right) dT \\ &= \Delta\overline{V} dP - \Delta\overline{S} dT \\ &= 0 \end{aligned}$$

and

$$\frac{dP}{dT} = \frac{\Delta\overline{S}}{\Delta\overline{V}} \tag{1.0.s.4}$$

where $\Delta\overline{S}$ and $\Delta\overline{V}$ are the entropy and volume changes that occur when one mole of the substance goes from phase α to phase β. Since $\Delta\overline{S} = \Delta\overline{H}/T$, the condition for equilibrium between phases α and β becomes

$$\frac{dP}{dT} = \frac{\Delta\overline{H}}{T\,\Delta\overline{V}} \tag{1.0.s.5}$$

Equation 1.0.s.5 is known as the **Clapeyron equation**.

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1.1: Phase Transitions of Pure Substances

Learning Objectives

- Define phase transitions and phase transition temperatures
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called condensation. When the rate of condensation becomes equal to the rate of vaporization, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a dynamic equilibrium, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's vapor pressure (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure **1.1.1**, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.

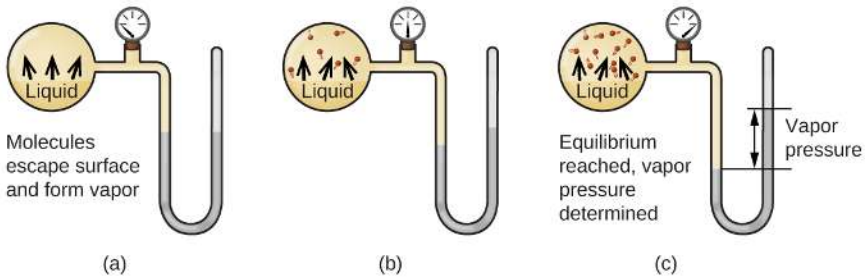
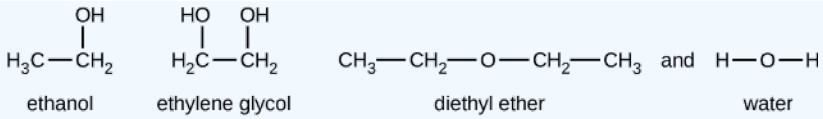


Figure **1.1.1**: In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example 1.1.1: Explaining Vapor Pressure in Terms of IMFs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:



Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two −OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure is the lowest.

? Exercise 1.1.1

At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Answer

All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:

$$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}$$

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure **1.1.2**. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.

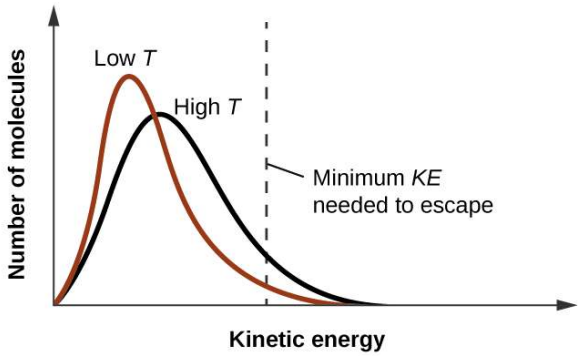


Figure **1.1.2**: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The boiling point of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The normal boiling point of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure **1.1.3** shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.

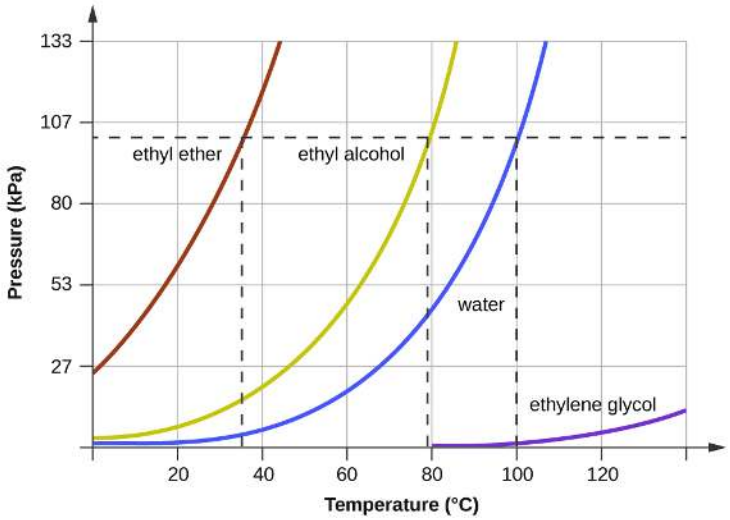


Figure **1.1.3**: The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

Example 1.1.2: A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure **1.1.3** to determine the boiling point of water at this elevation.

Solution

The graph of the vapor pressure of water versus temperature in Figure **1.1.3** indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

Exercise 1.1.2

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure **1.1.3** to determine the approximate atmospheric pressure at the camp.

Answer

Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the Clausius-Clapeyron equation:

$$P = Ae^{-\Delta H_{vap}/RT} \tag{1.1.1}$$

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and $\ln A$ is a constant whose value depends on the chemical identity of the substance.

Equation 1.1.1 is not the common way to present the Clausius-Clapeyron equation. The more common formulation starts by rearranging it into logarithmic form to yield the linear equation

$$\ln P = -\frac{\Delta H_{vap}}{RT} + \ln A$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the examples and exercises that follow. If at temperature T_1, the vapor pressure is P_1, and at temperature T_2, the vapor pressure is T_2, the corresponding linear equations are:

$$\ln P_1 = -\frac{\Delta H_{vap}}{RT_1} + \ln A$$

and

$$\ln P_2 = -\frac{\Delta H_{vap}}{RT_2} + \ln A$$

Since the constant, $\ln A$, is the same, these two equations may be rearranged to isolate $\ln A$ and then set them equal to one another

$$\ln P_1 + \frac{\Delta H_{vap}}{RT_1} = \ln P_2 + \frac{\Delta H_{vap}}{RT_2}$$

which can be combined to form

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.1.2}$$

Example 1.1.3: Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap}, can be determined by using the Clausius-Clapeyron equation (Equation 1.1.2):

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since we have two vapor pressure-temperature values

- $T_1 = 34.0°C = 307.2\,K$
- $P_1 = 10.0\,kPa$ and
- $T_2 = 98.8°C = 372.0\,K$
- $P_2 = 100\,kPa$

we can substitute them into this equation and solve for ΔH_{vap}. Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

$$\begin{aligned}\Delta H_{vap} &= \frac{R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \\ &= \frac{(8.3145\ J/mol \cdot K) \cdot \ln\left(\frac{100\ kPa}{10.0\ kPa}\right)}{\left(\frac{1}{307.2\ K} - \frac{1}{372.0\ K}\right)} \\ &= 33,800\ J/mol = 33.8\ kJ/mol\end{aligned}$$

Note that the pressure can be in any units, so long as they agree for both P values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

? Exercise 1.1.3

At 20.0 °C, the vapor pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapor pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

Answer

47,782 J/mol = 47.8 kJ/mol

✓ Example 1.1.4: Estimating Temperature (or Vapor Pressure)

For benzene (C_6H_6), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

Solution

If the temperature and vapor pressure are known at one point, along with the enthalpy of vaporization, ΔH_{vap}, then the temperature that corresponds to a different vapor pressure (or the vapor pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation (Equation 1.1.1):

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since the normal boiling point is the temperature at which the vapor pressure equals atmospheric pressure at sea level, we know one vapor pressure-temperature value (T_1 = 80.1 °C = 353.3 K, P_1 = 101.3 kPa, ΔH_{vap} = 30.8 kJ/mol) and want to find the temperature (T_2) that corresponds to vapor pressure P_2 = 83.4 kPa. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2. Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

$$\begin{aligned} T_2 &= \left(\frac{-R\cdot\ln\left(\frac{P_2}{P_1}\right)}{\Delta H_{vap}} + \frac{1}{T_1}\right)^{-1} \\ &= \left(\frac{-(8.3145\ \text{J/mol·K})\cdot\ln\left(\frac{83.4\ \text{kPa}}{101.3\ \text{kPa}}\right)}{30{,}800\ \text{J/mol}} + \frac{1}{353.3\ \text{K}}\right)^{-1} \\ &= 346.9\ \text{K or } 73.8°\text{C} \end{aligned}$$

? Exercise 1.1.4

For acetone $(CH_3)_2CO$, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapor pressure of acetone at 25.0 °C?

Answer

30.1 kPa

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta H_{vap} = 44.01\ kJ/mol$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \longrightarrow H_2O(l) \quad \Delta H_{con} = -\Delta H_{vap} = -44.01\ kJ/mol$$

Example 1.1.5: Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 1.1.4). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at T = 37 °C (normal body temperature); $\Delta H_{vap} = 43.46\ kJ/mol$ at 37 °C.



Figure 1.1.4: Evaporation of sweat helps cool the body. (credit: "Kullez"/Flickr)

Solution We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

$$1.5\ \cancel{L} \times \frac{1000\ \cancel{g}}{1\ \cancel{L}} \times \frac{1\ \cancel{mol}}{18\ \cancel{g}} \times \frac{43.46\ kJ}{1\ \cancel{mol}} = 3.6 \times 10^3\ kJ$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

Exercise 1.1.5: Boiling Ammonia

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Answer

28 kJ

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 1.1.5.

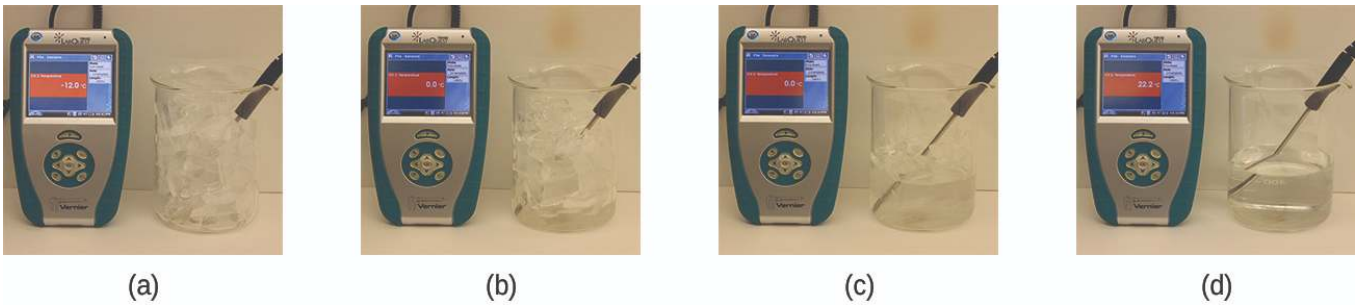


Figure **1.1.5**: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔHfus of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$\mathrm{H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{fus} = 6.01\ kJ/mol} \tag{1.1.3}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$\mathrm{H_2O_{(l)} \rightarrow H_2O_{(s)} \quad \Delta H_{frz} = -\Delta H_{fus} = -6.01\ kJ/mol} \tag{1.1.4}$$

Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as sublimation. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure **1.1.6**). The reverse of sublimation is called deposition, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



Figure **1.1.6**: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H_{\mathrm{sub}} = 26.1\ \mathrm{kJ/mol}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \quad \Delta H_{\mathrm{dep}} = -\Delta H_{\mathrm{sub}} = -26.1\ \mathrm{kJ/mol}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law.

$$\begin{aligned} \text{solid} &\longrightarrow \text{liquid} \quad \Delta H_{\mathrm{fus}} \\ \text{liquid} &\longrightarrow \text{gas} \quad \Delta H_{\mathrm{vap}} \\ \hline \text{solid} &\longrightarrow \text{gas} \quad \Delta H_{\mathrm{sub}} = \Delta H_{\mathrm{fus}} + \Delta H_{\mathrm{vap}} \end{aligned}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 1.1.7.

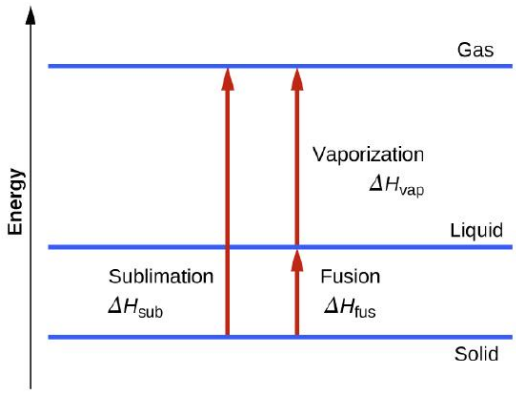


Figure 1.1.7: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure 1.1.8 shows a typical heating curve.

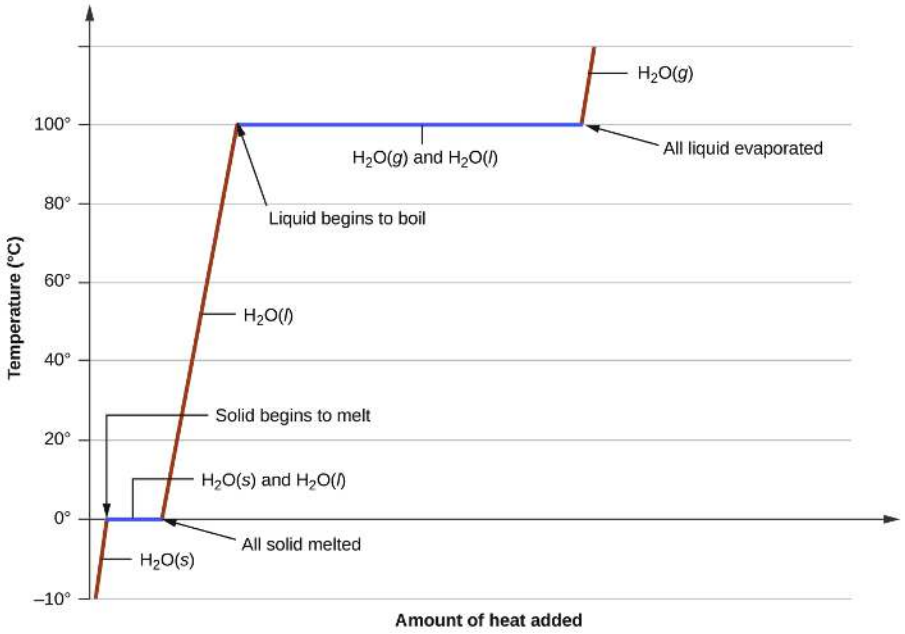


Figure **1.1.8**: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.

✔ Example **1.1.6**: Total Heat Needed to Change Temperature and Phase for a Substance

How much heat is required to convert 135 g of ice at −15 °C into water vapor at 120 °C?

Solution

The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = m \times c \times \Delta T$ (see previous chapter on thermochemistry). The heat needed to induce a given change in phase is given by $q = n \times \Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

$$q_{\text{total}} = (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}}$$

$$= (135\ \text{g} \cdot 2.09\ \text{J/g·°C} \cdot 15\text{°C}) + \left(135 \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot 6.01\ \text{kJ/mol}\right)$$

$$+(135\ \text{g} \cdot 4.18\ \text{J/g·°C} \cdot 100\text{°C}) + \left(135\ \text{g} \cdot \frac{1\ \text{mol}}{18.02\ \text{g}} \cdot 40.67\ \text{kJ/mol}\right)$$

$$+(135\ \text{g} \cdot 1.84\ \text{J/g·°C} \cdot 20\text{°C})$$

$$= 4230\ \text{J} + 45.0\ \text{kJ} + 56,500\ \text{J} + 305\ \text{kJ} + 4970\ \text{J}$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

$$= 4.23\ \text{kJ} + 45.0\ \text{kJ} + 56.5\ \text{kJ} + 305\ \text{kJ} + 4.97\ \text{kJ} = 416\ \text{kJ}$$

? Exercise 1.1.6

What is the total amount of heat released when 94.0 g water at 80.0 °C cools to form ice at −30.0 °C?

Answer

40.5 kJ

Summary

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

Key Equations

- $P = Ae^{-\Delta H_{\text{vap}}/RT}$
- $\ln P = -\dfrac{\Delta H_{\text{vap}}}{RT} + \ln A$
- $\ln\left(\dfrac{P_2}{P_1}\right) = \dfrac{\Delta H_{\text{vap}}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

Glossary

boiling point
temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Clausius-Clapeyron equation
mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

condensation
change from a gaseous to a liquid state

deposition
change from a gaseous state directly to a solid state

dynamic equilibrium
state of a system in which reciprocal processes are occurring at equal rates

freezing
change from a liquid state to a solid state

freezing point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

melting

change from a solid state to a liquid state

melting point

temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

normal boiling point

temperature at which a liquid’s vapor pressure equals 1 atm (760 torr)

sublimation

change from solid state directly to gaseous state

vapor pressure

(also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization

change from liquid state to gaseous state

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1.1.s: The Clausius-Clapeyron Equation

To use the Clapeyron equation we must know the enthalpy and volume differences at one equilibrium temperature and pressure. In general, these properties are readily measured. If we fix the pressure, we can measure the corresponding equilibrium temperature. We can obtain the enthalpy change at this pressure by measuring the heat required to convert a mole of the substance from one phase to the other. We can obtain the volume change from the molar volumes, which we can obtain by measuring the density of each phase. The enthalpy of the phase change varies only weakly as the equilibrium pressure and temperature vary. Similarly, for condensed phases, the densities are weak functions of temperature. This means that, for transitions between condensed phases, $\Delta\overline{H}/\Delta\overline{V}$ is approximately constant over a modest temperature range.

For a sublimation or vaporization process, the product is a gas. Then the molar volume of the product is a sensitive function of both pressure and temperature. However, the molar volume of the product phase is much greater than the molar volume of the initial solid or liquid phase. To a good approximation, the volume change for the process equals the volume of the gas produced. If we have an equation of state for the gas, the volume calculated from the equation of state is a good approximation to ΔV for the phase change. The ideal gas equation is usually adequate for this purpose. Then, $\Delta\overline{V} \approx RT/P$, and

$$\frac{dP}{dT} = \frac{P\Delta\overline{H}}{RT^2} \tag{1.1.s.1}$$

(The Clausius-Clapeyron equation)

This equation for the pressure–temperature relationship for a phase equilibrium involving a gas is called the Clausius-Clapeyron equation. Dividing both sides by the pressure, we can put the Clausius-Clapeyron equation into an alternative and often-useful form:

$$\frac{d\ln P}{dT} = \frac{\Delta\overline{H}}{RT^2} \tag{1.1.s.2}$$

If we can assume that $\Delta\overline{H}$ is independent of pressure, we can separate variables and integrate to obtain the Clausius-Clapeyron equation in integrated form. If we can assume further that $\Delta\overline{H}$ is constant, the integration yields

$$\int_{P_0}^{P} \frac{dP}{P} = \frac{\Delta\overline{H}}{R}\int_{T_0}^{T} \frac{dT}{T^2} \tag{1.1.s.3}$$

and

$$\ln\frac{P}{P_0} = -\frac{\Delta\overline{H}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{1.1.s.4}$$

where P_0 and T_0 are the initial equilibrium position.

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1.2: Solutions and their Concentrations

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Describe the major reasons that solutions are so important in the *practical* aspects of chemistry.
- Explain why expressing a concentration as "*x*-percent" can be ambiguous.
- Explain why the molarity of a solution will vary with its temperature, whereas molality and mole fraction do not.
- Given the necessary data, convert (in either direction) between any two concentration units, e.g. molarity - mole fraction.
- Show how one can prepare a given volume of a solution of a certain molarity, molality, or percent concentration from a solution that is more concentrated (expressed in the same units.)
- Calculate the concentration of a solution prepared by mixing given volumes to two solutions whose concentrations are expressed in the same units.

Solutions are *homogeneous* (single-phase) mixtures of two or more *components*. For convenience, we often refer to the majority component as the *solvent*; minority components are *solutes*; there is really no fundamental distinction between them. Solutions play a very important role in Chemistry because they allow intimate and varied encounters between molecules of different kinds, a condition that is essential for rapid chemical reactions to occur. Several more explicit reasons can be cited for devoting a significant amount of effort to the subject of solutions:

- For the reason stated above, most chemical reactions that are carried out in the laboratory and in industry, and that occur in living organisms, take place in solution.
- Solutions are so common; very few pure substances are found in nature.
- Solutions provide a convenient and accurate means of introducing known small amounts of a substance to a reaction system. Advantage is taken of this in the process of titration, for example.
- The physical properties of solutions are sensitively influenced by the balance between the intermolecular forces of like and unlike (solvent and solute) molecules. The physical properties of solutions thus serve as useful experimental probes of these intermolecular forces.

We usually think of a solution as a liquid made by adding a gas, a solid or another liquid *solute* in a liquid *solvent*. Actually, solutions can exist as gases and solids as well.

> Solid solutions are very common; most natural minerals and many metallic alloys are solid solutions.

Still, it is liquid solutions that we most frequently encounter and must deal with. Experience has taught us that sugar and salt dissolve readily in water, but that “oil and water don’t mix”. Actually, this is not strictly correct, since all substances have at least a slight tendency to dissolve in each other. This raises two important and related questions: why do solutions tend to form in the first place, and what factors limit their mutual solubilities?

Understanding Concentrations

Concentration is a general term that expresses the quantity of solute contained in a given amount of solution. Various ways of expressing concentration are in use; the choice is usually a matter of convenience in a particular application. You should become familiar with all of them.

Parts-per concentration

In the consumer and industrial world, the most common method of expressing the concentration is based on the quantity of solute in a fixed quantity of solution. The “quantities” referred to here can be expressed in weight, in volume, or both (i.e., the *weight* of solute in a given *volume* of solution.) In order to distinguish among these possibilities, the abbreviations (w/w), (v/v) and (w/v) are used.

In most applied fields of Chemistry, (w/w) measure is often used, and is commonly expressed as weight-percent concentration, or simply "percent concentration". For example, a solution made by dissolving 10 g of salt with 200 g of water contains "1 part of salt

per 20 g of water".

"*Cent*" is the Latin-derived prefix relating to the number 100 (L. *centum*), as in *century* or *centennial*. It also denotes 1/100th (from L. *centesimus*) as in *centimeter* and the monetary unit *cent*. It is usually more convenient to express such concentrations as "parts per 100", which we all know as "percent". So the solution described above is a "5% (w/w) solution" of NaCl in water. In clinical chemistry, (w/v) is commonly used, with weight expressed in grams and volume in mL (Example 8.1.1).

Example 8.1.1

The normal saline solution used in medicine for nasal irrigation, wound cleaning and intravenous drips is a 0.91% (w/v) solution of sodium chloride in water. How would you prepare 1.5 L of this solution?

Solution

The solution will contain 0.91 g of NaCl in 100 mL of water, or 9.1 g in 1 L. Thus you will add (1.5 × 9.1g) = 13.6 g of NaCl to 1.5 L of water.

Percent means parts per 100; we can also use parts per thousand (ppt) for expressing concentrations in grams of solute per kilogram of solution. For more dilute solutions, parts per million (ppm) and parts per billion (10^9; ppb) are used. These terms are widely employed to express the amounts of trace pollutants in the environment.

Example 8.1.2

Describe how you would prepare 30 g of a 20 percent (w/w) solution of KCl in water.

Solution

The weight of potassium chloride required is 20% of the total weight of the solution, or 0.2 × (3 0 g) = 6.0 g of KCl. The remainder of the solution (30 – 6 = 24) g consists of water. Thus you would dissolve 6.0 g of KCl in 24 g of water.

Weight/volume and volume/volume basis

It is sometimes convenient to base concentration on a fixed volume, either of the solution itself, or of the solvent alone. In most instances, a 5% by volume solution of a solid will mean 5 g of the solute dissolved in 100 ml of the solvent.

Example 8.1.3

Fish, like all animals, need a supply of oxygen, which they obtain from oxygen dissolved in the water. The minimum oxygen concentration needed to support most fish is around 5 ppm (w/v). How many moles of O_2 per liter of water does this correspond to?

Solution

5 ppm (w/v) means 5 grams of oxygen in one million mL (1000 L) of water, or 5 mg per liter. This is equivalent to (0.005 g) / (32.0 g mol^{-1}) = 1.6×10^{-4} mol.

If the solute is itself a liquid, volume/volume measure usually refers to the volume of solute contained in a fixed volume of *solution* (not *solvent*). The latter distinction is important because volumes of mixed substances are not strictly additive. These kinds of concentration measure are mostly used in commercial and industrial applications. The "proof" of an alcoholic beverage is the (v/v)-percent, multiplied by two; thus a 100-proof vodka has the same alcohol concentration as a solution made by adding sufficient water to 50 ml of alcohol to give 100 ml of solution.

Molarity: mole/volume basis

This is the method most used by chemists to express concentration, and it is the one most important for you to master. Molar concentration (molarity) is the number of moles of solute per liter of solution.

The important point to remember is that the volume of the *solution* is different from the volume of the *solvent*; the latter quantity can be found from the molarity only if the densities of both the solution and of the pure solvent are known. Similarly, calculation of

the weight-percentage concentration from the molarity requires density information; you are expected to be able to carry out these kinds of calculations, which are covered in most texts.

Example 8.1.4

How would you make 120 mL of a 0.10 M solution of potassium hydroxide in water?

Solution

The amount of KOH required is

$$(0.120\ \text{L}) \times (0.10\ \text{mol L}^{-1}) = 0.012\ \text{mol}.$$

The molar mass of KOH is 56.1 g, so the weight of KOH required is

$$(0.012\ mol) \times (56.1\ g\ mol^{-1}) = 0.67\ g \tag{1.2.1}$$

We would dissolve this weight of KOH in a volume of water that is less than 120 mL, and then add sufficient water to bring the volume of the solution up to 120 mL.

Note: if we had simply added the KOH to 120 mL of water, the molarity of the resulting solution would not be the same. This is because volumes of different substances are not strictly additive when they are mixed. Without actually measuring the volume of the resulting solution, its molarity would not be known.

Example 8.1.5

Calculate the molarity of a 60-% (w/w) solution of ethanol (C_2H_5OH) in water whose density is 0.8937 g mL^{-1}.

Solution

One liter of this solution has a mass of 893.7 g, of which

$$0.60 \times (893.7\ g) = 536.2\ g \tag{1.2.2}$$

consists of ethanol. The molecular weight of C_2H_5OH is 46.0, so the number of moles of ethanol present in one liter (that is, the molarity) will be

$$\frac{\frac{536.2\ g}{46.0\ g\ mol^{-1}}}{1L} = 11.6\ mol\ L^{-1} \tag{1.2.3}$$

Normality and Equivalents

Normality is a now-obsolete concentration measure based on the number of *equivalents* per liter of solution. Although the latter term is now also officially obsolete, it still finds some use in clinical- and environmental chemistry and in electrochemistry. Both terms are widely encountered in pre-1970 textbooks and articles.

The *equivalent weight* of an *acid* is its molecular weight divided by the number of titratable hydrogens it carries. Thus for sulfuric acid H_2SO_4, one mole has a mass of 98 g, but because both hydrogens can be neutralized by strong base, its equivalent weight is 98/2 = 49 g. A solution of 49 g of H_2SO_4per liter of water is 0.5 molar, but also "1 normal" (1*N* = 1 eq/L). Such a solution is "equivalent" to a 1*M* solution of HCl in the sense that each can be neutralized by 1 mol of strong base.

solution of $FeCl_3$ is said to be "3 normal" (3 *N*) because it dissociates into three moles/L of chloride ions.

Although molar concentration is widely employed, it suffers from one serious defect: since volumes are temperature-dependent (substances expand on heating), so are molarities; a 0.100 M solution at 0° C will have a smaller concentration at 50° C. For this reason, molarity is not the preferred concentration measure in applications where physical properties of solutions and the effect of temperature on these properties is of importance.

Mole fraction: mole/mole basis

This is the most fundamental of all methods of concentration measure, since it makes no assumptions at all about volumes. The mole fraction of substance *i* in a mixture is defined as

$$X_i = \frac{n_i}{\sum_j n_j} \tag{1.2.4}$$

in which n_j is the number of moles of substance *j*, and the summation is over all substances in the solution. Mole fractions run from zero (substance not present) to unity (the pure substance). The sum of all mole fractions in a solution is, by definition, unity:

$$\sum_i X_i = 1 \tag{1.2.5}$$

Example 8.1.6

What fraction of the molecules in a 60-% (w/w) solution of ethanol in water consist of H_2O?

Solution

From the previous problem, we know that one liter of this solution contains 536.2 g (11.6 mol) of C_2H_5OH. The number of moles of H_2O is

$$(\ (893.7 - 536.2)\ \text{g}) / (18.0\ \text{g mol}^{-1}) = 19.9\ \text{mol}.$$

The mole fraction of water is thus

$$\frac{19.9}{19.9 + 11.6} = 0.63 \tag{1.2.6}$$

Thus 63% of the molecules in this solution consist of water, and 37% are ethanol.

In the case of ionic solutions, each kind of ion acts as a separate component.

Example 8.1.7

Find the mole fraction of water in a solution prepared by dissolving 4.5 g of $CaBr_2$ in 84.0 mL of water.

Solution

The molar mass of $CaBr_2$ is 200 g, and 84.0 mL of H_2O has a mass of very close to 84.0 g at its assumed density of 1.00 g mL^{-1}. Thus the number of moles of $CaBr_2$ in the solution is

$$\frac{4.50\ g}{200\ g/mol} = 0.0225\ mol \tag{1.2.7}$$

Because this salt is completely dissociated in solution, the solution will contain 0.268 mol of Ca^{2+} and (2 × .268) = 0.536 of Br^-. The number of moles of water is

$$(84\ \text{g}) / (18\ \text{g mol}^{-1}) = 4.67\ \text{mol}.$$

The mole fraction of water is then

$$\frac{0.467\ \cancel{mol}}{0.268 + 0.536 + 4.67\ \cancel{mol}} = \frac{0.467}{5.47} = 0.854 \tag{1.2.8}$$

Thus H_2O constitutes 85 out of every 100 molecules in the solution.

Molality: mole/weight basis

A 1-molal solution contains one mole of solute per 1 kg of solvent. Molality is a hybrid concentration unit, retaining the convenience of mole measure for the solute, but expressing it in relation to a temperature-independent mass rather than a volume.

Molality, like mole fraction, is used in applications dealing with certain physical properties of solutions; we will see some of these in the next lesson.

Example 8.1.8

Calculate the molality of a 60-% (w/w) solution of ethanol in water.

Solution

From the above problems, we know that one liter of this solution contains 11.6 mol of ethanol in

$$(893.7 – 536.2) = 357.5 \text{ g}$$

of water. The molarity of ethanol in the solution is therefore

$$(11.6 \text{ mol}) / (0.3575 \text{ kg}) = 32.4 \text{ mol kg}^{-1}.$$

Conversion between Concentration Measures

Anyone doing practical chemistry must be able to convert one kind of concentration measure into another. The important point to remember is that any conversion involving molarity requires a knowledge of the *density* of the solution.

Example 8.1.9

A solution prepared by dissolving 66.0 g of urea $(NH_2)_2CO$ in 950 g of water had a density of 1.018 g mL^{-1}. Express the concentration of urea in

a. weight-percent
b. mole fraction
c. molarity
d. molality

Solution

a) The weight-percent of solute is $(100\%)^{-1}$ (66.0 g) / (950 g) = 6.9%

The molar mass of urea is 60, so the number of moles is

$$(66 \text{ g}) /(60 \text{ g mol}^{-1}) = 1.1 \text{ mol.}$$

The number of moles of H_2O is

$$(950 \text{ g}) / (18 \text{ g mol}^{-1}) = 52.8 \text{ mol.}$$

b) Mole fraction of urea:

$$(1.1 \text{ mol}) / (1.1 + 52.8 \text{ mol}) = 0.020$$

c) molarity of urea: the volume of 1 L of solution is

$$(66 + 950)\text{g} / (1018 \text{ g L}^{-1})= 998 \text{ mL.}$$

The number of moles of urea (from a) is 1.1 mol.
Its molarity is then

$$(1.1 \text{ mol}) / (0.998 \text{ L}) = 1.1 \text{ mol L}^{-1}.$$

d) The molality of urea is (1.1 mol) / (.066 + .950) kg = 1.08 mol kg^{-1}.

Example 8.1.10

Ordinary dry air contains 21% (v/v) oxygen. About many moles of O_2 can be inhaled into the lungs of a typical adult woman with a lung capacity of 4.0 L?

Solution

The number of molecules (and thus the number of moles) in a gas is directly proportional to its volume (Avogadro's law), so the mole fraction of O_2 is 0.21. The molar volume of a gas at 25° C is

$$(298/271) \times 22.4 \text{ L mol}^{-1} = 24.4 \text{ L mol}^{-1}$$

so the moles of O_2 in 4 L of air will be

$$(4 / 24.4) \times (0.21 \text{ mol}) \times (24.4 \text{ L mol}^{-1}) = 0.84 \text{ mol } O_2.$$

Dilution calculations

These kinds of calculations arise frequently in both laboratory and practical applications. If you have a thorough understanding of concentration definitions, they are easily tackled. The most important things to bear in mind are

- Concentration is inversely proportional to volume;
- Molarity is expressed in mol L^{-1}, so it is usually more convenient to express volumes in liters rather than in mL;
- Use the principles of unit cancelations to determine what to divide by what.

Example 8.1.11

Commercial hydrochloric acid is available as a 10.17 molar solution. How would you use this to prepare 500 mL of a 4.00 molar solution?

Solution

The desired solution requires (0.50 L) × (4.00 M $L^{-1)}$ = 2.0 mol of HCl. This quantity of HCl is contained in (2.0 mol) / (10.17 M L^{-1}) = 0.197 L of the concentrated acid. So one would measure out 197 mL of the concentrated acid, and then add water to make the total volume of 500 mL.

Example 8.1.12

Calculate the molarity of the solution produced by adding 120 mL of 6.0 M HCl to 150 mL of 0.15 M HCl. What important assumption must be made here?

Solution

The assumption, of course, is that the density of HCl within this concentration range is constant, meaning that their volumes will be additive.

Moles of HCl in first solution:

$$(0.120 \text{ L}) \times (6.0 \text{ mol L}^{-1}) = 0.72 \text{ mol HCl}$$

Moles of HCl in second solution:

$$(0.150 \text{ L}) \times (0.15 \text{ mol L}^{-1}) = 0.02 \text{ mol HCl}$$

Molarity of mixture:

$$(0.72 + 0.02) \text{ mol} / (.120 + .150) \text{ L} = 4.3 \text{ mol L}^{-1}.$$

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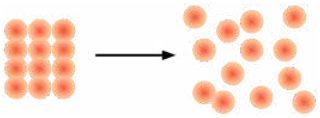
1.3: Thermodynamics of Solutions

Learning Objectives

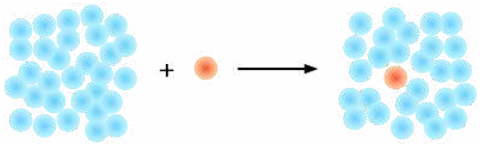
Make sure you thoroughly understand the following essential ideas:

- Describe the two fundamental processes that must occur whenever a solute dissolves in a solvent, and discuss the effects of the absorption or release of energy on the extent of these processes.
- Another factor entering into the process of solution formation is the increase (or occasionally, the decrease) in the entropy — that is, the degree to which thermal energy is dispersed or "diluted". Explain this in your own terms.
- Explain how the adage "like dissolves like" reflects the effects mentioned above. What is the principal physical property of a molecule that defines this "likeness"?
- What do we mean when we describe a liquid such as water as "associated"? Explain how this relates to the the solubility of solutes in such liquids.

You may recall that in the earlier unit on phase equilibria, we pointed out that aggregations of molecules that are more disordered tend to be the ones that are favored at higher temperature, whereas those that possess the lowest potential energy are favored at lower temperatures. This is a general principle that applies throughout the world of matter; the stable form at any given temperature will always be that which leads to the best balance between low potential energy and high molecular disorder. To see how these considerations are applied to solutions, think about the individual steps that must be carried out when a solute is dissolved in a solvent:



1. If the solute is a solid or liquid, it must first be *dispersed* — that is, its molecular units must be pulled apart. This requires energy, and so this step always works against solution formation.



2. The solute must then be introduced into the solvent. Whether this is energetically favorable or unfavorable depends on the nature of the solute and solvent. If the solute is A and the solvent is B, then what is important is the strength of the attractive forces between A-A and B-B molecules, compared to those between A-B pairs; if the latter are greater, then the potential energy will be lower when the substances are mixed and solution formation will be favored.

If step **2** releases more energy than is consumed in step **1**, this will favor solution formation, and we can generally expect the solute to be soluble in the solvent. Even if the dissolution process is slightly endothermic, there is a third important factor, the *entropy* increase, that will very often favor the dissolved state.

Entropy of Solution

As anyone who has shuffled a deck of cards knows, disordered arrangements of objects are statistically more favored simply because there are more ways in which they can be realized. And as the number of objects increases, the more does statistics govern their most likely arrangements. The numbers of objects (molecules) we deal with in Chemistry is so huge that their tendency to become as spread out as possible becomes overwhelming. However, in doing so, the thermal energy they carry with them is also spread and dispersed, so the availability of this energy, as measured by the temperature, is also of importance. Chemists use the term "entropy" to denote this aspect of molecular randomness.

Readers of this section who have had some exposure to thermodynamics will know that solubility, like all equilibria, is governed by the *Gibbs free energy change* for the process, which incorporates the entropy change at a fundamental level. A proper

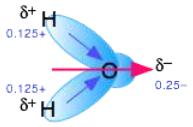
understanding of these considerations requires some familiarity with thermodynamics, which most students do not encounter until well into their second semester of Chemistry. If you are not there yet, do not despair; you are hereby granted temporary permission to think of molecular "disorder" and entropy simply in terms of "spread-outedness".

Thus in the very common case in which a small quantity of solid or liquid dissolves in a much larger volume of solvent, the solute becomes more spread out in space, and the number of equivalent ways in which the solute can be distributed within this volume is greatly increased. This is the same as saying that the entropy of the solute increases.

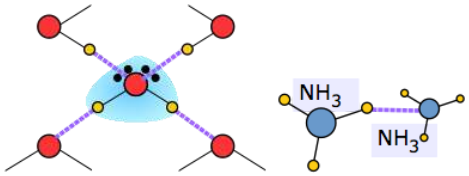
If the energetics of dissolution are favorable, this increase in entropy means that the conditions for solubility will always be met. Even if the energetics are slightly endothermic, the entropy effect can still allow the solution to form, although perhaps limiting the maximum concentration that can be achieved. In such a case, we may describe the solute as being *slightly soluble* in a certain solvent. What this means is that a greater volume of solvent will be required to completely dissolve a given mass of solute.

Enthalpy of Solution

Polar molecules are those in which electric charge is distributed asymmetrically. The most familiar example is ordinary water, in which the highly electronegative oxygen atom pulls part of the electric charge cloud associated with each O–H bond closer to itself. Although the H_2O molecule is electrically neutral overall, this charge imbalance gives rise to a permanent *electric dipole moment*.

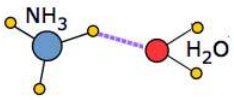


Chemists use the term "Associated" liquids to refer to liquids in which the effects of hydrogen bonding dominate the local structure. Water is the most important of these, but ammonia NH_3 and hydrogen cyanide HCN are other common examples.



Thus liquid water consists of an extended network of H_2O molecules linked together by dipole-dipole attractions that we call *hydrogen bonds*. Because these are much weaker than ordinary chemical bonds, they are continually being disrupted by thermal forces. As a result, the extended structure is highly disordered (in contrast to that of solid ice) and continually changing.

When a solute molecule is introduced into an associated liquid, a certain amount of energy must be expended in order to break the local hydrogen-bond structure and make space for the new molecule. If the solute is itself an ion or a polar molecule, new ion-dipole or dipole-dipole attractions come into play. In favorable cases these may release sufficient potential energy to largely compensate for the energy required to incorporate the solute into the structure.

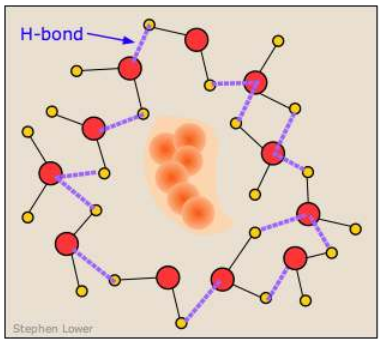


An extreme example of this occurs when ammonia dissolves in water. Each NH_3 molecule can form three hydrogen bonds, so the resulting solution is even more hydrogen-bonded than is pure water — accounting for the considerable amount of heat released in the process and the extraordinarily large solubility of ammonia in water.

Nonpolar solutes are Sparingly Soluble in Water: The Hydrophobic effect

When a nonpolar solute such as oxygen or hexane is introduced into an associated liquid, we might expect that the energy required to break the hydrogen bonds to make space for the new molecule is not compensated by the formation of new attractive interactions, suggesting that the process will be energetically unfavorable. We can therefore predict that solutes of these kinds will be only sparingly soluble in water, and this is indeed the case.

It turns out, however, that this is not an entirely correct explanation for the small solubility of non polar solutes in water. It is now known that the H_2O molecules that surround a non-polar intruder and find themselves unable to form energy-lowering polar or hydrogen-bonded interactions with it will rearrange themselves into a configuration that maximizes the hydrogen bonding between the water molecules themselves. In doing so, this creates a cage-like shell around the solute molecule. In terms of the energetics of the process, these new H_2O-H_2O interactions largely compensate for the lack of solute-H_2O interactions.



However, this shell of highly organized water molecules exacts its own toll on the solubility by reducing the entropy of the system. Dissolution of a solute normally increases the entropy by spreading the solute molecules (and the thermal energy they contain) through the larger volume of the solvent. But in this case, the H_2O molecules within the highly structured shell surrounding the solute molecule are themselves constrained to this location, and their number is sufficiently great to reduce the entropy by far more than the dissolved solute increases it.

The implications of the hydrophobic effect extend far beyond the topic of solubility. It governs the way that proteins fold, the formation of soap bubbles, and the formation of cell membranes. The small solubility of a non polar solute in an associated liquid such as water results more from the negative entropy change rather than from energetic considerations. This phenomenon is known as the *hydrophobic effect*. In the next section, we will explore the ways in which these energy-and-entropy considerations come together in various kinds of solutions.

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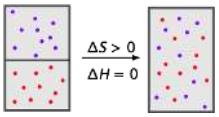
1.3A: Solutions of Gaseous Solutes in Gaseous Solvents

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

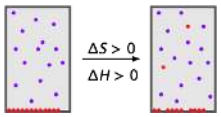
- Why are gases the only state of matter that never fail to form solutions?

Mixtures of gases are really solutions, but we tend not to think of them this way because they mix together freely and with no limits to their compositions; we say that gases are *miscible in all proportions*.



To the extent that gases behave ideally (because they consist mostly of empty space), their mixing does not involve energy changes at all; the mixing of gases is driven entirely by the increase in entropy (*S*) as each kind of molecule occupies and shares the space and kinetic energy of the other. Your nose can be a remarkably sensitive instrument for detecting components of gaseous solutions, even at the parts-per-million level. The olfactory experiences resulting from cooking cabbage, eating asparagus, and bodily emanations that are not mentionable in polite society are well known.

Can solids or liquids "dissolve" in a gaseous solvent? In a very narrow sense they can, but only to a very small extent. Dissolution of a condensed phase of matter into a gas is formally equivalent to evaporation (of a liquid) or sublimation (of a solid), so the process really amounts to the mixing of gases.



The energy required to remove molecules from their neighbors in a liquid or solid and into the gaseous phase is generally too great to be compensated by the greater entropy they enjoy in the larger volume of the mixture, so solids tend to have relatively low vapor pressures. The same is true of liquids at temperatures well below their boiling points. These two cases of gaseous solutions can be summarized as follows:

gaseous solvent, solute →	**gas**	**liquid**
energy to disperse solute	nil	la
energy to introduce into gas	nil	r
increase in entropy	large	la
miscibility	complete	very

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1.3B: Solutions of Gaseous Solutes in Liquid Solvents

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Explain why, in contrast, gases tend to be only slightly soluble in liquids and solids. And why are some combinations, such as the dissolution of ammonia or hydrogen chloride in water, significant exceptions to this rule?
- State Henry's law and explain
- Why do fish in rivers and streams sometimes become asphyxiated (oxygen-starved) in hot weather?

Solutions of Gases in Liquids

Gases dissolve in liquids, but usually only to a small extent. When a gas dissolves in a liquid, the ability of the gas molecules to move freely throughout the volume of the solvent is greatly restricted. If this latter volume is small, as is often the case, the gas is effectively being compressed. Both of these effects amount to a decrease in the entropy of the gas that is not usually compensated by the entropy increase due to mixing of the two kinds of molecules. Such processes greatly restrict the solubility of gases in liquids.

liquid solvent, solute →	gas
energy to disperse solute	nil
energy to introduce into solvent	medium to large
increase in entropy	negative
miscibility	**usually very limited**

Solubility of gases in water

One important consequence of the entropy decrease when a gas dissolves in a liquid is that the solubility of a gas decreases at higher temperatures; this is in contrast to most other situations, where a rise in temperature usually leads to increased solubility. Bringing a liquid to its boiling point will completely remove a gaseous solute. Some typical gas solubilities, expressed in the number of moles of gas at 1 atm pressure that will dissolve in a liter of water at 25° C, are given below:

solute	**formula**	**solubility, mol L^{-1} atm^{-1}**
ammonia	NH_3	57
carbon dioxide	CO_2	0.0308
methane	CH_4	0.00129
nitrogen	N_2	0.000661
oxygen	O_2	0.00126
sulfur dioxide	SO_2	1.25

As we indicated above, the only gases that are readily soluble in water are those whose polar character allows them to interact strongly with it.

Ammonia is remarkably soluble in water

Inspection of the above table reveals that ammonia is a champion in this regard. At 0° C, one liter of water will dissolve about 90 g (5.3 mol) of ammonia. The reaction of ammonia with water according to

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \qquad (1.3B.1)$$

makes no significant contribution to its solubility; the equilibrium lies heavily on the left side (as evidenced by the strong odor of ammonia solutions). Only about four out of every 1000 NH_3molecules are in the form of ammonium ions at equilibrium. This is truly impressive when one calculates that this quantity of NH_3 would occupy (5.3 mol) × (22.4 L mol^{-1}) = 119 L at STP. Thus one volume of water will dissolve over 100 volumes of this gas. It is even more impressive when you realize that in order to compress 119 L of an ideal gas into a volume of 1 L, a pressure of 119 atm would need to be applied! This, together with the observation that dissolution of ammonia is accompanied by the liberation of a considerable amount of heat, tells us that the high solubility of ammonia is due to the formation of more hydrogen bonds (to H_2O) than are broken within the water structure in order to accommodate the NH_3 molecule.

If we actually compress 90 g of pure NH_3 gas to 1 L, it will liquefy, and the vapor pressure of the liquid would be about 9 atm. In other words, the escaping tendency of NH_3 molecules from H_2O is only about 1/9th of what it is from liquid NH_3. One way of interpreting this is that the strong intermolecular (dipole-dipole) attractions between NH_3 and the solvent H_2O give rise to a force that has the effect of a negative pressure of 9 atm.

The Ammonia Fountain

This classic experiment nicely illustrates the high solubility of gaseous ammonia in water. A flask fitted with a tube as shown is filled with ammonia gas and inverted so that the open end of tube is submerged in a container of water. A small amount of water is pushed up into the flask to get the process started. As the gas dissolves in the water, its pressure is reduced, creating a partial vacuum that draws additional water into the flask. The effect can be made more dramatic by adding an indicator dye such as phenolphthalein to the water, which turns pink as the water emerges from the "fountain" and becomes alkaline.



In old textbooks, ammonia's extraordinarily high solublility in water was incorrectly attributed to the formation of the non-existent compound "ammonium hydroxide" NH_4OH. Although this formula is still occasionally seen, the name ammonium hydroxide is now used as a synonym for "aqueous ammonia" whose formula is simply NH_3*(aq)*.

As can also be seen in the above table, the gases CO_2 and SO_2 also exhibit higher solubilities in water. The main product in each case is a loosely-bound *hydrate* of the gas, denoted by CO_2*(aq)* or SO_2*(aq)*. A very small fraction of the hydrate $CO_2 \cdot H_2O$ then combines to form *carbonic acid* H_2CO_3.

Solubility of gases decreases with Temperature

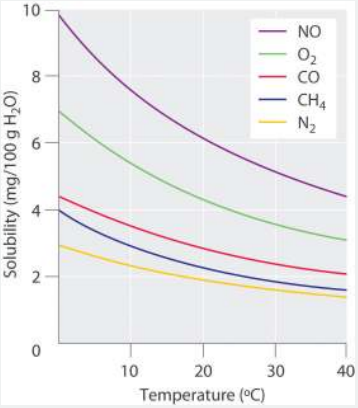
Recall that entropy is a measure of the ability of thermal energy to spread and be shared and exchanged by molecules in the system. Higher temperature exerts a kind of multiplying effect on a positive entropy change by increasing the amount of thermal energy available for sharing. Have you ever noticed the tiny bubbles that form near the bottom of a container of water when it is placed on a hot stove? These bubbles contain air that was previously dissolved in the water, but reaches its solubility limit as the water is

warmed. You can completely rid a liquid of any dissolved gases (including unwanted ones such as Cl_2 or H_2S) by boiling it in an open container.

This is quite different from the behavior of most (but not all) solutions of solid or liquid solutes in liquid solvents. The reason for this behavior is the very large entropy increase that gases undergo when they are released from the confines of a condensed phase .

Solubility of Oxygen in water

Fresh water at sea level dissolves 14.6 mg of oxygen per liter at 0°C and 8.2 mg/L at 25°C. These saturation levels ensure that fish and other gilled aquatic animals are able to extract sufficient oxygen to meet their respiratory needs. But in actual aquatic environments, the presence of decaying organic matter or nitrogenous runoff can reduce these levels far below saturation. The health and survival of these organisms is severely curtailed when oxygen concentrations fall to around 5 mg/L.



The temperature dependence of the solubility of oxygen in water is an important consideration for the well-being of aquatic life; thermal pollution of natural waters (due to the influx of cooling water from power plants) has been known to reduce the dissolved oxygen concentration to levels low enough to kill fish. The advent of summer temperatures in a river can have the same effect if the oxygen concentration has already been partially depleted by reaction with organic pollutants.

Solubility of gases increases with pressure: Henry's Law

The pressure of a gas is a measure of its "escaping tendency" from a phase. So it stands to reason that raising the pressure of a gas in contact with a solvent will cause a larger fraction of it to "escape" into the solvent phase. The direct-proportionality of gas solubility to pressure was discovered by William Henry (1775-1836) and is known as *Henry's Law*. It is usually written as

$$P = k_H C \tag{1.3B.2}$$

with

- P is the partial pressure of the gas above the liquid,
- C is the concentration of gas dissolved in the liquid, and
- k_H is the *Henry's law constant*, which can be expressed in various units, and in some instances is defined in different ways, so be very careful to note these units when using published values.

For Table 7b.2.X, k_H is given as

$$k_H = \frac{\text{partial pressure of gas in atm}}{\text{concentration in liquid } mol\ L^{-1}} \tag{1.3B.3}$$

Table 7b.2.X: *Henry's law constants in water at 25° C, L atm mol^{-1}*

gas	He	N_2	O_2	CO_2	CH_4	NH_3
K_H	2703	1639	769	29.4	0.00129	57

Example 8.2.1

Some vendors of bottled waters sell pressurized "oxygenated water" that is (falsely) purported to enhance health and athletic performance by supplying more oxygen to the body.

a. How many moles of O_2 will be in equilibrium with one liter of water at 25° C when the partial pressure of O_2 above the water is 2.0 atm?
b. How many mL of air (21% O_2 v/v) must you inhale in order to introduce an equivalent quantity of O_2 into the lungs (where it might actually do some good?)

Solution:

a. Solving Henry's law for the concentration, we get

$$C = \frac{P}{k_H} = \frac{2.0\ atm}{769\ L\ atm\ mol^{-1}} = 0.0026\ mol\ L^{-1} \tag{1.3B.4}$$

a. At 25° C, 0.0026 mol of O_2 occupies (22.4 L) × (.0026 mol) × (298/273) = 0.063 L. The equivalent volume of air would be (0.063 L) (.21) = 0.303 L. Given that the average tidal volume of the human lung is around 400 mL, this means that taking one extra breath would take in more O_2 than is present in 1 L of "oxygenated water".

Carbonated beverages: the history of "Fizz-ics"

Artificially carbonated water was first prepared by Joseph Priestley (who later discovered oxygen) in 1767 and was commercialized in 1783 by Joseph Schweppe, a Swiss-German jeweler. Naturally-carbonated spring waters have long been reputed to have curative values, and these became popular tourist destinations in the 19th century. The term "seltzer water" derives from one such spring in Niederselters, Germany. Of course, carbonation produced by fermentation has been known since ancient times. The tingling sensation that carbonated beverages produce in the mouth comes from the carbonic acid produced when bubbles of carbon dioxide come into contact with the mucous membranes of the mouth and tongue:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{1.3B.5}$$

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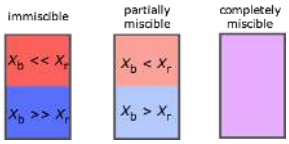
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1.3C: Solutions of Liquid Solutes in Liquid Solvents

Whereas all gases will mix to form solutions regardless of the proportions, liquids are much more fussy. Some liquids, such as ethyl alcohol and water, are miscible in all proportions. Others, like the proverbial oil and water, are not; each liquid has only a limited solubility in the other, and once either of these limits is exceeded, the mixture separates into two phases.

solute →	**liquid**
energy to disperse solute	varies
energy to introduce into solvent	varies
increase in entropy	moderate
miscibility	**"like dissolves like"**

The reason for this variability is apparent from the table. Mixing of two liquids can be exothermic, endothermic, or without thermal effect, depending on the particular substances. Whatever the case, the energy factors are not usually very large, but neither is the increase in randomness; the two factors are frequently sufficiently balanced to produce limited miscibility.



The range of possibilities is shown here in terms of the mole fractions *X* of two liquids A and B. If A and B are only slightly miscible, they separate into two layers according to their relative densities. Note that when one takes into account trace levels, no two liquids are totally immiscible.

Like Dissolves Like

A useful general rule is that liquids are completely miscible when their intermolecular forces are very similar in nature; "like dissolves like". Thus water is miscible with other liquids that can engage in hydrogen bonding, whereas a hydrocarbon liquid in which London or dispersion forces are the only significant intermolecular effect will only be completely miscible with similar kinds of liquids.

Substances such as the alcohols, $CH_3(CH_2)_nOH$, which are hydrogen-bonding (and thus hydrophilic) at one end and hydrophobic at the other, tend to be at least partially miscible with both kinds of solvents. If *n* is large, the hydrocarbon properties dominate and the alcohol has only a limited solubility in water. Very small values of *n* allow the –OH group to dominate, so miscibility in water increases and becomes unlimited in ethanol ($n = 1$) and methanol ($n = 0$), but miscibility with hydrocarbons decreases owing to the energy required to break alcohol-alcohol hydrogen bonds when the non polar liquid is added.

These considerations have become quite important in the development of alternative automotive fuels based on mixing these alcohols with gasoline. At ordinary temperatures the increased entropy of the mixture is great enough that the unfavorable energy factor is entirely overcome, and the mixture is completely miscible. At low temperatures, the entropy factor becomes less predominant, and the fuel mixture may separate into two phases, presenting severe problems to the fuel filter and carburetor.

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1.3D: Solutions of Solid Solutes in Liquid Solvents

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- A key to understanding the solubility of ionic solids in water are the concepts of lattice energy and hydration energy. Explain the meaning of these terms, and sketch out a diagram that shows how these are related to the "heat of solution".

Molecular Solids in Liquid Solvents

The stronger intermolecular forces in solids require more input of energy to disperse the molecular units into a liquid solution, but there is also a considerable increase in entropy that can more than compensate if the intermolecular forces are not too strong, and if the solvent has no strong hydrogen bonds that must be broken in order to introduce the solute into the liquid.

solvent →	non polar liquid	polar liquid
energy to disperse solute	moderate	moderate
energy to introduce into solvent	small	moderate
increase in entropy	moderate	moderate
miscibility	**moderate**	**small**

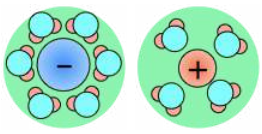
For example, at 25° C and 1 atm pressure, 20 g of iodine crystals will dissolve in 100 ml of ethyl alcohol, but the same quantity of water will dissolve only 0.30 g of iodine. As the molecular weight of the solid increases, the intermolecular forces holding the solid together also increase, and solubilities tend to fall off; thus the solid linear hydrocarbons $CH_3(CH_2)_nCH_3$ ($n > 20$) show diminishing solubilities in hydrocarbon liquids.

Ionic Solids in Liquid Solvents

Since the Coulombic forces that bind ions and highly polar molecules into solids are quite strong, we might expect these solids to be insoluble in just about any solvent. Ionic solids are insoluble in most non-aqueous solvents, but the high solubility of some (including NaCl) in water suggests the need for some further explanation.

solvent →	non polar	polar (water)
energy to disperse solute	large	large (endothermic)
energy to introduce into liquid	small	highly negative (exothermic)
increase in entropy	moderate	moderate to slightly negative
miscibility	very small	small to large

The key factor here turns out to be the interaction of the ions with the solvent. The electrically-charged ions exert a strong coulombic attraction on the end of the water molecule that has the opposite partial charge.



As a consequence, ions in solution are always *hydrated*; that is, they are quite tightly bound to water molecules through ion-dipole interaction. The number of water molecules contained in the *primary hydration shell* varies with the radius and charge of the ion.

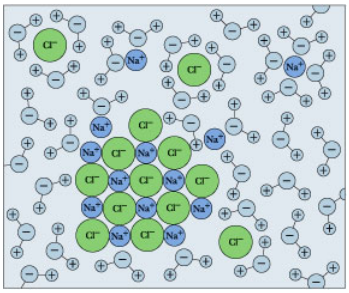
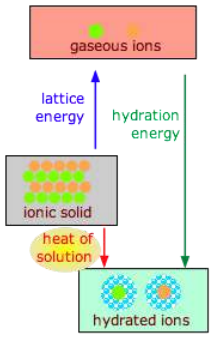


Figure **1.3*D*.1**: Hydration shells around some ions in a sodium chloride solution. The average time an ion spends in a shell is about 2-4 nanoseconds. But this is about two orders of magnitude longer than the lifetime of an individual H_2O–H_2O hydrogen bond.

Lattice and Hydration Energies



The dissolution of an ionic solid MX in water can be thought of as a sequence of two (hypothetical) steps:

$$MX(s) \rightarrow M^+(g) + X^-(g) \tag{1.3D.1}$$

$$M^+(g) + X^-(g) + H_2O(l) \rightarrow M^+(aq) + X^-(aq) \tag{1.3D.2}$$

The enthalpy difference of the first step is the lattice energy and is always positive; the enthalpy difference of the second step is the hydration energy and is always negative)

- The first reaction is always endothermic; it takes a lot of work to break up an ionic crystal lattice (Table **1.3*D*.1**).
- The hydration step is always exothermic as H_2O molecules are attracted into the electrostatic field of the ion (Table **1.3*D*.2**).
- The heat (enthalpy) of solution is the sum of the lattice and hydration energies, and can have either sign.

***Table* 1.3*D*.1**: *Hydration Energies (kJ mol^{-1})*

$H^+(g)$	*–1075*	$F^-(g)$	*–503*
$Li^+(g)$	–515	$Cl^-(g)$	–369
$Na^+(g)$	–405	$Br^-(g)$	–336
$K^+(g)$	–321	$I^-(g)$	–398
$Mg^{2+}(g)$	–1922	$OH^-(g)$	–460
$Ca^{2+}(g)$	–1592	NO_3^-	–328
$Sr^{2+}(g)$	–1445	SO_4^{2-}	–1145

Single-ion hydration energies (Table **1.3*D*.1**) cannot be observed directly, but are obtained from the differences in hydration energies of salts having the given ion in common. When you encounter tables such as the above in which numeric values are related to different elements, you should always stop and see if you can make sense of any obvious trends. In this case, the things to

look for are the size and charge of the ions as they would affect the electrostatic interaction between two ions or between an ion and a [polar] water molecule.

Table* 1.3*D*.2*: Lattice Energies (kJ/mol^{-1})

F^-	Cl^-	Br^-	I^-	
Li^+	+1031	+848	+803	+759
Na^+	+918	+780	+742	+705
K^+	+817	+711	+679	+651
Mg^{2+}	+2957	+2526	+2440	+2327
Ca^{2+}	+2630	+2258	+2176	+2074
Sr^{2+}	+2492	+2156	+2075	+1963

Lattice energies are not measured directly, but are estimates based on electrostatic calculations which are reliable only for simple salts. Enthalpies of solution are observable either directly or (for sparingly soluble salts,) indirectly. Hydration energies are not measurable; they are estimated as the sum the other two quantities. It follows that any uncertainty in the lattice energies is reflected in those of the hydration energies. For this reason, tabulated values of the latter will vary depending on the source.

Example 1.3*D*.1: Calcium Chloride

When calcium chloride, $CaCl_2$, is dissolved in water, will the temperature immediately after mixing rise or fall?

Solution:

Estimate the heat of solution of $CaCl_2$.

- lattice energy of solid $CaCl_2$: +2258 kJ mol^{-1}
- hydration energy of the three gaseous ions: (–1562 –381 – 381) = –2324 kJ mol^{-1}
- heat of solution:

$$(2258 - 2324)\ \text{kJ mol}^{-1} = \mathbf{-66\ kJ\ mol^{-1}}$$

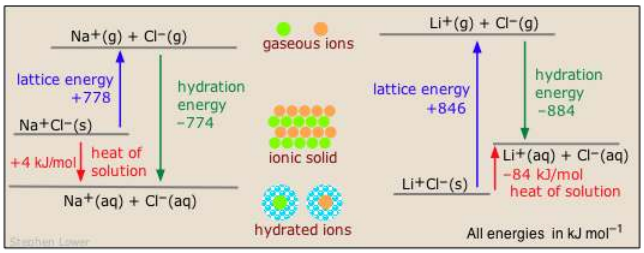
Since the process is exothermic, this heat will be released to warm the solution.

As often happens for a quantity that is the sum of two large terms having opposite signs, the overall dissolution process can come out as either endothermic or exothermic, and examples of both kinds are common.

Table 1.3*D*.3: Energy terms associated with the dissolution of some salts (kJ mol^{-1})

substance →	**LiF**	**NaI**	**KBr**	**CsI**	**LiCl**	**NaCl**	**KCl**	**AgCl**
lattice energy	1021	682	669	586	846	778	707	910
hydration energy	1017	686	649	552	884	774	690	844
enthalpy of solution	+3	–4	+20	+34	–38	+4	+17	+66

Two common examples illustrate the contrast between exothermic and endothermic heats of solution of ionic solids:



Hydration Entropy can make a Difference!

Hydration shells around some ions in a sodium chloride solution. The average time an ion spends in a shell is about 2-4 nanoseconds. But this is about two orders of magnitude longer than the lifetime of an individual H_2O–H_2O hydrogen bond. The balance between the lattice energy and hydration energy is a major factor in determining the solubility of an ionic crystal in water, but there is another factor to consider as well. We generally assume that there is a rather large increase in the entropy when a solid is dispersed into the liquid phase. However, in the case of ionic solids, each ion ends up surrounded by a shell of oriented water molecules. These water molecules, being constrained within the hydration shell, are unable to participate in the spreading of thermal energy throughout the solution, and reduce the entropy. In some cases this effect predominates so that dissolution of the salt leads to a net decrease in entropy. Recall that any process in which the the entropy diminishes becomes less probable as the temperature increases; this explains why the solubilities of some salts decrease with temperature.

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1.4: Colligative Properties

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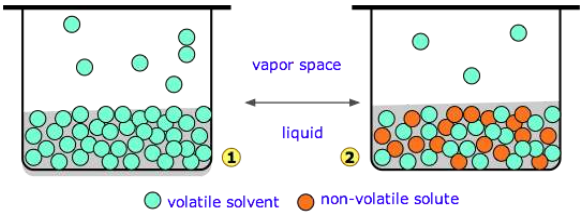
1.4.0: Colligative Properties- Raoult's Law

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- State *Raoult's law* in your own words, and explain why it makes sense.
- What do we mean by the *escaping tendency* of a molecule from a phase? How might we be able to observe or measure it?
- Explain why *boiling point elevation* follows naturally from Raoult's law.
- Explaining *freezing point depression* is admittedly a bit more difficult, but you should nevertheless be able to explain how the application of salt on an ice-covered road can cause the ice to melt.

The tendency of molecules to escape from a liquid phase into the gas phase depends in part on how much of an increase in entropy can be achieved in doing so. Evaporation of solvent molecules from the liquid always leads to a large increase in entropy because of the greater volume occupied by the molecules in the gaseous state. But if the liquid solvent is initially "diluted" with solute, its entropy is already larger to start with, so the amount by which it can increase on entering the gas phase will be less. There will accordingly be less tendency for the solvent molecules to enter the gas phase, and so the vapor pressure of the solution diminishes as the concentration of solute increases and that of solvent decreases.



The number 55.5 mol L^{-1} (= 1000 g L^{-1} ÷ 18 g mol^{-1}) is a useful one to remember if you are dealing a lot with aqueous solutions; this represents the concentration of water in pure water. (Strictly speaking, this is the *molal* concentration of H_2O; it is only the molar concentration at temperatures around 4° C, where the density of water is closest to 1.000 g cm^{-1}.)

Diagram 1 (above left) represents pure water whose concentration in the liquid is 55.5 M. A tiny fraction of the H_2O molecules will escape into the vapor space, and if the top of the container is closed, the pressure of water vapor builds up until equilibrium is achieved. Once this happens, water molecules continue to pass between the liquid and vapor in both directions, but at equal rates, so the partial pressure of H_2O in the vapor remains constant at a value known as the *vapor pressure* of water at the particular temperature.

In Figure **1.4.0.1**, we have replaced a fraction of the water molecules with a substance that has zero or negligible vapor pressure — a *nonvolatile solute* such as salt or sugar. This has the effect of diluting the water, reducing its escaping tendency and thus its vapor pressure.

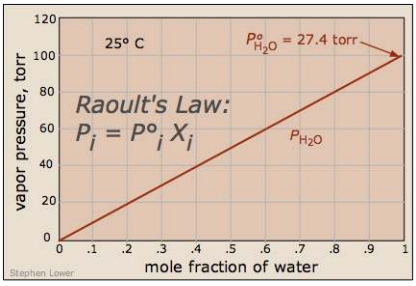
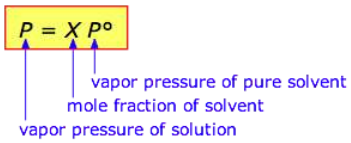


Figure **1.4.0.1**:

What's important to remember is that the reduction in the vapor pressure of a solution of this kind is directly proportional to the fraction of the [volatile] solute molecules in the liquid — that is, to the mole fraction of the solvent. The reduced vapor pressure is given by *Raoult's law*(1886):



From the definition of mole fraction, you should understand that in a two-component solution (i.e., a solvent and a single solute),

$$\chi_{solvent} = 1 - \chi_{solute}. \tag{1.4.0.1}$$

Example 1.4.0.1

Estimate the vapor pressure of a 40 % (W/W) solution of ordinary cane sugar ($C_{22}O_{11}H_{22}$, 342 g mol^{-1}) in water. The vapor pressure of pure water at this particular temperature is 26.0 torr.

Solution

100 g of solution contains (40 g) ÷ (342 g mol^{-1}) = 0.12 mol of sugar and (60 g) ÷ (18 g mol^{-1}) = 3.3 mol of water. The mole fraction of water in the solution is

$$\frac{3.3}{3.3 + 12} = 0.96 \tag{1.4.0.2}$$

and its vapor pressure will be 0.96 × 26.0 torr = 25.1 torr.

Example 1.4.0.2

The vapor pressure of water at 10° C is 9.2 torr. Estimate the vapor pressure at this temperature of a solution prepared by dissolving 1 mole of $CaCl_2$ in 1 L of water.

Solution

Each mole of $CaCl_2$ dissociates into one mole of Ca^{2+} and two moles of Cl^{1-}, giving a total of three moles of solute particles. The mole fraction of water in the solution will be

$$\frac{55.5}{3 + 55.5} = 0.95 \tag{1.4.0.3}$$

The vapor pressure will be 0.95 × 9.2 torr = 8.7 torr.

Since the sum of all mole fractions in a mixture must be unity, it follows that the more moles of solute, the smaller will be the mole fraction of the solvent. Also, if the solute is a salt that dissociates into ions, then the proportion of solvent molecules will be even smaller.

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1.4.1: Colligative Properties- Boiling Point Elevation and Freezing Point Depression

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Explain why boiling point elevation follows naturally from Raoult's law.
- Explaining freezing point depression is admittedly a bit more difficult, but you should nevertheless be able to explain how the application of salt on an ice-covered road can cause the ice to melt.

The colligative properties really depend on the escaping tendency of solvent molecules from the liquid phase. You will recall that the vapor pressure is a direct measure of escaping tendency, so we can use these terms more or less interchangeably.

Boiling Point Elevation

If addition of a nonvolatile solute lowers the vapor pressure of the solution via Raoult's law , then it follows that the temperature must be raised to restore the vapor pressure to the value corresponding to the pure solvent. In particular, the temperature at which the vapor pressure is 1 atm will be higher than the normal boiling point by an amount known as the boiling point elevation . The exact relation between the boiling point of the solution and the mole fraction of the solvent is rather complicated, but for dilute solutions the elevation of the boiling point is directly proportional to the *molal* concentration of the solute:

$$\Delta_B = K_B \frac{\text{moles of solute}}{\text{kg of solution}}$$

K_B: molal boiling point elevation constant (K mol^{-1} kg)

Δ_B: boiling point elevation (K)

Bear in mind that the proportionality constant K_B is a property of the ***solvent*** because this is the only component that contributes to the vapor pressure in the model we are considering in this section.

Table 1.4.1.1: Boiling point elevation constants

solvent	normal bp, °C	K_b , K mol^{-1} kg
water	100	0.514
ethanol	79	1.19
acetic acid	118	2.93
carbon tetrachloride	76.5	5.03

Example 1.4.1.1

Sucrose ($C_{22}O_{11}H_{22}$, 342 g mol^{-1}), like many sugars, is highly soluble in water; almost 2000 g will dissolve in 1 L of water, giving rise to what amounts to pancake syrup. Estimate the boiling point of such a sugar solution.

Solution

moles of sucrose:

$$\frac{2000\,g}{342\,g\,mol^{-1}} = 5.8\,mol \tag{1.4.1.1}$$

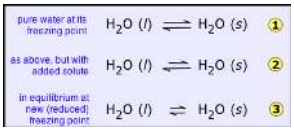
mass of water: assume 1000 g (we must know the density of the solution to find its exact value)

The molality of the solution is (5.8 mol) ÷ (1.0 kg) = 5.8 m.

Using the value of K_b from the table, the boiling point will be raised by (0.514 K mol^{-1} kg) × (5.8 mol kg^{-1}) = 3.0 K, so the boiling point will be 103° C.

Freezing Point Depression

The freezing point of a substance is the temperature at which the solid and liquid forms can coexist indefinitely — that is, they are in equilibrium. Under these conditions molecules pass between the two phases at equal rates because their escaping tendencies from the two phases are identical. Suppose that a liquid solvent and its solid (water and ice, for example) are in equilibrium (① below), and we add a non-volatile solute (such as salt, sugar, or automotive antifreeze liquid) to the water. This will have the effect of reducing the mole fraction of H_2O molecules in the liquid phase, and thus reduce the tendency of these molecules to escape from it, not only into the vapor phase (as we saw above), but also into the solid (ice) phase. This will have no effect on the rate at which H_2O molecules escape from the ice into the water phase, so the system will no longer be in equilibrium and the ice will begin to melt ②.



If we wish to keep the solid from melting, the escaping tendency of molecules from the solid must be reduced. This can be accomplished by reducing the *temperature*; this lowers the escaping tendency of molecules from both phases, but it affects those in the solid more than those in the liquid, so we eventually reach the new, lower freezing point where the two quantities are again in exact balance and both phases can coexist ③.

If you prefer to think in terms of vapor pressures, you can use the same argument if you bear in mind that the vapor pressures of the solid and liquid must be the same at the freezing point. Dilution of the liquid (the solvent) by the nonvolatile solute reduces the vapor pressure of the solvent according to Raoult's law, thus reducing the temperature at which the vapor pressures of the liquid and frozen forms of the solution will be equal. As with boiling point elevation, in dilute solutions there is a simple linear relation between the freezing point depression and the molality of the solute:

$$\Delta T_f = K_f \frac{\text{moles of solute}}{\text{kg of solvent}} \tag{1.4.1.2}$$

Note that K_f values are all *negative*!

Table **1.4.1.2**: Freezing point depression constants

Solvent	Normal Freezing Point (°C)	K_f (K mol^{-1} kg)
water	0.0	–1.86
acetic acid	16.7	–3.90
benzene	5.5	–5.10
camphor	180	–40.0
cyclohexane	6.5	–20.2
phenol	40	–7.3

Salting Roads

The use of salt to de-ice roads is a common application of this principle. The solution formed when some of the salt dissolves in the moist ice reduces the freezing point of the ice. If the freezing point falls below the ambient temperature, the ice melts. In very cold weather, the ambient temperature may be below that of the salt solution, and the salt will have no effect. The effectiveness of a de-icing salt depends on the number of particles it releases on dissociation and on its solubility in water:

name	Formula	lowest practi
ammonium sulfate	$(NH_4)_2SO_4$	–7
calcium chloride	$CaCl_2$	–29
potassium chloride	KCl	–15
sodium chloride	NaCl	–9
urea	$(NH_2)_2CO$	–7

Automotive radiator antifreezes are mostly based on ethylene glycol, $(CH_2OH)_2$. Owing to the strong hydrogen-bonding properties of this double alcohol, this substance is miscible with water in all proportions, and contributes only a very small vapor pressure of its own. Besides lowering the freezing point, antifreeze also raises the boiling point, increasing the operating range of the cooling system. The pure glycol freezes at –12.9°C and boils at 197°C, allowing water-glycol mixtures to be tailored to a wide range of conditions.

Example 1.4.1.2

Estimate the freezing point of an antifreeze mixture is made up by combining one volume of ethylene glycol (MW = 62, density 1.11 g cm^{-3}) with two volumes of water.

Solution

Assume that we use 1 L of glycol and 2 L of water (the actual volumes do not matter as long as their ratios are as given.) The mass of the glycol will be 1.10 kg and that of the water will be 2.0 kg, so the total mass of the solution is 3.11 kg. We then have:

- *number of moles of glycol:* (1110 g) ÷ (62 g mol^{-1}) = 17.9 mol
- *molality of glycol:* (17.9 mol) ÷ (2.00 kg) = 8.95 mol kg^{-1}
- *freezing point depression:* ΔT_F = (–1.86 K kg^{-1} mol) × (8.95 mol kg^{-1}) = –16.6 K so the solution will freeze at about –17°C.

Any ionic species formed by dissociation will also contribute to the freezing point depression. This can serve as a useful means of determining the fraction of a solute that is dissociated.

Example 1.4.1.3

An aqueous solution of nitrous acid (HNO_2, MW = 47) freezes at –0.198 .C. If the solution was prepared by adding 0.100 mole of the acid to 1000 g of water, what percentage of the HNO_2 is dissociated in the solution?

Solution

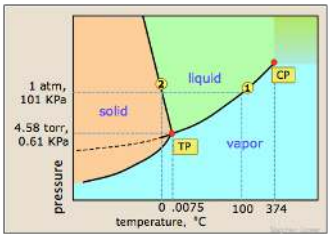
The nominal molality of the solution is (.001 mol) ÷ (1.00 kg) = 0.001 mol kg^{-1}.

But the *effective* molality according to the observed ΔT_F value is given by

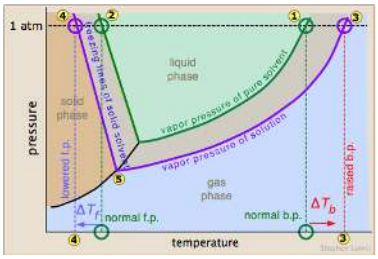
$\Delta T_F \div K_F$ = (–.198 K) ÷(–1.86 K kg mol^{-1}) = 0.106 mol kg^{-1}; this is the total number of moles of species present after the dissociation reaction $HNO_2 \rightarrow H^+ + NO^-$ has occurred. If we let x = $[H^+] = [NO_2^-]$, then by stoichiometry, $[HNO_2]$ = 0.100 - x and .106 - x = 2x and x = .0355. The fraction of HNO_2 that is dissociated is .0355 ÷ 0.100 = .355, corresponding to 35.5% dissociation of the acid.

Another Perspective of Freezing Point Depression and Boiling Point Elevation

A simple *phase diagram* can provide more insight into these phenomena. You may already be familiar with the phase map for water below.



The one shown below expands on this by plotting lines for both pure water and for its "diluted" state produced by the introduction of a non-volatile solute.



The normal boiling point of the pure solvent is indicated by point ① where the vapor pressure curve intersects the 1-atm line — that is, where the escaping tendency of solvent molecules from the liquid is equivalent to 1 atmosphere pressure. Addition of a non-volatile solute reduces the vapor pressures to the values given by the blue line. This shifts the boiling point to the right ③, corresponding to the increase in temperature ΔT_b required to raise the escaping tendency of the H_2O molecules back up to 1 atm.

To understand freezing point depression, notice that the vapor pressure line intersects the curved black vapor pressure line of the solid (ice), which corresponds to a new triple point ⑤ at which all three phases (ice, water vapor, and liquid water) are in equilibrium and thus exhibit equal escaping tendencies. This point is by definition the origin of the freezing (solid-liquid) line, which intersects the 1-atm line at a reduced freezing point ΔT_f, indicated by ④.

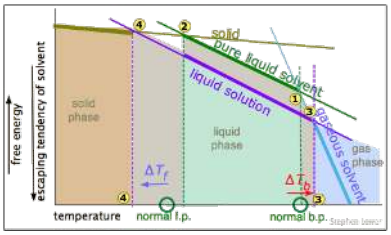
Note that the above analysis assumes that the solute is soluble only in the liquid solvent, but not in its solid form. This is generally more or less true. For example, when arctic ice forms from seawater, the salts get mostly "squeezed" out. This has the interesting effect of making the water that remains more saline, and hence more dense, causing it to sink to the bottom part of the ocean where it gets taken up by the south-flowing deep current.

A Thermodynamics Perspective on Freezing and Boiling

Those readers who have some knowledge of thermodynamics will recognize that what we have been referring to as "escaping" tendency is really a manifestation of the *Gibbs Energy*. This schematic plot shows how the *G*'s for the solid, liquid, and gas phases of a typical substance vary with the temperature.

> *The rule is that the phase with the most negative free energy rules.*

The phase that is most stable (and which therefore is the only one that exists) is always the one having the most negative free energy (indicated here by the thicker portions of the plotted lines.) The melting and boiling points correspond to the respective temperatures where the solid and liquid ② and liquid and vapor ① have identical free energies.



As we saw above, adding a solute to the liquid dilutes it, making its free energy more negative, with the result that the freezing and boiling points are shifted to the left and right, respectively.

The relationships shown in these plots depend on the differing slopes of the lines representing the free energies of the phases as the temperature changes. These slopes are proportional to the entropy of each phase. Because gases have the highest entropies, the slope of the "gaseous solvent" line is much greater than that of the others. Note that this plot is not to scale.

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1.4.2: Colligative Properties - Osmotic Pressure

Learning Objectives

- Define a semipermeable membrane in the context of osmotic flow.
- Explain, in simple terms, what fundamental process "drives" osmotic flow.
- What is osmotic pressure, and how is it measured?
- Osmotic pressure can be a useful means of estimating the molecular weight of a substance, particularly if its molecular weight is quite large. Explain in your own words how this works.
- What is reverse osmosis, and what is its principal application?
- Explain the role of osmotic pressure in food preservation, and give an example.
- Describe the role osmosis plays in the rise of water in plants (where is the semipermeable membrane?), and why it cannot be the only cause in very tall trees.

Osmosis is the process in which a liquid passes through a membrane whose pores permit the passage of solvent molecules but are too small for the larger solute molecules to pass through.

Semipermeable Membranes and Osmotic flow

Figure **1.4.2.1** shows a simple osmotic cell. Both compartments contain water, but the one on the right also contains a solute whose molecules (represented by green circles) are too large to pass through the membrane. Many artificial and natural substances are capable of acting as semi-permeable membranes. The walls of most plant and animal cells fall into this category.

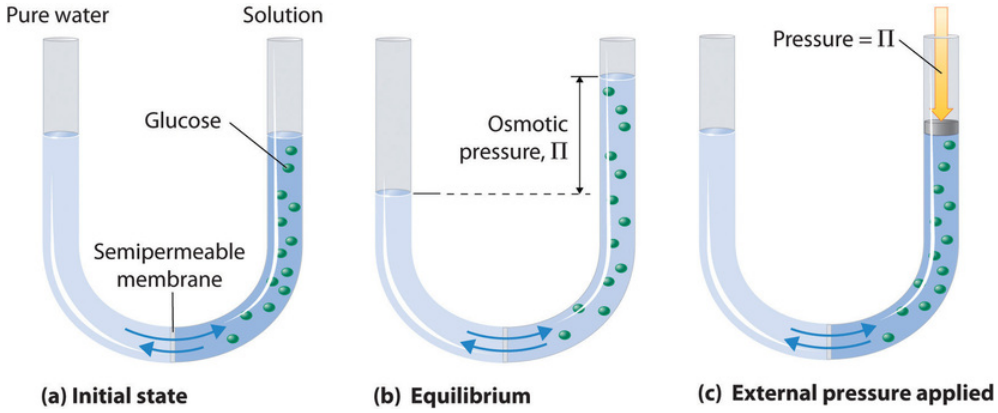


Figure **1.4.2.1**: Osmotic Pressure. (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), *equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.*

If the cell is set up so that the liquid level is initially the same in both compartments, you will soon notice that the liquid rises in the left compartment and falls in the right side, indicating that water molecules from the right compartment are migrating through the semipermeable membrane and into the left compartment. This migration of the solvent is known as osmotic flow, or simply osmosis.

The escaping tendency of a substance from a phase increases with its concentration in the phase. What is the force that drives the molecules through the membrane? This is a misleading question, because there is no real “force” in the physical sense other than the thermal energies all molecules possess. Osmosis is a consequence of simple statistics: the randomly directed motions of a collection of molecules will cause more to leave a region of high concentration than return to it; the escaping tendency of a substance from a phase increases with its concentration in the phase.

Diffusion and Osmotic Flow

Suppose you drop a lump of sugar into a cup of tea, without stirring. Initially there will be a very high concentration of dissolved sugar at the bottom of the cup, and a very low concentration near the top. Since the molecules are in random motion, there will be more sugar molecules moving from the high concentration region to the low concentration region than in the opposite direction. The motion of a substance from a region of high concentration to one of low concentration is known as *diffusion*. Diffusion is a consequence of a *concentration gradient* (which is a measure of the difference in escaping tendency of the substance in different regions of the solution).

There is really no special force on the individual molecules; diffusion is purely a consequence of statistics. Osmotic flow is simply diffusion of a solvent through a membrane impermeable to solute molecules. Now take two solutions of differing solvent concentration, and separate them by a semipermeable membrane (Figure **1.4.2.2**). Being semipermeable, the membrane is essentially invisible to the solvent molecules, so they diffuse from the high concentration region to the low concentration region just as before. This flow of solvent constitutes *osmotic flow*, or *osmosis*.

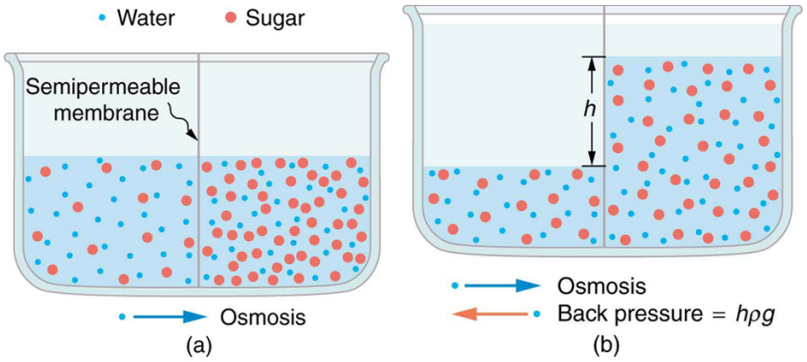


***Figure* 1.4.2.2:** *Osmosis osmotic flow(a) Two sugar-water solutions of different concentrations, separated by a semipermeable membrane that passes water but not sugar. Osmosis will be to the right, since water is less concentrated there. (b) The fluid level rises until the back pressure ρgh equals the relative osmotic pressure; then, the net transfer of water is zero. (CC-BY; OpenStax).*

Figure **1.4.2.2** shows water molecules (blue) passing freely in both directions through the semipermeable membrane, while the larger solute molecules remain trapped in the left compartment, diluting the water and reducing its escaping tendency from this cell, compared to the water in the right side. This results in a net osmotic flow of water from the right side which continues until the increased hydrostatic pressure on the left side raises the escaping tendency of the diluted water to that of the pure water at 1 atm, at which point osmotic equilibrium is achieved.

> *Osmotic flow is simply diffusion of a solvent through a membrane impermeable to solute molecules.*

In the absence of the semipermeable membrane, diffusion would continue until the concentrations of all substances are uniform throughout the liquid phase. With the semipermeable membrane in place, and if one compartment contains the pure solvent, this can never happen; no matter how much liquid flows through the membrane, the solvent in the right side will always be more concentrated than that in the left side. Osmosis will continue indefinitely until we run out of solvent, or something else stops it.

Osmotic equilibrium and osmotic pressure

One way to stop osmosis is to raise the hydrostatic pressure on the solution side of the membrane. This pressure squeezes the solvent molecules closer together, raising their escaping tendency from the phase. If we apply enough pressure (or let the pressure build up by osmotic flow of liquid into an enclosed region), the escaping tendency of solvent molecules from the solution will eventually rise to that of the molecules in the pure solvent, and osmotic flow will case. The pressure required to achieve *osmotic equilibrium* is known as the *osmotic pressure*. Note that the osmotic pressure is the pressure required to *stop* osmosis, not to sustain it.

Osmotic pressure is the pressure required to *stop* osmotic flow It is common usage to say that a solution “has” an osmotic pressure of *"x* atmospheres". It is important to understand that this means nothing more than that a pressure of this value must be applied to

the solution to **prevent** flow of pure solvent into this solution through a semipermeable membrane separating the two liquids.

Osmotic Pressure and Solute Concentration

The Dutch scientist Jacobus Van't Hoff (1852-1911) was one of the giants of physical chemistry. He discovered this equation after a chance encounter with a botanist friend during a walk in a park in Amsterdam; the botanist had learned that the osmotic pressure increases by about 1/273 for each degree of temperature increase. van't Hoff immediately grasped the analogy to the ideal gas law. The osmotic pressure Π of a solution containing n moles of solute particles in a solution of volume V is given by the *van 't Hoff equation*:

$$\Pi = \frac{nRT}{V} \tag{1.4.2.1}$$

in which

- R is the gas constant (0.0821 L atm mol^{-1} K^{-1}) and
- T is the absolute temperature.

> In contrast to the need to employ solute molality to calculate the effects of a non-volatile solute on changes in the freezing and boiling points of a solution, we can use solute molarity to calculate osmotic pressures.

Note that the fraction n/V corresponds to the molarity (M) of a solution of a non-dissociating solute, or to twice the molarity of a totally-dissociated solute such as $NaCl$. In this context, molarity refers to the summed total of the concentrations of all solute species. Hence, Equation 1.4.2.1 can be expressed as

$$\Pi = MRT \tag{1.4.2.2}$$

Recalling that Π is the Greek equivalent of *P*, the re-arranged form $\Pi V = nRT$ of the above equation should look familiar. Much effort was expended around the end of the 19th century to explain the similarity between this relation and the *ideal gas law*, but in fact, the Van't Hoff equation turns out to be only a very rough approximation of the real osmotic pressure law, which is considerably more complicated and was derived after van 't Hoff's formulation. As such, this equation gives valid results only for extremely dilute ("ideal") solutions.

According to the Van't Hoff equation, an ideal solution containing 1 mole of dissolved particles per liter of solvent at 0° C will have an osmotic pressure of 22.4 atm.

Example 1.4.2.1

Sea water contains dissolved salts at a total ionic concentration of about 1.13 mol L^{-1}. What pressure must be applied to prevent osmotic flow of pure water into sea water through a membrane permeable only to water molecules?

Solution

This is a simple application of Equation 1.4.2.2.

$$\begin{aligned}\Pi &= MRT \\ &= (1.13\ mol/L)(0.0821\ L\,atm\,mol^{-1}\ K^{-1})(298\ K) \\ &= 27.6\ atm\end{aligned}$$

Molecular Weight Determination by Osmotic Pressure

Since all of the colligative properties of solutions depend on the concentration of the solvent, their measurement can serve as a convenient experimental tool for determining the concentration, and thus the molecular weight, of a solute. Osmotic pressure is especially useful in this regard, because a small amount of solute will produce a much larger change in this quantity than in the boiling point, freezing point, or vapor pressure. even a 10^{-6} molar solution would have a measurable osmotic pressure. Molecular weight determinations are very frequently made on proteins or other high molecular weight polymers. These substances, owing to their large molecular size, tend to be only sparingly soluble in most solvents, so measurement of osmotic pressure is often the only practical way of determining their molecular weights.

Example 1.4.2.2: average molecular weight

The osmotic pressure of a benzene solution containing 5.0 g of polystyrene per liter was found to be 7.6 torr at 25°C. Estimate the average molecular weight of the polystyrene in this sample.

Solution:

osmotic pressure:

$$\Pi = \frac{7.6\,torr}{760\,torr\,atm^{-1}} = 0.0100\,atm$$

Using the form of the van 't Hoff equation (Equation 1.4.2.1), $PV = nRT$, the number of moles of polystyrene is

$$n = (0.0100\text{ atm})(1\text{ L}) \div (0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K}) = 4.09 \times 10^{-4}\text{ mol}$$

Molar mass of the polystyrene:

$$(5.0\text{ g}) \div (4.09 \times 10^{-4}\text{ mol}) = \mathbf{12200\text{ g mol}^{-1}}.$$

The experiment to demonstrate this is quite simple: pure solvent is introduced into one side of a cell that is separated into two parts by a semipermeable membrane. The polymer solution is placed in the other side, which is enclosed and connected to a manometer or some other kind of pressure gauge. As solvent molecules diffuse into the solution cell the pressure builds up; eventually this pressure matches the osmotic pressure of the solution and the system is in osmotic equilibrium. The osmotic pressure is read from the measuring device and substituted into the van't Hoff equation to find the number of moles of solute.

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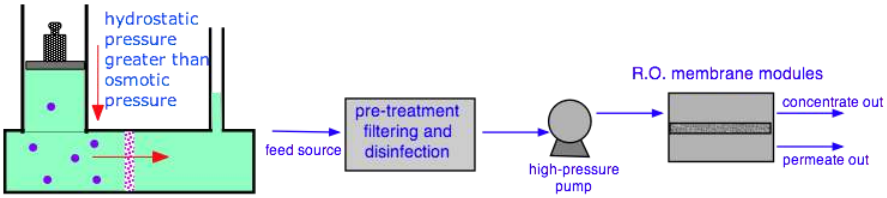
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1.4.3: Reverse Osmosis

Learning Objectives

- What is reverse osmosis, and what is its principal application?
- Explain the role of osmotic pressure in food preservation, and give an example.
- Describe the role osmosis plays in the rise of water in plants (where is the semipermeable membrane?), and why it cannot be the only cause in very tall trees.

If it takes a pressure of Π atm to bring about osmotic equilibrium, then it follows that applying a hydrostatic pressure greater than this to the high-solute side of an osmotic cell will force water to flow back into the fresh-water side. This process, known as *reverse osmosis*, is now the major technology employed to desalinate ocean water and to reclaim "used" water from power plants, runoff, and even from sewage. It is also widely used to deionize ordinary water and to purify it for for industrial uses (especially beverage and food manufacture) and drinking purposes.



Pre-treatment commonly employs activated-carbon filtration to remove organics and chlorine (which tends to damage RO membranes). Although bacteria are unable to pass through semipermeable membranes, the latter can develop pinhole leaks, so some form of disinfection is often advised. The efficiency and cost or RO is critically dependent on the properties of the semipermeable membrane.

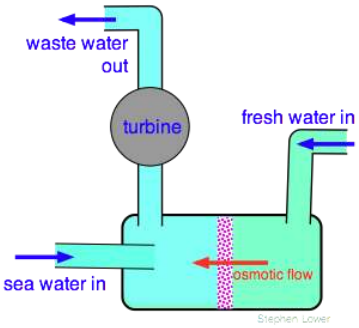


(left) Large-scale RO plants use multiple membrane cartridges. This one, in Tampa Bay FL, supplies desalinated drinking water to 2.4 million residents. (right) Many smaller RO units, suitable for home use, can fit under a kitchen sink.

Osmotic Generation of Electric Power

The osmotic pressure of seawater is almost 26 atm. Since a pressure of 1 atm will support a column of water 10.6 m high, this means that osmotic flow of fresh water through a semipermeable membrane into seawater could in principle support a column of the latter by 26 x 10.3 = 276 m (904 ft)!

So imagine an osmotic cell in which one side is supplied with fresh water from a river, and the other side with seawater. Osmotic flow of fresh water into the seawater side forces the latter up through a riser containing a turbine connected to a generator, thus providing a constant and fuel-less source of electricity. The key component of such a scheme, first proposed by an Israeli scientist in 1973 and known as *pressure-retarded osmosis* (PRO) is of course a semipermeable membrane capable of passing water at a sufficiently high rate.



The world's first experimental PRO plant was opened in 2009 in Norway. Its capacity is only 4 kW, but it serves as proof-in-principle of a scheme that is estimated capable of supplying up to 2000 terawatt-hours of energy worldwide. The semipermeable membrane operates at a pressure of about 10 atm and passes 10 L of water per second, generating about 1 watt per m^2 of membrane. PRO is but one form of *salinity gradient power* that depends on the difference between the salt concentrations in different bodies of water.

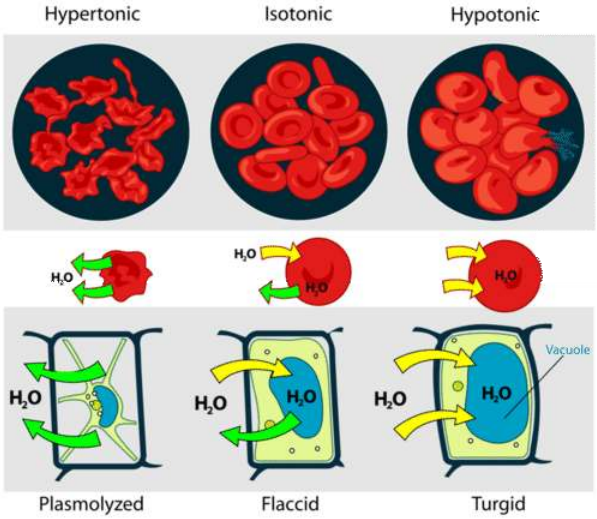
> *1 atm is equivalent to 1034 g cm^{-2}, so from the density of water we get (1034 g cm^{-2}) ÷ (1 g cm^{-3}) = 1034 cm = 10.3 m.*

Osmosis in Biology and Physiology

Because many plant and animal cell membranes and tissues tend to be permeable to water and other small molecules, osmotic flow plays an essential role in many physiological processes.

Normal saline solution

The interiors of cells contain salts and other solutes that dilute the intracellular water. If the cell membrane is permeable to water, placing the cell in contact with pure water will draw water into the cell, tending to rupture it. This is easily and dramatically seen if red blood cells are placed in a drop of water and observed through a microscope as they burst. This is the reason that "normal saline solution", rather than pure water, is administered in order to maintain blood volume or to infuse therapeutic agents during medical procedures.



In order to prevent irritation of sensitive membranes, one should always add some salt to water used to irrigate the eyes, nose, throat or bowel. Normal saline contains 0.91% w/v of sodium chloride, corresponding to 0.154 M, making its osmotic pressure close to that of blood.

Food preservation

The drying of fruit, the use of sugar to preserve jams and jellies, and the use of salt to preserve certain meats, are age-old methods of preserving food. The idea is to reduce the water concentration to a level below that in living organisms. Any bacterial cell that wanders into such a medium will have water osmotically drawn out of it, and will die of dehydration. A similar effect is noticed by anyone who holds a hard sugar candy against the inner wall of the mouth for an extended time; the affected surface becomes dehydrated and noticeably rough when touched by the tongue.

In the food industry, what is known as *water activity* is measured on a scale of 0 to 1, where 0 indicates no water and 1 indicates all water. Food spoilage micro-organisms, in general, are inhibited in food where the water activity is below 0.6. However, if the pH of the food is less than 4.6, micro-organisms are inhibited (but not immediately killed] when the water activity is below 0.85.

Diarrhea

The presence of excessive solutes in the bowel draws water from the intestinal walls, giving rise to diarrhea. This can occur when a food is eaten that cannot be properly digested (as, for example, milk in lactose-intolerant people). The undigested material contributes to the solute concentration, raising its osmotic pressure. The situation is made even worse if the material undergoes bacterial fermentation which results in the formation of methane and carbon dioxide, producing a frothy discharge.

Water Transport in Plants

Osmotic flow plays an important role in the transport of water from its source in the soil to its release by transpiration from the leaves, it is helped along by hydrogen-bonding forces between the water molecules. Capillary rise is not believed to be a significant factor.

Water enters the roots via osmosis, driven by the low water concentration inside the roots that is maintained by both the active [non-osmotic] transport of ionic nutrients from the soil and by the supply of sugars that are photosynthesized in the leaves. This generates a certain amount of *root pressure* which sends the water molecules on their way up through the vascular channels of the stem or trunk. But the maximum root pressures that have been measured can push water up only about 20 meters, whereas the tallest trees exceed 100 meters. Root pressure can be the sole driver of water transport in short plants, or even in tall ones such as trees that are not in leaf. Anyone who has seen apparently tender and fragile plants pushing their way up through asphalt pavement cannot help but be impressed!

But when taller plants are actively transpiring (losing water to the atmosphere], osmosis gets a boost from what plant physiologists call *cohesion tension* or *transpirational pull*. As each H_2O molecule emerges from the opening in the leaf it pulls along the chain of

molecules beneath it. So hydrogen-bonding is no less important than osmosis in the overall water transport process. If the soil becomes dry or saline, the osmotic pressure outside the root becomes greater than that inside the plant, and the plant suffers from "water tension", i.e., wilting.

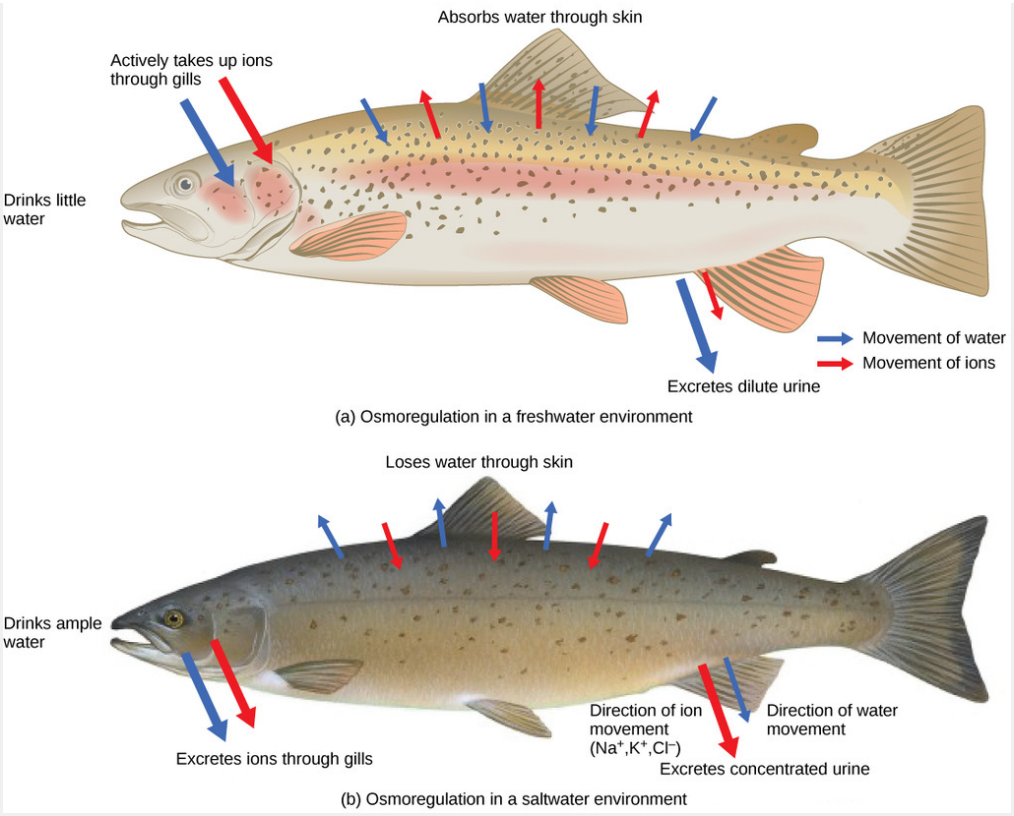
Do fish drink water? Do they Urinate?

The following section is a bit long, but for those who are interested in biology it offers a beautiful example of how the constraints imposed by osmosis have guided the evolution of ocean-living creatures into fresh-water species . It concerns ammonia NH_3, a product of protein metabolism that is generated within all animals, but is highly toxic and must be eliminated.

Marine invertebrates (those that live in seawater) are covered in membranes that are fairly permeable to water and to small molecules such as ammonia. So water can diffuse in either direction as required, and ammonia can diffuse out as quickly as it forms. Nothing special here.

Invertebrates that live in fresh water do have problem: the salt concentrations within their bodies are around 1%, much greater than in fresh water. For this reason they have evolved surrounding membranes that are largely impermeable to salts (to prevent their diffusion out of the body) and to water (to prevent osmotic flow in.) But these organisms must also be able to exchange oxygen and carbon dioxide with their environment. The special respiratory organs (gills) that mediate this process, as a consequence of being permeable to these two gases, will also allow water molecules (whose sizes are comparable to those of the respiratory gases) to pass through. In order to protect fresh-water invertebrates from the disastrous effects of unlimited water inflow through the gill membranes, these animals possess special excretory organs that expel excess water back into the environment. Thus in such animals, there is a constant flow of water passing through the body. Ammonia and other substances that need to be excreted are taken up by this stream which constitutes a continual flow of dilute urine.

Fishes fall into two general classes: most fish have bony skeletons and are known as teleosts. Sharks and rays have cartilage instead of bones, and are called elasmobranchs. For the teleosts that live in fresh water, the situation is very much the same as with fresh-water invertebrates; they take in and excrete water continuously. The fact that an animal lives in the water does not mean that it enjoys an unlimited supply of water. Marine teleosts have a more difficult problem. Their gills are permeable to water, as are those of marine invertebrates. But the salt content of seawater (about 3%), being higher than the about 1% in the fish's blood, would draw water out of the fish. Thus these animals are constantly losing water, and would be liable to desiccation if water could freely pass out of their gills. Some does, of course, and with it goes most of its nitrogen in the form of NH_3.



Salmon physiology responds to freshwater and seawater to maintain osmotic balance. Fish are osmoregulators, but must use different mechanisms to survive in (a) freshwater or (b) saltwater environments. Image used withpermission (CC BY 3.0; OpenStax).

Thus most of the waste nitrogen exits not through the usual excretory organs as with most vertebrates, but through the gills. But in order to prevent excessive loss of water, the gills have reduced permeability to this water, and with it, to comparably-sized NH_3. So in order to prevent ammonia toxicity, the remainder of it is converted to a non-toxic substance (trimethylamine oxide $(CH_3)_3NO$) which is excreted via the kidneys.

The marine elasmobranchs solve the loss-of-water problem in another way: they convert waste ammonia to urea $(NH_3)_2CO$ which is highly soluble and non-toxic. Their kidneys are able to control the quantity of urea excreted so that their blood retains about 2-2.5 percent of this substance. Combined with the 1 percent of salts and other substances in their blood, this raises the osmotic pressure within the animal to slightly above that of seawater, Thus the same mechanism that protects them from ammonia poisoning also ensures them an adequate water supply.

Contributors

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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1.5: Ideal vs. Real Solutions

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Describe the physical reasons that a binary liquid solution might exhibit non-ideal behavior

The popular liquor vodka consists mainly of ethanol (ethyl alcohol) and water in roughly equal portions. Ethanol and water both have substantial vapor pressures, so both components contribute to the total pressure of the gas phase above the liquid in a closed container of the two liquids. One might expect the vapor pressure of a solution of ethanol and water to be directly proportional to the sums of the values predicted by Raoult's law for the two liquids individually, but in general, this does not happen. The reason for this can be understood if you recall that Raoult's law reflects a single effect: the smaller proportion of vaporizable molecules (and thus their reduced escaping tendency) when the liquid is diluted by otherwise "inert" (non-volatile) substance.

Ideal Solutions

There are some solutions whose components follow Raoult's law quite closely. An example of such a solution is one composed of hexane C_6H_{14} and heptane C_7H_{16}. The total vapor pressure of this solution varies in a straight-line manner with the mole fraction composition of the mixture.

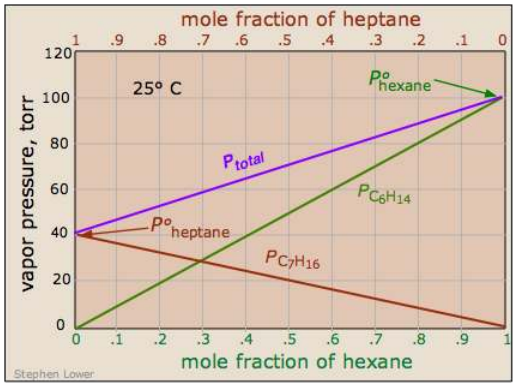


Figure 1.5.1: Raoult's law plot for a mixture of hexane and heptane.

Note that the mole fraction scales at the top and bottom run in opposite directions, since by definition,

$$\chi_{hexane} = 1 - \chi_{heptane} \tag{1.5.1}$$

If this solution behaves ideally, then is the sum of the Raoult's law plots for the two pure compounds:

$$P_{total} = P_{heptane} + P_{hexane} \tag{1.5.2}$$

An *ideal solution* is one whose vapor pressure follows Raoult's law throughout its range of compositions. Experience has shown solutions that approximate ideal behavior are composed of molecules having very similar structures. Thus hexane and heptane are both linear hydrocarbons that differ only by a single $–CH_2$ group. This provides a direct clue to the underlying cause of non-ideal behavior in solutions of volatile liquids. In an ideal solution, the interactions are there, but they are all energetically identical. Thus in an ideal solution of molecules A and B, A—A and B—B attractions are the same as A—B attractions. This is the case only when the two components are chemically and structurally very similar.

Ideal Solutions vs. Ideal Gases

The ideal solution differs in a fundamental way from the definition of an ideal gas, defined as a hypothetical substance that follows the ideal gas law. The kinetic molecular theory that explains ideal gas behavior assumes that the molecules occupy no space and that intermolecular attractions are totally absent.

The definition of an ideal gas is clearly inapplicable to liquids, whose volumes directly reflect the volumes of their component molecules. And of course, the very ability of the molecules to form a condensed phase is due to the attractive forces between

the molecules. So the most we can say about an ideal solution is that the attractions between its all of its molecules are identical — that is, A-type molecules are as strongly attracted to other A molecules as to B-type molecules. Ideal solutions are perfectly democratic: there are no favorites.

Real Solutions

Real solutions are more like real societies, in which some members are "more equal than others." Suppose, for example, that unlike molecules are more strongly attracted to each other than are like molecules. This will cause A–B pairs that find themselves adjacent to each other to be energetically more stable than A–A and B–B pairs. At compositions in which significant numbers of both kind of molecules are present, their tendencies to escape the solution — and thus the vapor pressure of the solution, will fall below what it would be if the interactions between all the molecules were identical. This gives rise to a *negative deviation* from Raoult's law. The chloroform-acetone system, illustrated above, is a good example.

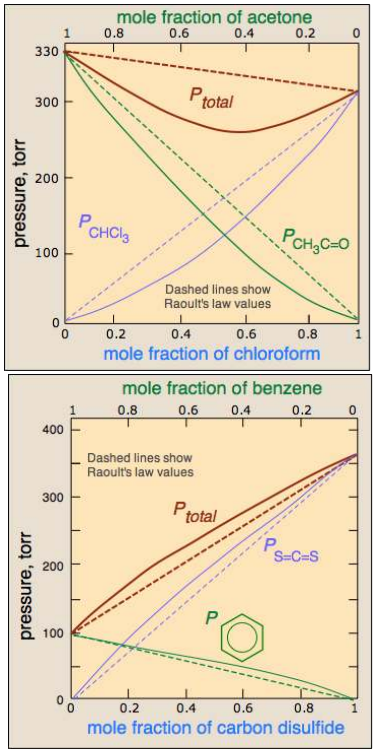


Figure **1.5.2**: *Systems with negative deviation (left) and positive deviation (right) of Raoult's law.*

Conversely, if like molecules of each kind are more attracted to each other than to unlike ones, then the molecules that happen to be close to their own kind will be stabilized. At compositions approaching 50 mole-percent, A and B molecules near each other will more readily escape the solution, which will therefore exhibit a higher vapor pressure than would otherwise be the case. It should not be surprising molecules as different as benzene and CS_2 should interact more strongly with their own kind, hence the positive deviation illustrated here.

You will recall that all gases approach ideal behavior as their pressures approach zero. In the same way, as the mole fraction of either component approaches unity, the behavior of the solution approaches ideality. This is a simple consequence of the fact that at these limits, each molecule is surrounded mainly by its own kind, and the few A-B interactions will have little effect. Raoult's law is therefore a limiting law:

$$P_i = \lim_{x_i \to 0} P^o \chi_i \tag{1.5.3}$$

it gives the partial pressure of a substance in equilibrium with the solution more and more closely as the mole fraction of that substance approaches unity.

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1.6: Distillation

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- Sketch out a typical *boiling point diagram* for a binary liquid solution, and use this to show how a simple one-stage *distillation* works.
- Explain the role of the *lever rule* in fractional distillation
- Describe the purpose and function of a *fractionating column*
- Sketch out boiling point diagrams for high- and low-boiling *azeotropes*
- Describe the role of distillation in *crude oil refining*, and explain, in a very general way, how further processing is used to increase the yield of gasoline motor fuel.

Distillation is a process whereby a mixture of liquids having different vapor pressures is separated into its components. At first one might think that this would be quite simple: if you have a solution consisting of liquid A that boils at 50°C and liquid B with a boiling point of 90°C, all that would be necessary would be to heat the mixture to some temperature between these two values; this would boil off all the A (whose vapor could then be condensed back into pure liquid A), leaving pure liquid B in the pot. But that overlooks that fact that these liquids will have substantial vapor pressures at *all* temperatures, not only at their boiling points.

Vapor Pressure vs. Composition Phase Diagrams

To fully understand distillation, we will consider an ideal binary liquid mixture of **A** and **B**. If the mole fraction of A in the mixture is χ_A, then by the definition of mole fraction, that of B is

$$\chi_B = 1 - \chi_A \tag{1.6.1}$$

Since distillation depends on the different vapor pressures of the components to be separated, let's first consider the vapor pressure vs. composition plots (Figure **1.6.1**) for a hypothetical mixture at some arbitrary temperature at which both liquid and gas phases can exist, depending on the total pressure.

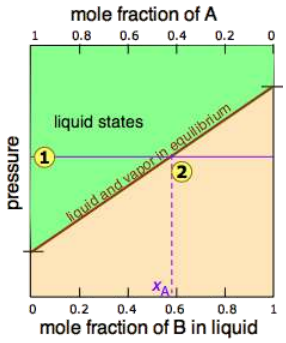


Figure **1.6.1**: Liquid-Vapor Equilibrium curve.

In Figure **1.6.2**, all states of the system (i.e., combinations of pressure and composition) in which the solution exists solely as a **liquid** are shaded in green. Since liquids are more stable at higher pressures, these states occupy the upper part of the diagram. At any given total vapor pressure such as at ①, the composition of the vapor in equilibrium with the liquid (designated by x_A) corresponds to the intercept with the diagonal equilibrium line at ②. The diagonal line is just an expression of the linearity between vapor pressure and composition according to Raoult's law.

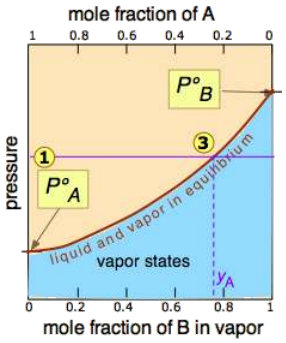


Figure **1.6.2**: Liquid-Vapor Equilibrium curve.

The blue shading in Figure **1.6.2** shows all the states in which the **vapor** is the only stable phase. The upper boundary of this region is defined by the equilibrium line which in this case is curved. As before, the intersection ③ of the pressure line ① with the equilibrium curve defines the mole fractions of **A** and **B** present in the vapor. (Note that mole fractions of gases, which we are dealing with here, are conventionally represented by y, hence y_A and y_B). The curvature of the equilibrium line arises from the need to combine Raoult's law with Dalton's law of partial pressures which applies to gaseous mixtures.

Both Figure **1.6.1** and **1.6.2** above refer to the **same** solution at the same total vapor pressure ①. We can therefore combine them into a single plot, like Figure **1.6.3**.

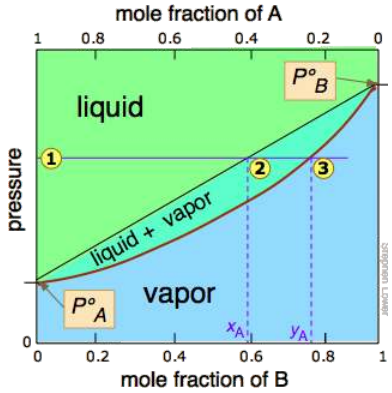


Figure **1.6.3**

The two liquid-vapor equilibrium lines (one curved, the other straight) now enclose an area in which liquid and vapor can **coexist**; outside of this region, the mixture will consist entirely of liquid or of vapor. At this particular pressure ①, the intercept ② with the upper boundary of the two-phase region gives the mole fractions of A and B in the liquid phase, while the intercept ③ with the lower boundary gives the mole fractions of the two components in the vapor.

? Exercise 1.6.1

Take a moment to study Figure **1.6.5** and to confirm that

- because both intercepts occur on equilibrium lines, they describe the *compositions* of the liquid and vapor that can simultaneously exist;
- the compositions of the vapor and liquid are not the same;
- in the vapor, the mole fraction of **B** (the more volatile component of the solution) is greater than that in the liquid;
- in the liquid, the mole fraction of **A** (the less volatile component) is smaller than that of the vapor.

The vapor in equilibrium with a solution of two or more liquids is **always** richer in the more volatile component.

Temperatures vs. Composition Phase Diagrams (Boiling Point Diagrams)

The rule shown above suggests that if we heat a mixture sufficiently to bring its total vapor pressure into the two-phase region, we will have a means of separating the mixture into two portions which will be enriched in the more volatile and less volatile

components respectively. This is the principle on which distillation is based. But what temperature is required to achieve this? Again, we will spare you the mathematical details, but it is possible to construct a plot similar to the Figure **1.6.4** except that the vertical axis represents *temperature* rather than pressure. This kind of plot is called a *boiling point diagram*.

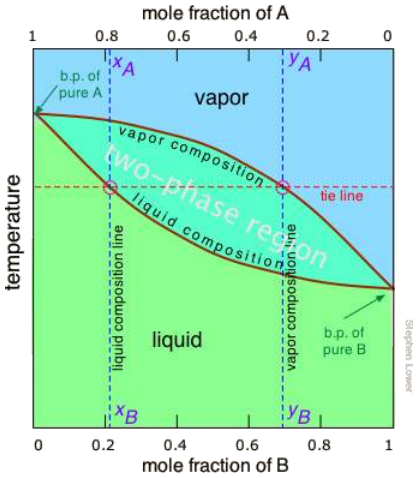


Figure **1.6.4**: Boiling point diagram of a volatile two-component system.

Important Properties of Boiling Point Diagrams

Some important things to understand about Figure **1.6.6**:

- The shape of the two-phase region is bi-convex, as opposed to the half-convex shape of the pressure-composition plot.
- The slope of the two-phase region is opposite to what we saw in the previous plot, and the areas corresponding to the single-phase regions are reversed. This simply reflects the fact that liquids having a higher vapor pressure boil at lower temperatures, and *vice versa*.
- The horizontal line that defines the temperature is called the *tie line*. Its intercepts with the two equilibrium curves specify the composition of the liquid and vapor in equilibrium with the mixture at the given temperature.
- The vapor composition line is also known as the *dew point line* — the temperature at which condensation begins on cooling.
- The liquid composition line is also called the *bubble point line* — the temperature at which boiling begins on heating.

The tie line shown in Figure **1.6.6** is for one particular temperature. But when we heat a liquid to its boiling point, the composition will change as the more volatile component (**B** in these examples) is selectively removed as vapor. The remaining liquid will be

enriched in the less volatile component, and its boiling point will consequently rise. To understand this process more thoroughly, let us consider the situation at several points during the distillation of an equimolar solution of **A** and **B**.

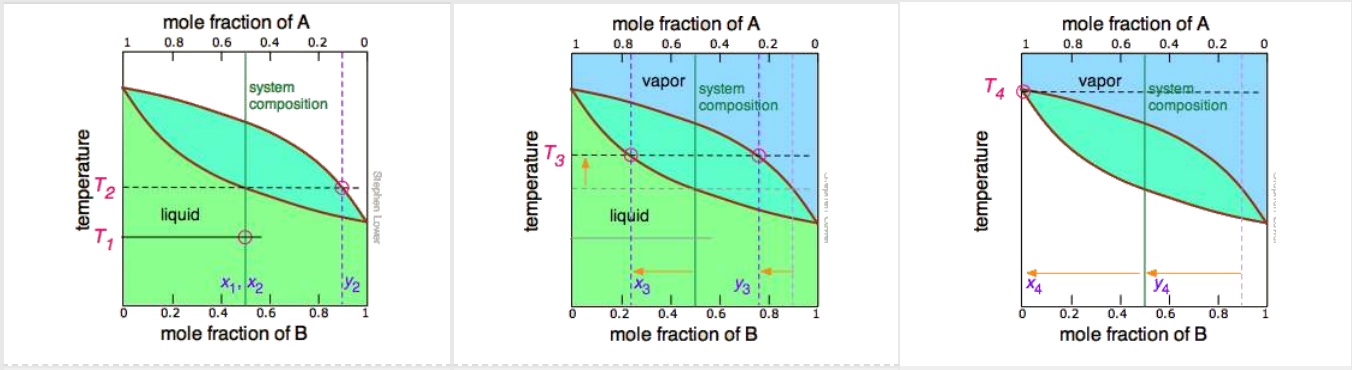


Figure **1.6.5*A***: We begin with the liquid at T_1, below its boiling point. When the temperature rises to T_2, boiling begins and the first vapor (and thus the first drop of condensate) will have the composition y_2.

***Figure* 1.6.5*B*:** As the more volatile component B is boiled off, the liquid and vapor/condensate compositions shift to the left (orange arrows).

***Figure* 1.6.5*C*:** At T_4, the last trace of liquid disappears. The system is now entirely vapor, of composition y_4.

Notice that the vertical green *system composition* line remains in the same location in the three plots because the "system" is defined as consisting of both the liquid in the "pot" and that in the receiving container which was condensed from the vapor. The principal ideas you should take away from this are that

- distillation can never completely separate two volatile liquids;
- the composition of the vapor and thus of the condensed distillate changes continually as each drop forms, starting at y_2 and ending at y_4 in this example;
- if the liquid is completely boiled away, the composition of the distillate will be the same as that of the original solution.

Laboratory Distillation Setup

The apparatus used for a simple laboratory batch distillation is shown here. The purpose of the thermometer is to follow the progress of the distillation; as a rough rule of thumb, the distillation should be stopped when the temperature rises to about half-way between the boiling points of the two pure liquids, which should be at least 20-30 C° apart (if they are closer, then *fractional distillation*, described below, becomes necessary).

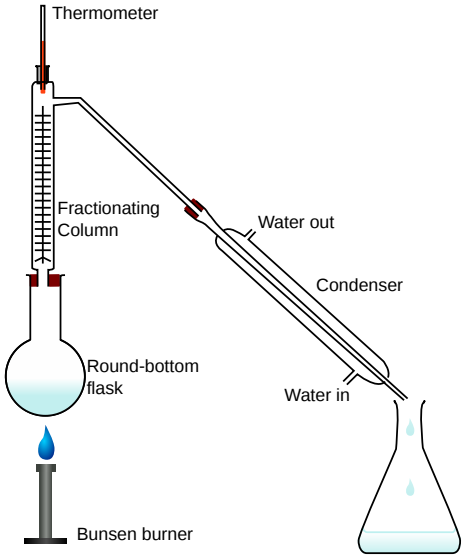


Figure **1.6.6**: Fractional distillation setup. An Erlenmeyer flask is used as a receiving flask. Here the distillation head and fractionating column are combined in one piece. (CC BY-SA 3.0; Theresa knott via Wikipedia)

Condensers are available in a number of types. The simple *Liebig condenser* shown above is the cheapest and therefore most commonly used in student laboratories. Several other classic designs increase the surface area separating the vapor/distillate and cooling water, leading to greater heat exchange efficiency and allowing higher throughput.

Fractional Distillation

Although distillation can never achieve complete separation of volatile liquids, it can in principal be carried out in such a way that any desired degree of separation can be achieved if the solution behaves ideally and one is willing to go to the trouble. The general procedure is to distill only a fraction of the liquid, the smaller the better. The condensate, now enriched in the more volatile component, is then collected and re-distilled (again, only a small fraction), thus obtaining a condensate even-more-enriched in the more volatile component. If we repeat this sequence many times, we can eventually obtain almost-pure, if minute, samples of the two components.

But since this would hardly be practical, there is a better way. In order to understand it, you need to know about the *lever rule*, which provides a simple way of determining the relative *quantities* (not just the compositions) of two phases in equilibrium. The lever rule is easily derived from **Raoult's** and **Dalton's laws**, but we will simply illustrate it graphically (Figure 1.6.7). The plot shows the boiling point diagram of a simple binary mixture of composition ①. At the temperature corresponding to the tie line, the composition of the liquid corresponds to ② and that of the vapor to ③ .

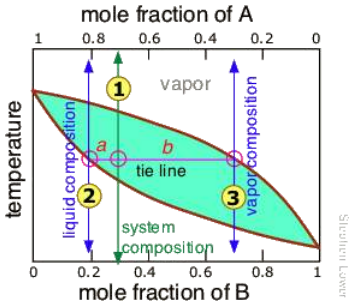


Figure* 1.6.7*:

So now for the lever rule: the relative quantities of the liquid and the vapor we identified above are given by the lengths of the tie-line segments labeled *a* and *b*. Thus in this particular example, in which *b* is about four times longer than *a*, we can say that the mole ratio of vapor (of composition ③) to liquid (composition ②) is 4.

Steps in Fractional Distillation

It is not practical to carry out an almost-infinite number of distillation steps to obtain nearly-infinitesimal quantities of the two pure liquids we wish to separate. So instead of collecting each drop of condensate and re-distilling it, we will distil half of the mixture in each step. Suppose you want to separate a liquid mixture composed of 20 mole-% B and 80 mole-% A, with A being the more volatile.

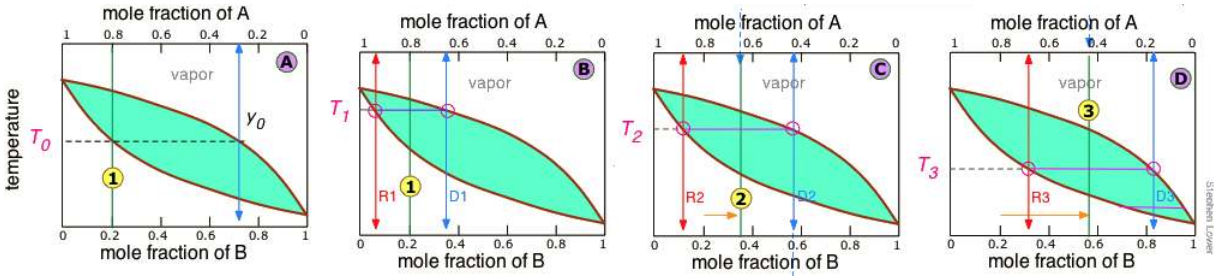


Figure* 1.6.8*: *Steps in Fractional Distillation*

Ⓐ As we heat the mixture whose overall composition is indicated by ①, the first vapor is formed at $T_0$and has the composition y_0, found by extending the horizontal dashed line until it meets the vapor curve. This vapor is clearly enriched in

B; if it is condensed, the resulting liquid will have a mole fraction x_B approaching that of A in the original liquid. But this is only the first drop, we don't want to stop there!

Ⓑ As the liquid continues to boil, the boiling temperature rises. When it reaches T_1, we will have boiled away half of the liquid. At this point, the "system" composition (liquid plus vapor) is still the same (①), but is now equally divided between the liquid, which we call "residue" R_1, and the condensed vapor, the *distillate* D_1.

> *How do we know it is equally divided? We have picked T_1 so that the tie line is centered on the system concentration, so by the lever rule, R_1 and D_1 contain equal numbers of moles.*

Ⓒ We now take the condensed liquid D_1 having the composition ②, and distill half of it, obtaining distillate of composition D_2.

Ⓓ .. and then carry out yet another distillation, this time using D_3 as our feedstock.

Ⓔ Our four-stage fractionation has enriched the more volatile solute from 20 to slightly over 80 mole-percent in D_4. The less volatile component A is most concentrated in R_1. R_2 through R_4 are thrown away (but not down the sink, please!)

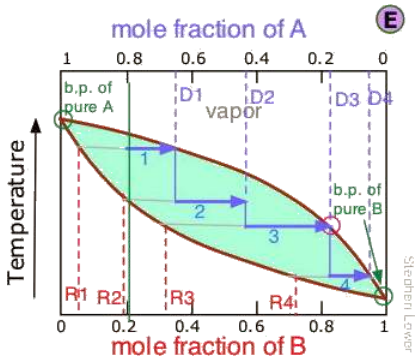


Figure* 1.6.9*: *Boiling point diagrams illustrating fractional distillation"*

This may be sufficient for some purposes, but we might wish to do much better, using perhaps 1000 stages instead of just 4. What could be more tedious?

Fractionation with reflux

Not to worry! The multiple successive distillations can be carried out "virtually" by inserting a *fractionating column* between the boiling flask and the condenser.

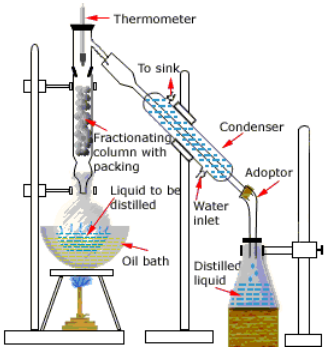


Figure* 1.6.10*:

These columns are made with indentations or are filled with materials that provide a large surface area extending through the vertical temperature gradient (higher temperature near the bottom, lower temperature at the top.) The idea is that hot vapors condense at various levels in the column and the resulting liquid drips down (*refluxes*) to a lower level where it is vaporized, which corresponds roughly to a re-distillation.



Vigreux columns having multiple indentations are widely used (above right). Simple columns can be made by filling a glass tube with beads, short glass tubes, or even stainless steel kitchen-type scouring pads. More elaborate ones have spinning steel ribbons.

Separation efficiency: theoretical plates

The operation of fractionating columns can best be understood by reference to a bubble-cap column. The one shown here consists of four sections, or "plates" through which hot vapors rise and bubble up through pools of condensate that collect on each plate. The intimate contact between vapor and liquid promotes equilibration and re-distillation at successively higher temperatures at each higher plate in the column. Unlike the case of the step-wise fractional distillation we discussed above, none of the intermediate residues is thrown away; they simply drip down back into the pot where their fractionation journey begins again, always leading to a further concentration of the less-volatile component in the remaining liquid. At the same time, the vapor emerging from the top plate (5) provides a continuing flow of volatile-enriched condensate, although in diminishing quantities as it is depleted in the boiling pot.

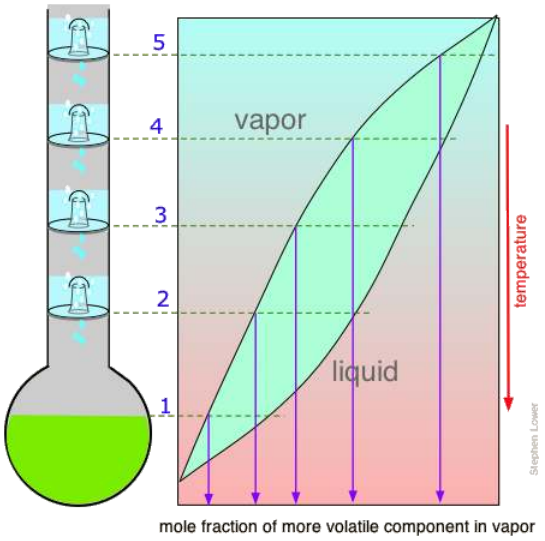


Figure* 1.6.11*:

If complete equilibrium is attained between the liquid and vapor at each stage, then we can describe the system illustrated above as providing "five theoretical plates" of separation (remember that the pot represents the first theoretical plate.) Equilibrium at each stage requires a steady-state condition in which the quantity of vapor moving upward at each stage is equal to the quantity of liquid draining downward — in other words, the column should be operating in total reflux, with no net removal of distillate. So any real distillation process will be operated at a reflux ratio that provides optimum separation in a reasonable period of time.

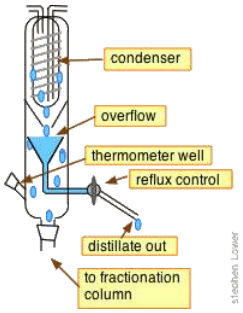


Figure* 1.6.11*: Reflux ratio can be adjusted by placing a special control head on top of the fractionation column. The laboratory-type device shown here illustrates the general concept. Reflux control is mainly of importance in large-scale industrial operations.

Some of the more advanced laboratory-type devices (such as some spinning-steel band columns) are said to offer up to around 200 theoretical plates of separating power.

Azeotropes: the Limits of Distillation

The boiling point diagrams presented in the foregoing section apply to solutions that behave in a reasonably ideal manner — that is, to solutions that do not deviate too far from Raoult's law. As we explained above, mixtures of liquids whose intermolecular interactions are widely different do not behave ideally, and may be impossible to separate by ordinary distillation. The reason for this is that under certain conditions, the compositions of the liquid and of the vapor in equilibrium with it become identical, precluding any further separation. These cross-over points appear as "kinks" in the boiling point diagrams.

High- and low-boiling azeotropes

Thus in this boiling point diagram for a mixture exhibiting a positive deviation from Raoult's law, successive fractionations of mixtures correspond to either ① or ② bring the distillation closer to the azeotropic composition indicated by the dashed vertical line. Once this point is reached, further distillation simply yields more of the same "high-boiling" azeotrope.

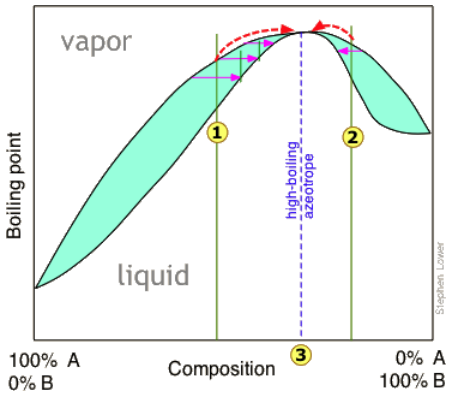


Figure* 1.6.12*: *Maximum Bioling Azeotrope*

Distillation of a mixture having a negative deviation from Raoult's law leads to a similar stalemate, in this case yielding a "low-boiling" azeotrope. High- and low-boiling azeotropes are commonly referred to as *constant-boiling mixtures*, and they are more common than most people think.

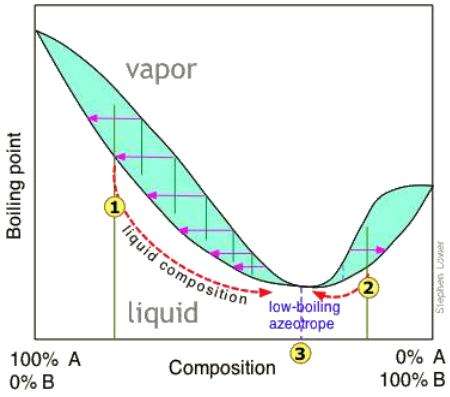


Figure **1.6.13**: Maximum Bioling Azeotrope

"Breaking" an azeotrope

There are four general ways of dealing with azeotropes. The first two of these are known collectively as *azeotropic distillation*.

- **Addition of a third substance** that alters the intermolecular attractions is the most common trick. The drawback is that another procedure is usually needed to remove this other substance.
- **Pressure-swing distillation** takes advantage of the fact that boiling point (*T*,*X*) diagrams are two-dimensional slices of a (*T*,*X*,*P*) diagram in which the pressure is the third variable. This means that the azeotropic composition depends on the pressure, so distillation at some pressure other than 1 atm may allow one to "jump" the azeotrope.
- **Use of a molecular sieve** — a porous material that selectively absorbs one of the liquids, most commonly water when the latter is present at a low concentration.
- **Give up.** It often happens that the azeotropic composition is sufficiently useful that it's not ordinarily worth the trouble of obtaining a more pure product. This accounts for the concentrations of many commercial chemicals such as mineral acids.

Some constant-boiling mixtures with water

mixture	azeotrope
Ethanol	98%, high, 78.1°C
Hydrochloric acid	20.2% high, 108.6°C
Hydrofluoric acid	35.6%, 111.3°C
Nitric acid	68%, 120.5°C
Sulfuric acid	98.3%, 338°C

Distillation of Ethanol

Ethanol is one of the major industrial chemicals, and is of course the essential component of beverages that have been a part of civilization throughout recorded history. Most ethanol is produced by fermentation of the starch present in food grains, or of sugars formed by the enzymatic degradation of cellulose. Because ethanol is toxic to the organisms whose enzymes mediate the fermentation process, the ethanol concentration in the fermented mixture is usually limited to about 15%. The liquid phase of the mixture is then separated and distilled.

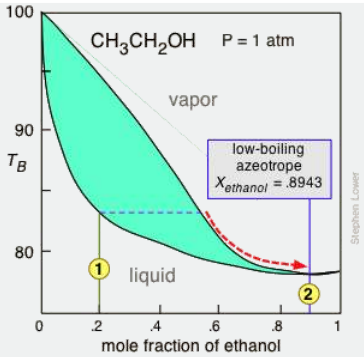


Figure* 1.6.8*:

T

he normal boiling point of ethanol is 78.4°C, but its formation of a low-boiling

azeotrope

with water limits the maximum concentration that can be obtained

b

y ordinary distillation to 95.6 volume-% (89.5 mole-%). This concentration is adequate for many applications, for which the product is commonly sold as "95% ethan

o

l".

For applications requiring anhydrous ethanol ("absolute ethanol"), the most common method is the use of zeolite-based molecular sieves to absorb the remaining water. Addition of benzene can break the azeotrope, and this was the most common production method in earlier years. For certain critical uses where the purest ethanol is required, it is synthesized directly from ethylene.

Special Distillation Methods

Here be briefly discuss two distillation methods that students are likely to encounter in more advanced organic lab courses.

Vacuum distillation: Many organic substances become unstable at high temperatures, tending to decompose, polymerize or react with other substances at temperatures around 200° C or higher. A liquid will boil when its vapor pressure becomes equal to the pressure of the gas above it, which is ordinarily that of the atmosphere. If this pressure is reduced, boiling can take place at a lower temperature. (Even pure water will boil at room temperature under a partial vacuum.) "Vacuum distillation" is of course a misnomer; a more accurate term would be "reduced-pressure distillation". Vacuum distillation is very commonly carried out in the laboratory and will be familiar to students who take more advanced organic lab courses. It is also sometimes employed on a large industrial scale.

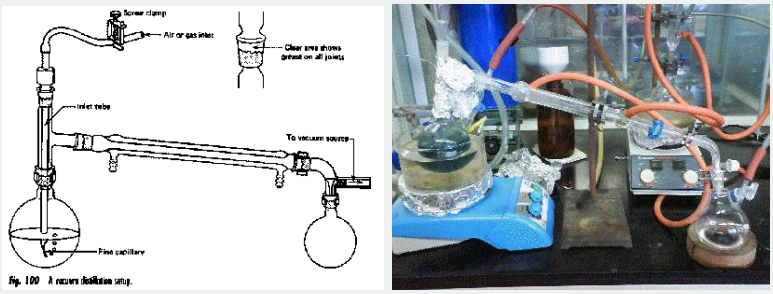


Figure* 1.6.9: vacuum connection at lower right*

The vacuum distillation setup is similar that employed in ordinary distillation, with a few additions:

- The vacuum line is connected to the bent adaptor above the receiving flask.
- In order to avoid uneven boiling and superheating ("bumping"), the boiling flask is usually provided with a fine capillary ("ebulliator") through which an air leak produces bubbles that nucleate the boiling liquid.
- The vacuum is usually supplied by a mechanical pump, or less commonly by a water aspirator or a "house vacuum" line.

- The boiling flask is preferably heated by a water- or steam bath, which provides more efficient heat transfer to the flask and avoids localized overheating. Prior to about 1960, open flames were commonly used in student laboratories, resulting in occasional fires that enlivened the afternoon, but detracted from the student's lab marks.
- A Claisen-type distillation head (below) provides a convenient means of accessing the boiling flask for inserting an air leak capillary or introducing additional liquid through a separatory funnel. This Claisen-Vigreux head includes a fractionation column.

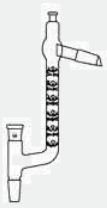


Figure **1.6.10***: A Claisen-type distillation head*

Steam Distillation: Strictly speaking, this topic does not belong in this unit, since steam distillation is used to separate *immiscible* liquids rather than solutions. But because immiscible liquid mixtures are not treated in elementary courses, we present a brief description of steam distillation here for the benefit of students who may encounter it in an organic lab course. A mixture of immiscible liquids will boil when their *combined* vapor pressures reach atmospheric pressure. This combined vapor pressure is just the sum of the vapor pressures of each liquid individually, and is independent of the quantities of each phase present.

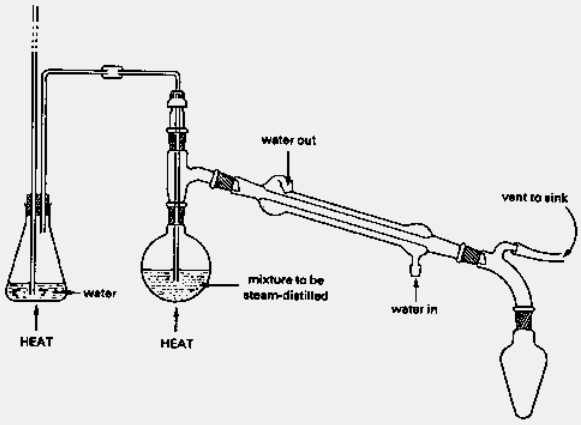


Figure **1.6.11**

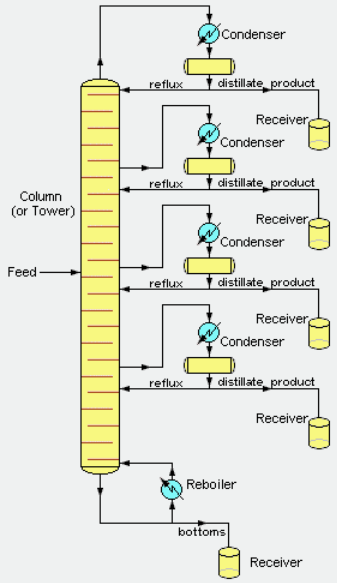
Because water boils at 100° C, a mixture of water and an immiscible liquid (an "oil"), even one that has a high boiling point, is guaranteed to boil *below* 100°, so this method is especially valuable for separating high boiling liquids from mixtures containing non-volatile impurities. Of course the water-oil mixture in the receiving flask must itself be separated, but this is usually easily accomplished by means of a separatory funnel since their densities are ordinarily different.

There is a catch, however: the lower the vapor pressure of the oil, the greater is the quantity of water that co-distills with it. This is the reason for using steam: it provides a source of water able to continually restore that which is lost from the boiling flask. Steam distillation from a water-oil mixture without the introduction of additional steam will also work, and is actually used for some special purposes, but the yield of product will be very limited. Steam distillation is widely used in industries such as petroleum refining (where it is often called "steam stripping") and in the flavors-and-perfumes industry for the isolation of essential oils

The term *essential oil* refers to the aromas ("essences") of these [mostly simple] organic liquids which occur naturally in plants, from which they are isolated by steam distillation or solvent extraction. Steam distillation was invented in the 13th Century by Ibn al-Baiter, one of the greatest of the scientists and physicians of the Islamic Golden Age in Andalusia.

Industrial-scale distillation and Petroleum fractionation

Distillation is one of the major "unit operations" of the chemical process industries, especially those connected with petroleum and biofuel refining, liquid air separation, and brewing. Laboratory distillations are typically batch operations and employ relatively simple fractionating columns to obtain a pure product. In contrast, industrial distillations are most often designed to produce mixtures having a desired boiling range rather than pure products.



Industrial operations commonly employ bubble-cap fractionating columns (seldom seen in laboratories), although packed columns are sometimes used. Perhaps the most distinctive feature of large scale industrial distillations is that they usually operate on a continuous basis in which the preheated crude mixture is preheated in a furnace and fed into the fractionating column at some intermediate point. A reboiler unit maintains the bottom temperature at a constant value. The higher-boiling components then move down to a level at which they vaporize, while the lighter (lower-boiling) material moves upward to condense at an appropriate point.

Petroleum is a complex mixture of many types of organic molecules, mostly hydrocarbons, that were formed by the effects of heat and pressure on plant materials (mostly algae) that grew in regions that the earth's tectonic movements buried over periods of millions of years. This mixture of liquid and gases migrates up through porous rock until it s trapped by an impermeable layer of sedimentary rock. The molecular composition of *crude oil* (the liquid fraction of petroleum) is highly variable, although its overall elemental makeup generally reflects that of typical plants.

element	carbon	hydrogen	nitrogen	oxygen	sulfur	metals
amount	83-87%	10-14%	0.1-2%	0.1-1.5%	0.5-6%	

The principal molecular constituents of crude oil are

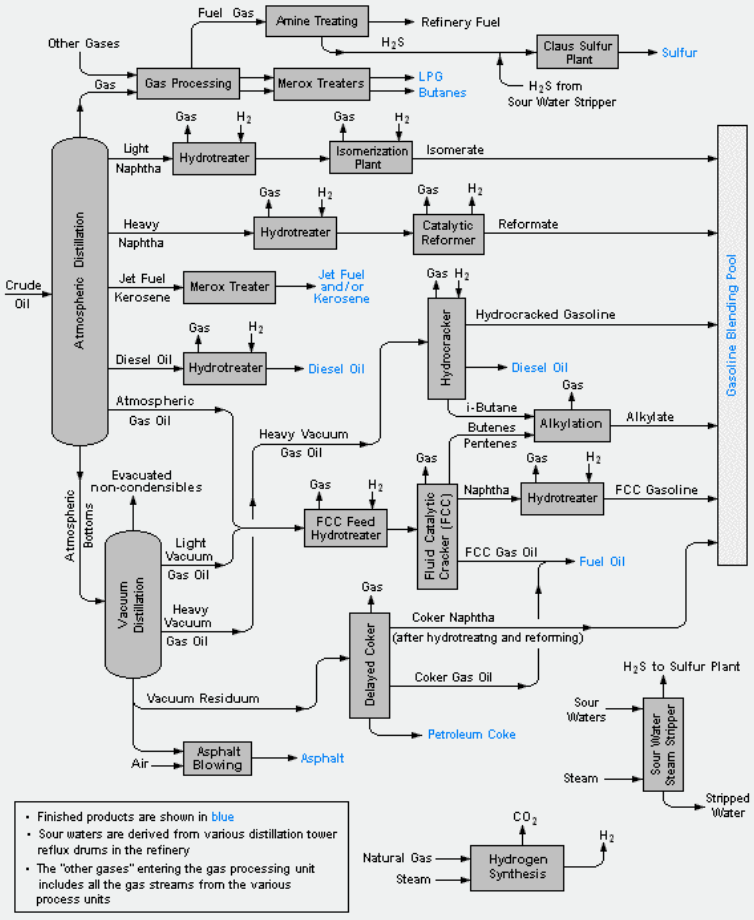
- alkanes: Also known as *paraffins*, these are saturated linear- or branched-chain molecules having the general formula C_nH_{2n+2} in which n is mostly between 5 and 40.
- unsaturated aliphatic: Linear- or branched chain molecules containing one or more double or triple bonds (alkenes or alkynes).
- Cycloalkanes:Also known as naphthenes these are saturated hydrocarbons C_nH_{2n} containing one or more ring structures.
- Aromatic hydrocarbons:These contain one or more fused benzene rings C_nH_n, often with hydrocarbon side-chains.

The word *gasoline* predates its use as a motor fuel; it was first used as a topical medicine to rid people of head lice, and to remove grease spots and stains from clothing. The first major step of refining is to fractionate the crude oil into various boiling ranges.

boiling range	fraction name	further processing
	butane and propane	gas processing
30 - 210°	straight-run gasoline	blending into motor gasoline
100 - 200°	naphtha	reforming into gasoline components
150 - 250°	kerosene	jet fuel blending
160 -400°	light gas oil	distillate fuel blending into diesel or fuel oil
315 - 540°	heavy gas oil	catalytic cracking: large molecules are broken up into smaller ones and recycled
>450°	asphalts, bottoms	may be vacuum-distilled into more fractions

Further processing and blending

About 16% of crude oil is diverted to the petrochemical industry where it is used to make ethylene and other feedstocks for plastics and similar products. Because the fraction of straight-run gasoline is inadequate to meet demand, some of the lighter fractions undergo reforming and the heavier ones cracking and are recycled into the gasoline stream. These processes necessitate a great amount of recycling and blending, into which must be built a considerable amount of flexibility in order to meet seasonal needs (more volatile gasolines and heating fuel oil in winter, more total gasoline volumes in the summer.)



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1.E: Physical Equilibrium (Exercises)

11.2: The Dissolution Process

Q11.2.1

How do solutions differ from compounds? From other mixtures?

S11.2.1

A solution can vary in composition, while a compound cannot vary in composition. Solutions are homogeneous at the molecular level, while other mixtures are heterogeneous.

Q11.2.2

Which of the principal characteristics of solutions can we see in the solutions of $\mathbf{K_2Cr_2O_7}$ shown in



Figure: When potassium dichromate ($\mathbf{K_2Cr_2O_7}$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

S11.2.2

The solutions are the same throughout (the color is constant throughout), and the composition of a solution of $K_2Cr_2O_7$ in water can vary.

Q11.2.3

When KNO_3 is dissolved in water, the resulting solution is significantly colder than the water was originally.

a. Is the dissolution of KNO_3 an endothermic or an exothermic process?
b. What conclusions can you draw about the intermolecular attractions involved in the process?
c. Is the resulting solution an ideal solution?

S11.2.3

(a) The process is endothermic as the solution is consuming heat. (b) Attraction between the K^+ and $\mathbf{NO_3^-}$ ions is stronger than between the ions and water molecules (the ion-ion interactions have a lower, more negative energy). Therefore, the dissolution process increases the energy of the molecular interactions, and it consumes the thermal energy of the solution to make up for the difference. (c) No, an ideal solution is formed with no appreciable heat release or consumption.

Q11.2.4

Give an example of each of the following types of solutions:

a. a gas in a liquid
b. a gas in a gas
c. a solid in a solid

S11.2.4

(a) CO_2 in water; (b) O_2 in N_2 (air); (c) bronze (solution of tin or other metals in copper)

Q11.2.5

Indicate the most important types of intermolecular attractions in each of the following solutions:

a. The solution in Figure.
b. NO(*l*) in CO(*l*)
c. $Cl_2(g)$ in $Br_2(l)$
d. HCl(*aq*) in benzene $C_6H_6(l)$
e. Methanol $CH_3OH(l)$ in $H_2O(l)$

S11.2.5

(a) ion-dipole forces; (b) dipole-dipole forces; (c) dispersion forces; (d) dispersion forces; (e) hydrogen bonding

Q11.2.5

Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane (C_7H_{16}, nonpolar solvent):

a. vegetable oil (nonpolar)
b. isopropyl alcohol (polar)
c. potassium bromide (ionic)

S11.2.5

(a) heptane; (b) water; (c) water

Q11.2.6

Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

S11.2.6

Heat is released when the total intermolecular forces (IMFs) between the solute and solvent molecules are stronger than the total IMFs in the pure solute and in the pure solvent: Breaking weaker IMFs and forming stronger IMFs releases heat. Heat is absorbed when the total IMFs in the solution are weaker than the total of those in the pure solute and in the pure solvent: Breaking stronger IMFs and forming weaker IMFs absorbs heat.

Q11.2.7

Solutions of hydrogen in palladium may be formed by exposing Pd metal to H_2 gas. The concentration of hydrogen in the palladium depends on the pressure of H_2 gas applied, but in a more complex fashion than can be described by Henry's law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal.

a. Determine the molarity of this solution (solution density = 1.8 g/cm^3).
b. Determine the molality of this solution (solution density = 1.8 g/cm^3).
c. Determine the percent by mass of hydrogen atoms in this solution (solution density = 1.8 g/cm^3).

S11.2.7

http://cnx.org/contents/mH6aqegx@2/The-Dissolution-Process

11.3: Electrolytes

Q11.3.1

Explain why the ions Na^+ and Cl^- are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules.

S11.3.2

Crystals of NaCl dissolve in water, a polar liquid with a very large dipole moment, and the individual ions become strongly solvated. Hexane is a nonpolar liquid with a dipole moment of zero and, therefore, does not significantly interact with the ions of

the NaCl crystals.

Q11.3.2

Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.

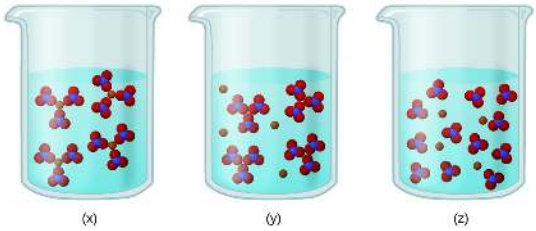
S11.3.2

HBr is an acid and so its molecules react with water molecules to form H_3O^+ and Br^- ions that provide conductivity to the solution. Though HBr is soluble in benzene, it does not react chemically but remains dissolved as neutral HBr molecules. With no ions present in the benzene solution, it is electrically nonconductive.

Q11.3.3

Consider the solutions presented:

(a) Which of the following sketches best represents the ions in a solution of $Fe(NO_3)_3(aq)$?



(b) Write a balanced chemical equation showing the products of the dissolution of $Fe(NO_3)_3$.

S11.3.3

(a) $Fe(NO_3)_3$ is a strong electrolyte, thus it should completely dissociate into Fe^{3+} and (NO_3^-) ions. Therefore, (z) best represents the solution. (b) $\mathbf{Fe(NO_3)_3(s) \longrightarrow Fe^{3+}(aq) + 3\,NO_3^-(aq)}$

Q11.3.4

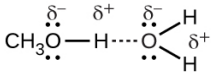
Compare the processes that occur when methanol (CH_3OH), hydrogen chloride (HCl), and sodium hydroxide (NaOH) dissolve in water. Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

S11.3.3

Methanol, $\boldsymbol{CH_3OH}$, dissolves in water in all proportions, interacting via hydrogen bonding.

Methanol:

$$\boldsymbol{CH_3OH_{(l)} + H_2O_{(l)} \longrightarrow CH_3OH_{(aq)}} \tag{1.E.1}$$



hydrogen bonding

Hydrogen chloride, HCl, dissolves in and reacts with water to yield hydronium cations and chloride anions that are solvated by strong ion-dipole interactions.

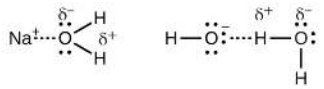
Hydrogen chloride:

$$\boldsymbol{HCl(g) + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}} \tag{1.E.2}$$

Sodium hydroxide, NaOH, dissolves in water and dissociates to yield sodium cations and hydroxide anions that are strongly solvated by ion-dipole interactions and hydrogen bonding, respectively.

Sodium hydroxide:

$$NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)} \tag{1.E.3}$$



Ion-dipole attraction hydrogen bonding

Q11.3.5

What is the expected electrical conductivity of the following solutions?

a. NaOH(*aq*)
b. HCl(*aq*)
c. $C_6H_{12}O_6$(*aq*) (glucose)
d. NH_3(*l*)

S11.3.5

(a) high conductivity (solute is an ionic compound that will dissociate when dissolved); (b) high conductivity (solute is a strong acid and will ionize completely when dissolved); (c) nonconductive (solute is a covalent compound, neither acid nor base, unreactive towards water); (d) low conductivity (solute is a weak base and will partially ionize when dissolved)

Q11.3.6

Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.

S11.3.6

A medium must contain freely mobile, charged entities to be electrically conductive. The ions present in a typical ionic solid are immobilized in a crystalline lattice and so the solid is not able to support an electrical current. When the ions are mobilized, either by melting the solid or dissolving it in water to dissociate the ions, current may flow and these forms of the ionic compound are conductive.

Q11.3.7

Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:

a. the solutions in Figure
b. methanol, CH_3OH, dissolved in ethanol, C_2H_5OH
c. methane, CH_4, dissolved in benzene, C_6H_6
d. the polar halocarbon CF_2Cl_2 dissolved in the polar halocarbon $CF_2ClCFCl_2$
e. O_2(*l*) in N_2(*l*)

S11.3.7

(a) ion-dipole; (b) hydrogen bonds; (c) dispersion forces; (d) dipole-dipole attractions; (e) dispersion forces

11.4: Solubility

Q11.4.1

Suppose you are presented with a clear solution of sodium thiosulfate, $Na_2S_2O_3$. How could you determine whether the solution is unsaturated, saturated, or supersaturated?

S11.4.1

Add a small crystal of $Na_2S_2O_3$. It will dissolve in an unsaturated solution, remain apparently unchanged in a saturated solution, or initiate precipitation in a supersaturated solution.

Q11.4.2

Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.

S11.4.2

The solubility of solids usually decreases upon cooling a solution, while the solubility of gases usually decreases upon heating.

Q11.4.3

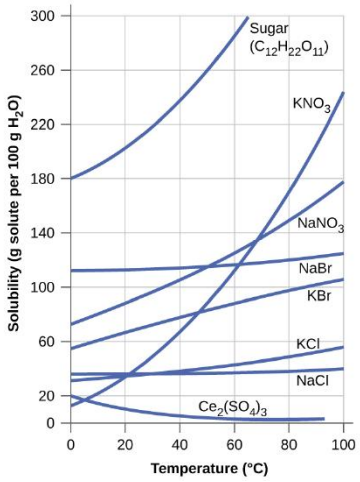
Suggest an explanation for the observations that ethanol, C_2H_5OH, is completely miscible with water and that ethanethiol, C_2H_5SH, is soluble only to the extent of 1.5 g per 100 mL of water.

S11.4.3

The hydrogen bonds between water and C_2H_5OH are much stronger than the intermolecular attractions between water and C_2H_5SH.

Q11.4.4

Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C using the following figure for useful data, and report the computed percentage to one significant digit.



This graph shows how the solubility of several solids changes with temperature.

S11.4.4

At 10 °C, the solubility of KBr in water is approximately 60 g per 100 g of water.

$$\% \; KBr = \frac{60 \; g \; KBr}{(60 + 100) \; g \; solution} = 40\% \tag{1.E.4}$$

Q11.4.5

Which of the following gases is expected to be most soluble in water? Explain your reasoning.

a. CH_4
b. CCl_4
c. $CHCl_3$

S11.4.5

(c) $CHCl_3$ is expected to be most soluble in water. Of the three gases, only this one is polar and thus capable of experiencing relatively strong dipole-dipole attraction to water molecules.

Q11.4.6

At 0 °C and 1.00 atm, as much as 0.70 g of O_2 can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O_2 dissolve in 1 L of water?

S11.4.6

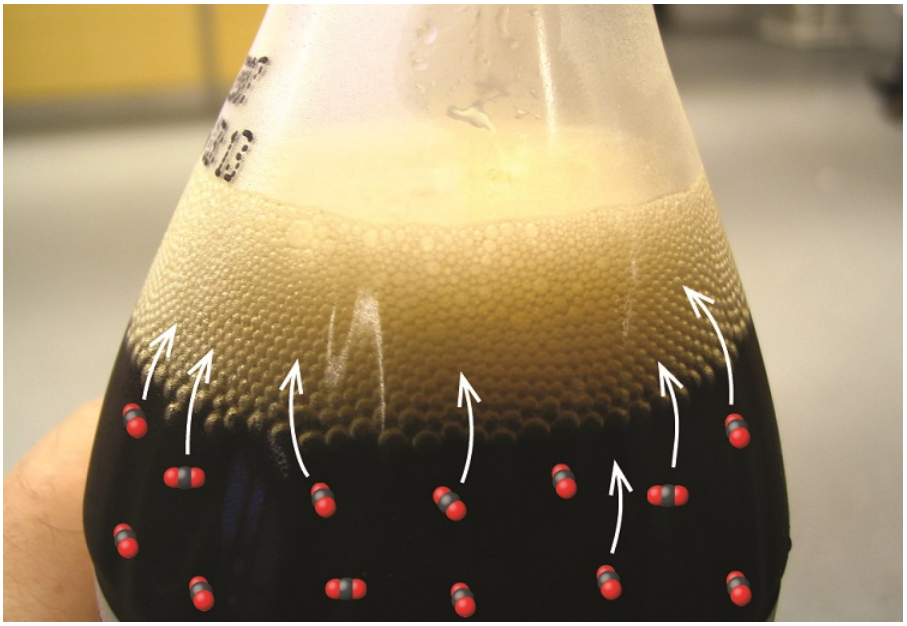
This problem requires the application of Henry's law. The governing equation is $C_g = kP_g$.

$$k = \frac{C_g}{P_g} = \frac{0.70\ g}{1.00\ atm} = 0.70\ g\ atm^{-1} \tag{1.E.5}$$

Under the new conditions, $C_g = 0.70\ g\ atm^{-1} \times 4.00\ atm = 2.80\ g$.

Q11.4.7

Refer to following figure for the following three questions:



a. How did the concentration of dissolved CO_2 in the beverage change when the bottle was opened?
b. What caused this change?
c. Is the beverage unsaturated, saturated, or supersaturated with CO_2?

S11.4.7

(a) It decreased as some of the CO_2 gas left the solution (evidenced by effervescence). (b) Opening the bottle released the high-pressure CO_2 gas above the beverage. The reduced CO_2 gas pressure, per Henry's law, lowers the solubility for CO_2. (c) The dissolved CO_2 concentration will continue to slowly decrease until equilibrium is reestablished between the beverage and the very low CO_2 gas pressure in the opened bottle. Immediately after opening, the beverage, therefore, contains dissolved CO_2 at a concentration greater than its solubility, a nonequilibrium condition, and is said to be supersaturated.

Q11.4.8

The Henry's law constant for CO_2 is $3.4 \times 10^{-2}\ M/atm$ at 25 °C. What pressure of carbon dioxide is needed to maintain a CO_2 concentration of 0.10 M in a can of lemon-lime soda?

S11.4.8

$$P_g = \frac{C_g}{k} = \frac{0.10\ M}{3.4 \times 10^{-2}\ M/atm} = 2.9\ atm \tag{1.E.6}$$

Q11.4.9

The Henry's law constant for O_2 is $1.3 \times 10^{-3}\ M/atm$ at 25 °C. What mass of oxygen would be dissolved in a 40-L aquarium at 25 °C, assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O_2 is 0.21 atm?

S11.4.9

Start with Henry's law

$$C_g = kP_g \tag{1.E.7}$$

and apply it to O_2

$$C(O_2) = (1.3 \times 10^{-3}\ M/atm)(0.21\ atm) = 2.7 \times 10^{-4}\ mol/L \tag{1.E.8}$$

The total amount is \((2.7 \times 10^{-4}\; mol/L)(40\;L=1.08 \times 10^{-2} \;mol\]

The mass of oxygen is $(1.08 \times 10^{-2}\ mol)(32.0\ g/mol) = 0.346\ g$

or, using two significant figures, $0.35\ g$.

Q11.4.10

How many liters of HCl gas, measured at 30.0 °C and 745 torr, are required to prepare 1.25 L of a 3.20-*M* solution of hydrochloric acid?

S11.4.10

First, calculate the moles of HCl needed. Then use the ideal gas law to find the volume required.

M = mol L−1

3.20M=xmol1.25L

x = 4.00 mol HCl

Before using the ideal gas law, change pressure to atmospheres and convert temperature from °C to kelvin.

\[1\;atmx=760torr745torr

x = 0.9803 atm

V=nRTP=(4.000molHCl)(0.08206LatmK−1mol−1)(303.15K)0.9803atm=102 L HCl

102 L HCl

more http://cnx.org/contents/2488fW6W@2/Solubility

11.5: Colligative Properties

Q11.5.1

Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?

Q11.5.2

What is the microscopic explanation for the macroscopic behavior illustrated in [link]?

S11.5.2

The strength of the bonds between like molecules is stronger than the strength between unlike molecules. Therefore, some regions will exist in which the water molecules will exclude oil molecules and other regions will exist in which oil molecules will exclude water molecules, forming a heterogeneous region.

Q11.5.3

Sketch a qualitative graph of the pressure versus time for water vapor above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.

Q11.5.4

A solution of potassium nitrate, an electrolyte, and a solution of glycerin ($C_3H_5(OH)_3$), a nonelectrolyte, both boil at 100.3 °C. What other physical properties of the two solutions are identical?

S11.5.4

Both form homogeneous solutions; their boiling point elevations are the same, as are their lowering of vapor pressures. Osmotic pressure and the lowering of the freezing point are also the same for both solutions.

Q11.5.5

What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

Q11.5.6

What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

S11.5.6

a. Find number of moles of HNO_3 and H_2O in 100 g of the solution. Find the mole fractions for the components.
b. The mole fraction of HNO_3 is 0.378. The mole fraction of H_2O is 0.622.

Q11.5.7

Calculate the mole fraction of each solute and solvent:

a. 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
b. 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
c. 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
d. 25 g of I_2 in 125 g of ethanol, C_2H_5OH

S11.5.7

a. $583\ g\ H_2SO_4 \times \frac{1\ mole\ H_2SO_4}{98.08\ g\ H_2SO_4} = 5.94\ mole\ H_2SO_4$ $\qquad$ $1.50\ kg\ H_2O \times \frac{1000\ g}{1\ kg} \times \frac{1\ mole\ H_2O}{18.02\ g\ H_2O} = 83.2\ moles\ H_2O$

Q11.5.8

Calculate the mole fraction of each solute and solvent:

a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C
b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

S11.5.8

a. $X_{Na_2CO_3} = 0.0119$; $X_{H_2O} = 0.988$;
b. $X_{NH_4NO_3} = 0.9927$; $X_{H_2O} = 0.907$;
c. $X_{Cl_2} = 0.192$; $X_{CH_2Cl_2} = 0.808$;
d. $X_{C_5H_9N} = 0.00426$; $X_{CHCl_3} = 0.997$

Q11.5.9

Calculate the mole fractions of methanol, CH_3OH; ethanol, C_2H_5OH; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)

Q11.5.10

What is the difference between a 1 *M* solution and a 1 *m* solution?

S11.5.10

In a 1 *M* solution, the mole is contained in exactly 1 L of solution. In a 1 *m* solution, the mole is contained in exactly 1 kg of solvent.

Q11.5.11

What is the molality of phosphoric acid, H_3PO_4, in a solution of 14.5 g of H_3PO_4 in 125 g of water?

Q11.5.12

What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

S11.5.12

(a) Determine the molar mass of HNO_3. Determine the number of moles of acid in the solution. From the number of moles and the mass of solvent, determine the molality. (b) 33.7 *m*

Q11.5.13

Calculate the molality of each of the following solutions:

a. 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery
b. 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection
c. 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH
d. 25 g of I_2 in 125 g of ethanol, C_2H_5OH

Q11.5.14

Calculate the molality of each of the following solutions:

a. 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0°C
b. 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack
c. 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2
d. 0.372 g of histamine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

S11.5.14

(a) 6.70×10^{-1} *m*; (b) 5.67 *m*; (c) 2.8 *m*; (d) 0.0358 *m*

Q11.5.15

The concentration of glucose, $C_6H_{12}O_6$, in normal spinal fluid is $\frac{75\text{ mg}}{100\text{ g}}$. What is the molality of the solution?

Q11.5.16

A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3. Calculate the molality of the solution.

S11.5.16

1.08 *m*

Q11.5.17

a. Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?
b. What is the boiling point of a solution of 115.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water?

S11.5.17

a. Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the boiling point of water and the boiling point of the solution; determine the new boiling point.

b. 100.5 °C

Q11.5.18

What is the boiling point of a solution of 9.04 g of I_2 in 75.5 g of benzene, assuming the I_2 is nonvolatile?

Q11.5.19

What is the freezing temperature of a solution of 115.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water, which freezes at 0.0 °C when pure?

S11.5.19

(a) Determine the molar mass of sucrose; determine the number of moles of sucrose in the solution; convert the mass of solvent to units of kilograms; from the number of moles and the mass of solvent, determine the molality; determine the difference between the freezing temperature of water and the freezing temperature of the solution; determine the new freezing temperature. (b) −1.8 °C

Q11.5.20

What is the freezing point of a solution of 9.04 g of I_2 in 75.5 g of benzene?

Q11.5.21

What is the osmotic pressure of an aqueous solution of 1.64 g of $Ca(NO_3)_2$ in water at 25 °C? The volume of the solution is 275 mL.

S11.5.21

(a) Determine the molar mass of $Ca(NO_3)_2$; determine the number of moles of $Ca(NO_3)_2$ in the solution; determine the number of moles of ions in the solution; determine the molarity of ions, then the osmotic pressure. (b) 2.67 atm

Q11.5.22

What is osmotic pressure of a solution of bovine insulin (molar mass, 5700 g mol^{-1}) at 18 °C if 100.0 mL of the solution contains 0.103 g of the insulin?

Q11.5.23

What is the molar mass of a solution of 5.00 g of a compound in 25.00 g of carbon tetrachloride (bp 76.8 °C; K_b = 5.02 °C/*m*) that boils at 81.5 °C at 1 atm?

S11.5.24

(a) Determine the molal concentration from the change in boiling point and K_b; determine the moles of solute in the solution from the molal concentration and mass of solvent; determine the molar mass from the number of moles and the mass of solute. (b) 2.1 × 10^2 g mol^{-1}

Q11.5.25

A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66 °C. Calculate the molar mass of the compound.

Q11.5.26

A 1.0 *m* solution of HCl in benzene has a freezing point of 0.4 °C. Is HCl an electrolyte in benzene? Explain.

S11.5.26

No. Pure benzene freezes at 5.5 °C, and so the observed freezing point of this solution is depressed by ΔT_f = 5.5 − 0.4 = 5.1 °C. The value computed, assuming no ionization of HCl, is ΔT_f = (1.0 m)(5.14 °C/*m*) = 5.1 °C. Agreement of these values supports the assumption that HCl is not ionized.

Q11.5.27

A solution contains 5.00 g of urea, $CO(NH_2)_2$, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?

Q11.5.28

A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at −1.94 °C. Calculate the molar mass of the substance.

S11.5.28

144 g mol^{-1}

Q11.5.29

Arrange the following solutions in order by their decreasing freezing points: 0.1 *m* Na_3PO_4, 0.1 *m* C_2H_5OH, 0.01 *m* CO_2, 0.15 *m* NaCl, and 0.2 *m* $CaCl_2$.

Q11.5.30

Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of NaCl, 0.020 mol of Na_2SO_4, and 0.030 mol of $MgCl_2$, assuming complete dissociation of these electrolytes.

S11.5.30

0.870 °C

Q11.5.31

How could you prepare a 3.08 *m* aqueous solution of glycerin, $C_3H_8O_3$? What is the freezing point of this solution?

Q11.5.32

A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide, CS_2 (K_b = 2.43 °C/*m*). If the boiling point elevation was 0.107 °C, what is the formula of a sulfur molecule in carbon disulfide?

S11.5.32

S_8

Q11.5.33

In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI_2?

Q11.5.34

Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of 1.32×10^{-3} atm at 25 °C. What is the molar mass of lysozyme?

S11.5.34

1.39×10^4 g mol^{-1}

Q11.5.35

The osmotic pressure of a solution containing 7.0 g of insulin per liter is 23 torr at 25 °C. What is the molar mass of insulin?

Q11.5.36

The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, $C_6H_{12}O_6$, is required to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C?

S11.5.36

54 g

Q11.5.37

What is the freezing point of a solution of dibromobenzene, $C_6H_4Br_2$, in 0.250 kg of benzene, if the solution boils at 83.5 °C?

Q11.5.38

What is the boiling point of a solution of NaCl in water if the solution freezes at −0.93 °C?

S11.5.38

100.26 °C

Q11.5.39

The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and K_b for ethanol is 1.20 °C/*m*. What is the molecular formula of fructose?

Q11.5.40

The vapor pressure of methanol, CH_3OH, is 94 torr at 20 °C. The vapor pressure of ethanol, C_2H_5OH, is 44 torr at the same temperature.

a. Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.
b. Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapor pressure of methanol and of ethanol above the solution at 20 °C.
c. Calculate the mole fraction of methanol and of ethanol in the vapor above the solution.

S11.5.40

(a) $X_{CH_3OH} = 0.590$; $X_{C_2H_5OH} = 0.410$; (b) Vapor pressures are: CH_3OH: 55 torr; C_2H_5OH: 18 torr; (c) CH_3OH: 0.75; C_2H_5OH: 0.25

Q11.5.41

The triple point of air-free water is defined as 273.15 K. Why is it important that the water be free of air?

Q11.5.42

Meat can be classified as fresh (not frozen) even though it is stored at −1 °C. Why wouldn't meat freeze at this temperature?

S11.5.42

The ions and compounds present in the water in the beef lower the freezing point of the beef below −1 °C.

Q11.5.43

An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K_f for camphor is 37.7 °C/*m*. What is the molecular formula of the solute? Show your calculations.

Q11.5.44

A sample of $HgCl_2$ weighing 9.41 g is dissolved in 32.75 g of ethanol, C_2H_5OH (K_b = 1.20 °C/*m*). The boiling point elevation of the solution is 1.27 °C. Is $HgCl_2$ an electrolyte in ethanol? Show your calculations.

S11.5.44

$$\Delta bp = K_b m = (1.20\,°C/m)\left(\frac{9.41\text{ g} \times \frac{1\text{ mol } HgCl_2}{271.496\text{ g}}}{0.03275\text{ kg}}\right) = 1.27\,°C$$

The observed change equals the theoretical change; therefore, no dissociation occurs.

https://chem.libretexts.org/@go/page/206916

Q11.5.45

A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about −1.4 °C. What is the formula of the salt? Show your calculations.

11.6: Colloids

Q11.6.1

Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.

S11.6.1

Colloidal System	Dispersed Phase	Dispersion Medium
starch dispersion	starch	water
smoke	solid particles	air
fog	water	air
pearl	water	calcium carbonate ($CaCO_3$)
whipped cream	air	cream
floating soap	air	soap
jelly	fruit juice	pectin gel
milk	butterfat	water
ruby	chromium(III) oxide (Cr_2O_3)	aluminum oxide (Al_2O_3)

Q11.6.2

Distinguish between dispersion methods and condensation methods for preparing colloidal systems.

S11.6.2

Dispersion methods use a grinding device or some other means to bring about the subdivision of larger particles. Condensation methods bring smaller units together to form a larger unit. For example, water molecules in the vapor state come together to form very small droplets that we see as clouds.

Q11.6.3

How do colloids differ from solutions with regard to dispersed particle size and homogeneity?

S11.6.3

Colloidal dispersions consist of particles that are much bigger than the solutes of typical solutions. Colloidal particles are either very large molecules or aggregates of smaller species that usually are big enough to scatter light. Colloids are homogeneous on a macroscopic (visual) scale, while solutions are homogeneous on a microscopic (molecular) scale.

Q11.6.4

Explain the cleansing action of soap.

S11.6.4

Soap molecules have both a hydrophobic and a hydrophilic end. The charged (hydrophilic) end, which is usually associated with an alkali metal ion, ensures water solubility The hydrophobic end permits attraction to oil, grease, and other similar nonpolar substances that normally do not dissolve in water but are pulled into the solution by the soap molecules.

Q11.6.5

How can it be demonstrated that colloidal particles are electrically charged?

S11.6.5

If they are placed in an electrolytic cell, dispersed particles will move toward the electrode that carries a charge opposite to their own charge. At this electrode, the charged particles will be neutralized and will coagulate as a precipitate.

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CHAPTER OVERVIEW

2: Chemical Equilibrium

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General Chemistry

In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

2.0: Prelude to Equilibrium
2.1: Chemical Equilibria
2.2: Free Energy and the Equilibrium Constant
2.3: Equilibrium Constants
2.4: Shifting Equilibria - Le Châtelier’s Principle
2.5: Equilibrium Calculations
2.E: Fundamental Equilibrium Concepts (Exercises)

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2.0: Prelude to Equilibrium

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

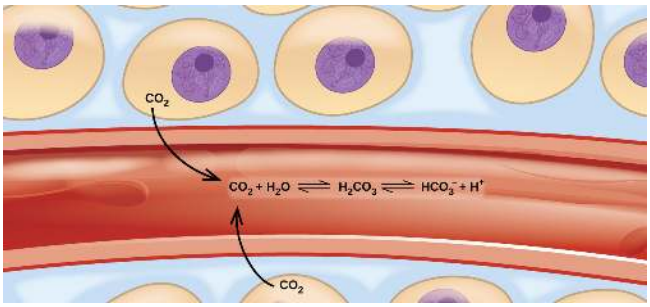


Figure **2.0.1**: Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (HCO_3^-) (Figure **2.0.1**). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

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2.1: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{2.1.1}$$

The color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 2.1.1).

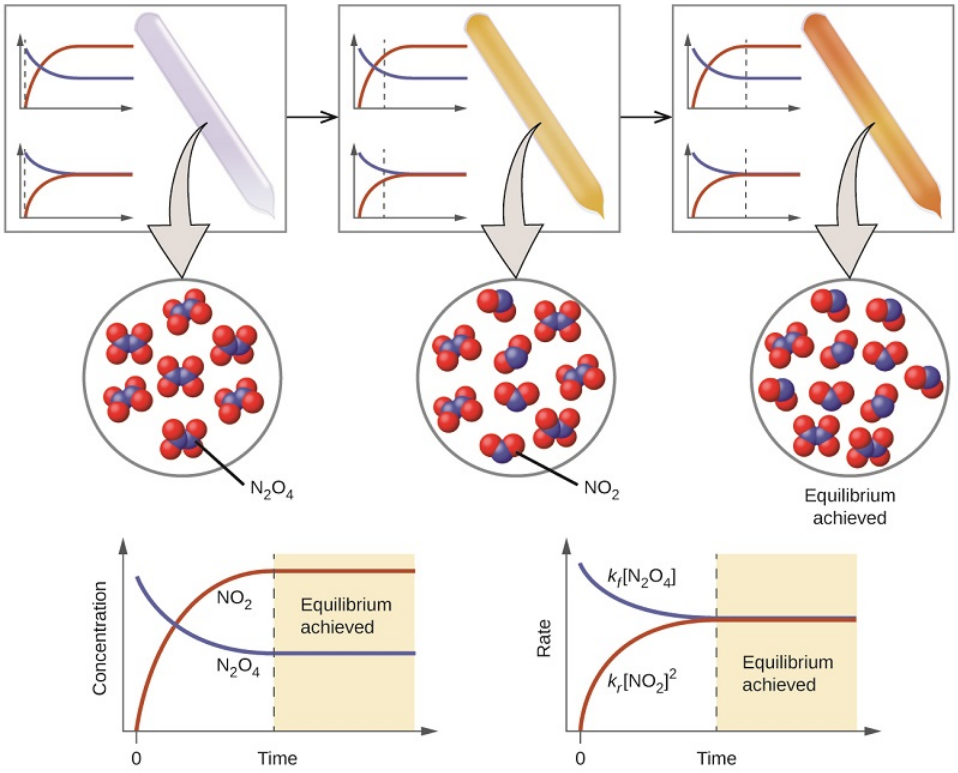


Figure 2.1.1: A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

The formation of NO_2 from N_2O_4 is a reversible reaction, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants.

Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure **2.1.2**).



Figure **2.1.2**: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure **2.1.1**.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure **2.1.1** shows the reaction:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g) \tag{2.1.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure **2.1.1**, the rate of the forward reaction

$$2\,NO_2\,(g) \rightarrow N_2O_4\,(g) \tag{2.1.3}$$

is equal to the rate of the backward reaction

$$N_2O_4\,(g) \rightarrow 2\,NO_2\,(g) \tag{2.1.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$H_2SO_4\,(l) + CaCO_3\,(s) \rightarrow CO_2\,(g) + H_2O\,(l) + CaSO_4\,(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure **2.1.3**). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."



Figure **2.1.3**: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure **2.1.4** shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.



Figure **2.1.4**: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: http://images-of-elements.com/bromine.php).

Contributors

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form

reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

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2.2: Free Energy and the Equilibrium Constant

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously: $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient Q versus the equilibrium constant K. Recall that if Q < K, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if Q > K, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If Q = K, then the system is at equilibrium, and no net reaction occurs. Table **2.2.1** summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table **2.2.1**: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K

*Spontaneous in the reverse direction.

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude of ΔG° and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follow (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{2.2.1}$$

If a reaction is carried out at constant temperature (ΔT = 0), then Equation 2.2.1 simplifies to

$$\Delta G = V\Delta P \tag{2.2.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 2.2.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_f}{P_i}\right) \tag{2.2.3}$$

If the initial state is the standard state with P_i = 1 atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT\ln P \tag{2.2.4}$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{2.2.5}$$

As you will soon discover, Equation 2.2.5 allows us to relate ΔG° and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{2.2.6}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} = (cG_C + dG_D) - (aG_A + bG_B) \tag{2.2.7}$$

Substituting Equation 2.2.5 for each term into Equation 2.2.7,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)] \tag{2.2.8}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) = \Delta G^\circ + RT \ln Q \tag{2.2.9}$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$,), and as you've learned in this chapter, ΔG = 0 for a system at equilibrium. Therefore, we can describe the relationship between ΔG° and K_p for gases as follows:

$$0 = \Delta G^\circ + RT \ln K_p \tag{2.2.10}$$

$$\Delta G^\circ = -RT \ln K_p \tag{2.2.11}$$

If the products and reactants are in their standard states and ΔG° < 0, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if ΔG° > 0, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If ΔG° = 0, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

Example 2.2.1

ΔG° is −32.7 kJ/mol of N_2 for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{2.2.12}$$

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm,
- and T = 100°C.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 2.2.9, calculate Q.
B. Determine if Q is >, <, or = to K

C. Substitute the values of ΔG° and Q into Equation 2.2.9 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 2.2.9. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7} \tag{2.2.13}$$

B Because ΔG° is −, K must be a number greater than 1

C Substituting the values of ΔG° and Q into Equation 2.2.9,

$$\begin{aligned} \Delta G = \Delta G^\circ + RT \ln Q &= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right] \\ &= -32.7 \text{ kJ} + (-44 \text{ kJ}) \\ &= -77 \text{ kJ/mol of } N_2 \end{aligned}$$

Because ΔG < 0 and Q < K (because Q < 1), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

Exercise 2.2.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and P_{NO_2} = 1.00 × 10^{-4} atm. The value of ΔG° for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

Example 2.2.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG° for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 10, ΔG°, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 2.2.11 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 10, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 2.2.11,

$$\Delta G^\circ = -RT \ln K_p \tag{2.2.14}$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_p \tag{2.2.15}$$

Inserting the value of ΔG° and the temperature (25°C = 298 K) into this equation,

$$\ln K_p = -\frac{(-32.7 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.2 \tag{2.2.16}$$

$$K_p = 5.4 \times 10^5 \tag{2.2.17}$$

Thus the equilibrium constant for the formation of ammonia at room temperature is product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

Exercise 2.2.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG° for this reaction is −70.5 kJ/mol of O_2.

Answer

2.2×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of K_p and K in Chapter 15 and showed that they are related:

$$K_p = K(RT)^{\Delta n} \tag{2.2.18}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, Δn = 0, so K_p = K. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 2.2.11 can be written in a more general form:

$$\Delta G° = -RT \ln K \tag{2.2.19}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 2.2.19 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 2.2.19 with $\Delta G° = \Delta H° - T\Delta S°$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K \tag{2.2.20}$$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.*

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 2.2.20, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{2.2.21}$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction (ΔH° < 0), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 2.2.21 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation

2.2.21 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 2.2.21 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \tag{2.2.22}$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \tag{2.2.23}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.2.24}$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature.

Example 2.2.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 13. What is K_p at 500°C? (Use the data from Example 10.)

Given: balanced chemical equation, ΔH°, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvins. Then substitute appropriate values into Equation 2.2.24 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 2.2.24 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2.2.25}$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8 \tag{2.2.26}$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10} \tag{2.2.27}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5} \tag{2.2.28}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 2.2.4

In the exercise in Example 2.2.3, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH°_f values in the exercise in Example 10 to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G° < 0$, then $K > 1$, and products are favored over reactants at equilibrium. Conversely, if $\Delta G° > 0$, then $K < 1$, and reactants are favored over products at equilibrium. If $\Delta G° = 0$, then $K=1$, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and $\Delta H°$ to estimate the equilibrium constant for a reaction at any other temperature.

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2.3: Equilibrium Constants

Learning Objectives

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol (⇌) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$mA + nB + \rightleftharpoons xC + yD \tag{2.3.1}$$

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n} \tag{2.3.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \tag{2.3.3}$$

is given by this expression:

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} \tag{2.3.4}$$

Example 2.3.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,O_{2(g)} \rightleftharpoons 2\,O_{3(g)}$
b. $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$
c. $4\,NH_{3(g)} + 7\,O_{2(g)} \rightleftharpoons 4\,NO_{2(g)} + 6\,H_2O_{(g)}$

Solution

a. $Q_c = \frac{[O_3]^2}{[O_2]^3}$
b. $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
c. $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Exercise 2.3.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
b. $C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g)$
c. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightleftharpoons 8\,CO_2(g) + 10\,H_2O(g)$

Answer a

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Answer b

$$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

Answer c

$$Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 2.3.1). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

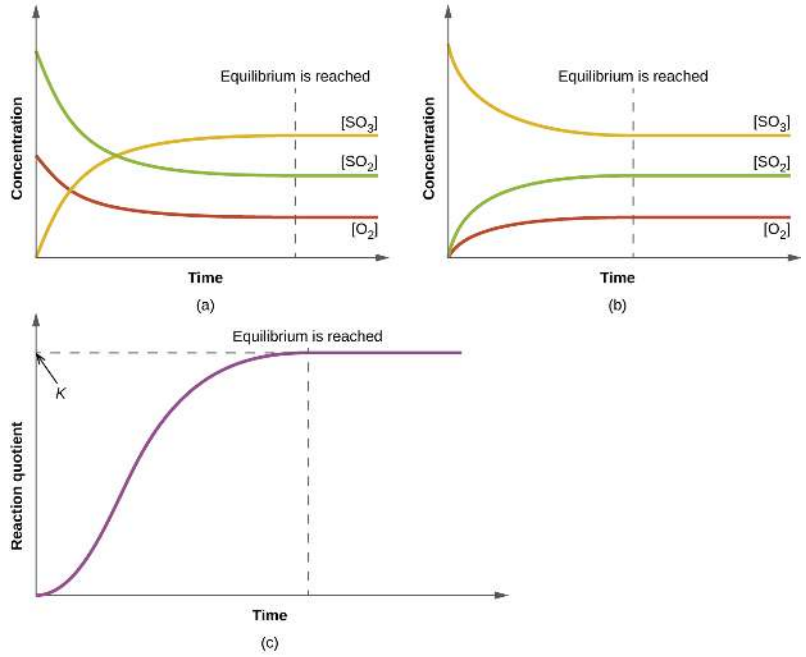


Figure 2.3.1: (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant (K) of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y\ldots}{[A]^m[B]^n\ldots} \tag{2.3.5}$$

This equation is a mathematical statement of the law of mass action: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

✔ Example 2.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, [NO_2] = 0.016 M and [N_2O_4] = 0.042 M.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[NO_2] = \frac{0.10\ \text{mol}}{1.0\ \text{L}} = 0.10\ M$, and [$N_2O_4$] = 0 *M*. Thus,

$$Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0}{0.10^2} = 0 \tag{2.3.6}$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2. \tag{2.3.7}$$

The equilibrium constant is 1.6 × 10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from concentrations instead of actual concentrations, and so K_c values are truly unitless.

Exercise 2.3.2

For the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

the concentrations at equilibrium are [SO_2] = 0.90 *M*, [O_2] = 0.35 *M*, and [SO_3] = 1.1 *M*. What is the value of the equilibrium constant, K_c?

Answer

K_c = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure **2.3.2** illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 0.640 \quad T = 800°C \tag{2.3.8}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure **2.3.2** when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

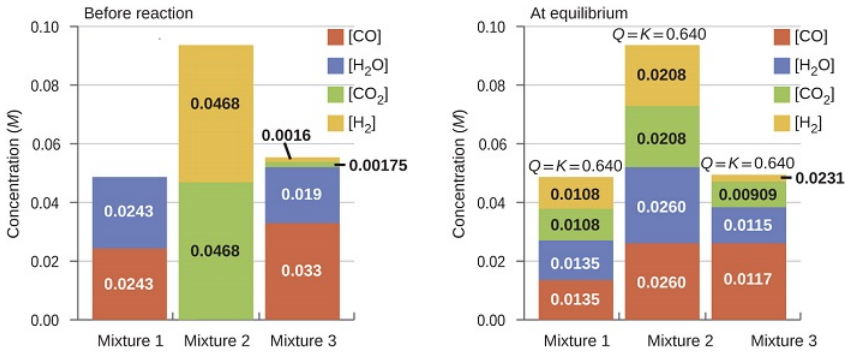


Figure **2.3.2**: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 2.3.8).

Example 2.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$$

with $K_c = 0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.0203 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

? Exercise 2.3.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$$

Answer a

Q_c = 6.45 × 10^3, shifts right.

Answer b

Q_c = 0.12, shifts left.

Answer c

Q_c = 0, shifts right

In Example **2.3.2**, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.

As a consequence of this last consideration, Q_c and K_c expressions do not contain terms for solids or liquids (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$C_2H_2(aq) + 2\,Br_2(aq) \rightleftharpoons C_2H_2Br_4(aq) \tag{2.3.9}$$

with associated equilibrium constant

$$K_c = \frac{[C2H2Br4]}{[C2H2][Br2]^2} \tag{2.3.10}$$

Example 2

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{2.3.11}$$

with associated equilibrium constant

$$K_c = \frac{[I3-]}{[I2][I-]} \tag{2.3.12}$$

Example 3

$$\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H_3O^+}(aq) \rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\,\mathrm{H_2O}(l) \tag{2.3.13}$$

with associated equilibrium constant

$$K_c = \frac{[Hg^2+]^2[HNO2]}{[Hg2^2+][NO3-][H3O+]^3} \tag{2.3.14}$$

Example 4

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \tag{2.3.15}$$

with associated equilibrium constant

$$K_c = \frac{[H3O+][F-]}{[HF]} \tag{2.3.16}$$

Example 5

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{2.3.17}$$

with associated equilibrium constant

$$K_c = \frac{[NH4+][OH-]}{[NH3]} \tag{2.3.18}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, its concentration **does not** appear as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{2.3.19}$$

with associated equilibrium constant

$$K_c = \frac{[C2H4][H2]}{[C2H6]} \tag{2.3.20}$$

Example 2

$$3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{O_3}(g) \tag{2.3.21}$$

with associated equilibrium constant

$$K_c = \frac{[O3]^2}{[O2]^3} \tag{2.3.22}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{2.3.23}$$

with associated equilibrium constant

$$K_c = \frac{[NH3]^2}{[N2][H2]^3} \tag{2.3.24}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{2.3.25}$$

with associated equilibrium constant

$$K_c = \frac{[CO2]^3[H2O]^4}{[C3H8][O2]^5} \tag{2.3.26}$$

Note that the concentration of $\mathrm{H_2O}_{(g)}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{2.3.27}$$

$$P = \left(\frac{n}{V}\right) RT \tag{2.3.28}$$

$$= MRT \tag{2.3.29}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{2.3.30}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{2.3.31}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of C_2H_6; $P_{\mathrm{H_2}}$, the partial pressure of H_2; and $P_{\mathrm{C_2H_6}}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{2.3.32}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{2.3.33}$$

with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \tag{2.3.34}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \tag{2.3.35}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \tag{2.3.36}$$

$$= K_c(RT)^{(x+y)-(m+n)} \tag{2.3.37}$$

$$= K_c(RT)^{\Delta n} \tag{2.3.38}$$

The relationship between K_c and K_P is

$$K_P = K_c(RT)^{\Delta n} \tag{2.3.39}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$, we have

$$\Delta n = (x + y) - (m + n) \tag{2.3.40}$$

Example 2.3.4: Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$
b. $\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$
c. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g) \tag{2.3.41}$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1 = K_c\,(RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^0 = K_c$$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-2} = \frac{K_c}{(RT)^2}$$

d) $K_P = K_c\,(\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Exercise 2.3.4

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
b. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$
c. $\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g)$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$\mathrm{CH_3OH}(g) \rightleftharpoons \mathrm{CO}(g) + 2\,\mathrm{H_2}(g) \tag{2.3.42}$$

What would be the value of K_P at this temperature?

Answer a

$K_P = K_c\,(RT)^{-1}$

Answer b

$K_P = K_c\,(RT)$

Answer c

$K_P = K_c (RT)$;

Answer d

160 or 1.6×10^2

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$\mathrm{PbCl_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \tag{2.3.43}$$

with associated equilibrium constant

$$K_c = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \tag{2.3.44}$$

Example 1

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{2.3.45}$$

with associated equilibrium constant

$$K_c = \frac{1}{[\mathrm{CO_2}]} \tag{2.3.46}$$

Example 1

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{2.3.47}$$

with associated equilibrium constant

$$K_c = \frac{[CS2]}{[S]^2} \tag{2.3.48}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g) \tag{2.3.49}$$

with associated equilibrium constant

$$K_c = [\mathrm{Br_2}] \tag{2.3.50}$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using **partial pressures** instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{2.3.51}$$

with associated equilibrium constant

$$K_P = \frac{1}{P_{\mathrm{CO_2}}} \tag{2.3.52}$$

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{2.3.53}$$

with associated equilibrium constant

$$K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{2.3.54}$$

Summary

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

Key Equations

- $Q = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_P = K_c\,(RT)^{\Delta n}$

Glossary

equilibrium constant (K)
value of the reaction quotient for a system at equilibrium

heterogeneous equilibria
equilibria between reactants and products in different phases

homogeneous equilibria
equilibria within a single phase

K_c
equilibrium constant for reactions based on concentrations of reactants and products

K_P
equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

law of mass action
when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (Q)
ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

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2.4: Shifting Equilibria - Le Châtelier's Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure **2.4.1** is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 2.4.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $\mathbf{Fe^{3+}}(aq) + \mathbf{SCN^-}(aq) \rightleftharpoons \mathbf{Fe(SCN)^{2+}}(aq)$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $\mathbf{Ag^+}(aq) + \mathbf{SCN^-}(aq) \rightleftharpoons \mathbf{AgSCN}(s)$. *The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the* $Fe(SCN)^{2+}$. *(credit: modification of work by Mark Ott).*

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathbf{H_{2(g)}} + \mathbf{I_{2(g)}} \rightleftharpoons 2\,\mathbf{HI}_{(g)} \tag{2.4.1}$$

$$K_c = 50.0 \text{ at } 400°\text{C} \tag{2.4.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[\mathbf{H_2}] = [\mathbf{I_2}] = 0.221\ M$ and $[\mathbf{HI}] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If $\mathbf{H_2}$ is introduced into the system so quickly that its

concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{2.4.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \tag{2.4.4}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \tag{2.4.5}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \quad \Delta H = -9.4\ \text{kJ (exothermic)} \tag{2.4.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) + \text{heat} \tag{2.4.7}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of $\mathbf{H_2}$ and $\mathbf{I_2}$ and a reduction in the concentration of **HI**. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the **HI** system increases the equilibrium constant: At the new equilibrium the concentration of **HI** has increased and the concentrations of $\mathbf{H_2}$ and $\mathbf{I_2}$ decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between $\mathbf{NO_2}$ and $\mathbf{N_2O_4}$ in this reaction

$$\mathbf{N_2O_4(g)} \rightleftharpoons \mathbf{2\,NO_2(g)} \quad \Delta H = 57.20\ \mathbf{kJ} \tag{2.4.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathbf{heat + N_2O_4(g)} \rightleftharpoons \mathbf{2\,NO_2(g)} \tag{2.4.9}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathbf{NO_2}$ molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless $\mathbf{N_2O_4}$ increases, and the concentration of brown $\mathbf{NO_2}$ decreases, causing the brown color to fade.

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$\mathbf{N_2(g) + 3\,H_2(g)} \rightleftharpoons \mathbf{2\,NH_3(g)} \tag{2.4.10}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.4.11}$$

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen ($\mathrm{N_2}$) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.4.12}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)} \quad \Delta H = -92.2\ \mathrm{kJ} \tag{2.4.13}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure **2.4.2**).

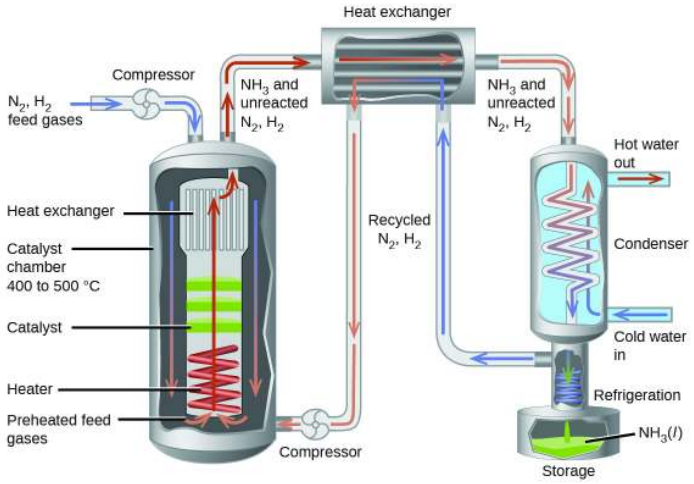


Figure **2.4.2**: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Table **2.4.1**: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

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2.5: Equilibrium Calculations

Learning Objectives

- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \tag{2.5.1}$$

If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 M, the change in the N_2 concentration, $\Delta[N_2]$, the final concentration minus the initial concentration, is 0.11 M. The change is positive because the concentration of N_2 increases.

The change in the H_2 concentration, $\Delta[H_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

$$\begin{aligned}\Delta[\mathrm{H_2}] &= 3 \times \Delta[\mathrm{N_2}] \\ &= 3 \times (0.11\ M) \\ &= 0.33\ M\end{aligned}$$

The change in concentration of NH_3, $\Delta[NH_3]$, is twice that of $\Delta[N_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is negative because the concentration of ammonia *decreases* as it decomposes.

$$\begin{aligned}\Delta[\mathrm{NH_3}] &= -2 \times \Delta[\mathrm{N_2}] \\ &= -2 \times (0.11\ M) \\ &= -0.22\ M\end{aligned}$$

We can relate these relationships directly to the coefficients in the equation

$$\begin{array}{ccccc} 2\,\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\,\mathrm{H_2}(g) \\ \Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] & & \Delta[\mathrm{N_2}] = 0.11\ M & & \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \end{array} \tag{2.5.2}$$ (2.5.3)

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2, we could represent it by the symbol x.

$$\Delta[\mathrm{N_2}] = x$$

The changes in the other concentrations would then be represented as:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$

$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \tag{2.5.4}$$
$$-2x \qquad x \qquad 3x \tag{2.5.5}$$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 2.5.1: Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{2.5.6}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{2.5.7}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{2.5.8}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad x \tag{2.5.9}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{2.5.10}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{2.5.11}$$

Solution

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{2.5.12}$$
$$x \qquad 2x \qquad -x \tag{2.5.13}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{2.5.14}$$
$$-x \qquad -x \qquad x \tag{2.5.15}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{2.5.16}$$
$$x \qquad 5x \qquad -3x \qquad -4x \tag{2.5.17}$$

Exercise 2.5.1

Complete the changes in concentrations for each of the following reactions:

(a)

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \tag{2.5.18}$$
$$\_\_\_\_ \qquad x \qquad \_\_\_\_ \tag{2.5.19}$$

(b)

$$C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g) \tag{2.5.20}$$
$$\_\_\_\_ \qquad -2x \tag{2.5.21}$$

(c)

$$4\,NH_3(g) + 7\,H_2O(g) \rightleftharpoons 4\,NO_2(g) + 6\,H_2O(g) \tag{2.5.22}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{2.5.23}$$

Answer a

$2x$, x, $-2x$

Answer b

x, $-2x$

Answer c

$4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant**. If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations**. If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations**. If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_P, K_P, and partial pressure. We will look at solving each of these cases in sequence.

Calculation of an Equilibrium Constant

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

Example **2.5.1** showed us how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE table—for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the initial concentrations of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the change that occurs as the system shifts toward equilibrium—do not forget to consider the reaction stoichiometry as described in a previous section of this chapter. The last row contains the concentrations once equilibrium has been reached.

Example 2.5.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{2.5.24}$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2.

	I_2	+	I^-	$\rightleftharpoons$	I_3^-
Initial concentration (M)	1.000×10^{-3}		1.000×10^{-3}		0
Change (M)	$-x$		$-x$		$+x$
Equilibrium concentration (M)	$1.000 \times 10^{-3} - x$		$1.000 \times 10^{-3} - x$		x

Since the equilibrium concentration of I_2 is given, we can solve for x. At equilibrium the concentration of I_2 is 6.61×10^{-4} M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$= 3.39 \times 10^{-4}\ M$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x = -3.39 \times 10^{-4}$	$-x$	$+x$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

We now calculate the value of the equilibrium constant.

$$K_c = Q_c = \frac{[I3-]}{[I2][I-]}$$

$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

Exercise 2.5.2

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Answer

$K_c = 4$

Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example 2.5.3: Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, $[N_2]$ = 0.036 mol/L and $[O_2]$ 0.0089 mol/L.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_c = Q_c = \frac{[NO]^2}{[N2][O2]}$$

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$Q_c = \frac{[NO]^2}{[N2][O2]}$$

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

$$= 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

? Exercise 2.5.3

The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer

1.53 mol/L

Calculation of Changes in Concentration

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
   - Write a balanced chemical equation for the reaction.
   - If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
   - Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol *x* and express the other changes in terms of the smallest change.
   - Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
   - Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for *x*, and check any assumptions used to find *x*.
   - Calculate the equilibrium concentrations.
4. Check the arithmetic.
   - Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.

In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example 2.5.4: Calculation of Concentration as a Reaction Equilibrates

Under certain conditions, the equilibrium constant for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 *M*?

Solution

Use the stepwise process described earlier.

1. *Determine the direction the reaction proceeds.*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.

- *Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \tag{2.5.25}$$
$$-x \qquad x \qquad x \tag{2.5.26}$$

- The changes in concentration and the expressions for the equilibrium concentrations are:

	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	$0 + x = x$	$0 + x = x$

- *Solve for the change and the equilibrium concentrations.*

$$K_c = \frac{[PCl3][Cl2]}{[PCl5]} = 0.0211$$
$$= \frac{(x)(x)}{(1.00 - x)}$$

This equation contains only one variable, *x*, the change in concentration. We can write the equation as a quadratic equation and solve for *x* using the quadratic formula.

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$
$$0.0211(1.00 - x) = x^2$$
$$x^2 + 0.0211x - 0.0211 = 0$$

An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for *x*:

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

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for *a*, *b*, and *c* yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$
$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$
$$= \frac{-0.0211 \pm 0.291}{2}$$

Hence

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

Quadratic equations often have two different solutions, one that is physically possible and one that is physically impossible (an extraneous root). In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, x = 0.135 M.

The equilibrium concentrations are

$[PCl_5] = 1.00 - 0.135 = 0.87\ M$
$[PCl_3] = x = 0.135\ M$
$[Cl_2] = x = 0.135\ M$

- *Check the arithmetic.*

$$K_c = \frac{[PCl3][Cl2]}{[PCl5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations check.

? Exercise 2.5.4A

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 M in CH_3CO_2H, 0.15 M in C_2H_5OH, 0.40 M in $CH_3CO_2C_2H_5$, and 0.40 M in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Answer

$[CH_3CO_2H]$ = 0.36 M, $[C_2H_5OH]$ = 0.36 M, $[CH_3CO_2C_2H_5]$ = 0.17 M, $[H_2O]$ = 0.17 M

? Exercise 2.5.4B

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, [HI] = 1.88 M

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products.

Consider the ionization of 0.150 M HA, a weak acid.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \quad K_c = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the "all reactant" starting point. Using x for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$		
Initial concentration (*M*)	0.150	0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.150 - x$	x	x

Setting up and solving the quadratic equation gives

$$K_c = \frac{[H+][A-]}{[HA]} = \frac{(x)(x)}{(0.150-x)} = 6.80 \times 10^{-4}$$
$$x^2 + 6.80 \times 10^{-4}x - 1.02 \times 10^{-4} = 0$$
$$x = -6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}(2)(1)$$
$$x = 0.00977\ M \text{ or } -0.0104\ M$$

Using the positive (physical) root, the equilibrium concentrations are

$$[\mathrm{HA}] = 0.150 - x = 0.140\ M$$
$$[\mathrm{H^+}] = [\mathrm{A^-}] = x = 0.00977\ M$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the "all product" starting point. Assuming all of the HA ionizes gives

$$[\mathrm{HA}] = 0.150 - 0.150 = 0\ M$$
$$[\mathrm{H^+}] = 0 + 0.150 = 0.150\ M$$
$$[\mathrm{A^-}] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and "*y*" to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$		
Initial concentration (*M*)	0	0.150	0.150
Change (*M*)	$+y$	$-y$	$-y$
Equilibrium concentration (*M*)	y	$0.150 - y$	$0.150 - y$

Setting up and solving the quadratic equation gives

$$K_c = \frac{[H+][A-]}{[HA]} = \frac{(0.150-y)(0.150-y)}{(y)} = 6.80 \times 10^{-4}$$
$$6.80 \times 10^{-4}y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$
$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$
$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$$y = 0.160\ M \text{ or } y = 0.140\ M$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[\mathrm{HA}] = y = 0.140\ M$$
$$[\mathrm{H^+}] = 0.150 - y = 0.010\ M$$
$$[\mathrm{A^-}] = 0.150 - y = 0.010\ M$$

Thus, the two approaches give the same results (to three *decimal places*), and show that *both* starting points lead to the same equilibrium conditions. The "all reactant" starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the "all product" starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts "close" to equilibrium will require only a "small" change in conditions (x) to reach equilibrium.

Recall that a small K_c means that very little of the reactants form products and a large K_c means that most of the reactants form products. If the system can be arranged so it starts "close" to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example 2.5.5: Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CN^-}(aq) \quad K_c = 4.9 \times 10^{-10} \tag{2.5.27}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

	$\mathrm{HCN}(aq) \rightleftharpoons$	$\mathrm{H^+}(aq)$ +	$\mathrm{CN^-}(aq)$
Initial concentration (M)	0.15	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.15 - x$	x	x

The exact solution may be obtained using the quadratic formula with

$$K_c = \frac{(x)(x)}{0.15 - x} \tag{2.5.28}$$

solving

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0 \tag{2.5.29}$$

$$x = 8.56 \times 10^{-6}\ M\ (3\ \text{sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2\ \text{sig. figs.}) \tag{2.5.30}$$

Thus $[\mathrm{H^+}] = [\mathrm{CN^-}] = x = 8.6 \times 10^{-6}\ M$ and $[\mathrm{HCN}] = 0.15 - x = 0.15\ M$.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, x must be small compared to 0.15 M. More formally, if $x \ll 0.15$, then $0.15 - x \approx 0.15$. If this assumption is true, then it simplifies obtaining x

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15} \tag{2.5.31}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15} \tag{2.5.32}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11} \tag{2.5.33}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M \tag{2.5.34}$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF $(0.15 - x) \approx 0.15\ M$, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\% \tag{2.5.35}$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

Exercise 2.5.5

What are the equilibrium concentrations in a 0.25 *M* NH_3 solution?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_c = 1.8 \times 10^{-5}$$

Assume that *x* is much less than 0.25 M and calculate the error in your assumption.

Answer

$[OH^-] = [NH_4^+] = 0.0021\ M$; [$NH_3$] = 0.25 *M*, error = 0.84%

The second example requires that the original information be processed a bit, but it still can be solved using a small *x* approximation.

Example 2.5.6: Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \quad K_c = 5.0 \times 10^{13} = \frac{[Cu(NH3)4^2+]}{[Cu^2+(aq)][NH3]^4} \tag{2.5.36}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 *M* NH_3 what are the concentrations when the system comes to equilibrium?

Solution The initial concentration of copper(II) is 0.010 *M*. The equilibrium constant is very large so it would be better to start with as much product as possible because "all products" is much closer to equilibrium than "all reactants." Note that Cu^{2+} is the limiting reactant; if all 0.010 *M* of it reacts to form product the concentrations would be

$$[Cu^{2+}] = 0.010 - 0.010 = 0\ M \tag{2.5.37}$$

$$[Cu(NH_3)_4{}^{2+}] = 0.010\ M \tag{2.5.38}$$

$$[NH_3] = 1.00 - 4 \times 0.010 = 0.96\ M \tag{2.5.39}$$

Using these "shifted" values as initial concentrations with *x* as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \rightleftharpoons$	$Cu(NH_3)_4{}^{2+}(aq)$
Initial concentration (*M*)	0	0.96	0.010
Change (*M*)	+*x*	+4*x*	−*x*
Equilibrium concentration (*M*)	*x*	0.96 + 4*x*	0.010 − *x*

Since we are starting close to equilibrium, *x* should be small so that

$$0.96 + 4x \approx 0.96\ M$$
$$0.010 - x \approx 0.010\ M$$
$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$
$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[Cu^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[NH_3] = 0.96 - 4x = 0.96\ M$$
$$[Cu(NH_3)_4{}^{2+}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (x) was very small. With only a small change required to get to equilibrium, the equation for x was greatly simplified and gave a valid result well within the 5% error maximum.

? Exercise 2.5.6

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 M NH_3 solution?

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6{}^{2+}(aq)$$

with $K_c = 5.5 \times 10^8$.

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (x) of the product shifts left. Calculate the error in your assumption.

Answer

$[Ni(NH_3)_6{}^{2+}] = 0.25\ M$, $[NH_3]$ = 0.50 M, $[Ni^{2+}] = 2.9 \times 10^{-8}$ M, error = 1.2×10^{-5}%

Summary

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of X is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium.

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2.E: Fundamental Equilibrium Concepts (Exercises)

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13.1: Chemical Equilibria Exercises

Q13.1.1

What does it mean to describe a reaction as “reversible”?

S13.1.1

The reaction can proceed in both the forward and reverse directions.

Q13.1.2

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

Q13.1.3

If a reaction is reversible, when can it be said to have reached equilibrium?

S13.1.3

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.

Q13.1.4

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

Q13.1.5

If the concentrations of products and reactants are equal, is the system at equilibrium?

S13.1.5

The concept of equilibrium does not imply equal concentrations, though it is possible.

13.2: Equilibrium Constant Exercises

Q13.2.1

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Q13.2.2

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown below:



S13.2.2

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

Q13.2.3

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

\[\ce{2NO2}(g) \rightleftharpoons \ce{N2O4}(g)\]

Q13.2.4

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

Q13.2.5

1. (a) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{AgCl}(s) \rightleftharpoons \mathbf{Ag^+}(aq) + \mathbf{Cl^-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
2. (b) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{Pb^{2+}}(aq) + \mathbf{2\,Cl^-}(aq) \rightleftharpoons \mathbf{PbCl_2}(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

S13.2.5

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \dfrac{1}{[Pb^2+][Cl-]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

Q13.2.6

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{CaCO_3}(s) \rightleftharpoons \mathbf{Ca^{2+}}(aq) + \mathbf{CO_3^-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{3\,Ba^{2+}}(aq) + \mathbf{2\,PO_4^{3-}}(aq) \rightleftharpoons \mathbf{Ba_3(PO_4)_2}(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

Q13.2.7

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $\mathbf{3\,C_2H_2}(g) \longrightarrow \mathbf{C_6H_6}(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

S13.2.7

Since $K_c = \dfrac{[C6H6]}{[C2H2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

Q13.2.8

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $\mathbf{KI}(aq) + \mathbf{I_2}(aq) \rightleftharpoons \mathbf{KI_3}(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

Q13.2.9

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

S13.2.9

$K_c > 1$

Q13.2.10

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

Q13.2.11

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{CH_4}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{CH_3Cl}(g) + \mathrm{HCl}(g)$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$
c. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
d. $\mathrm{BaSO_3}(s) \rightleftharpoons \mathrm{BaO}(s) + \mathrm{SO_2}(g)$
e. $\mathrm{P_4}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{P_4O_{10}}(s)$
f. $\mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{Br}(g)$
g. $\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$
h. $\mathrm{CuSO_4 \cdot 5\,H_2O}(s) \rightleftharpoons \mathrm{CuSO_4}(s) + 5\,\mathrm{H_2O}(g)$

S13.2.11

(a) $Q_c = \frac{[CH3Cl][HCl]}{[CH4][Cl2]}$; (b) $Q_c = \frac{[NO]^2}{[N2][O2]}$; (c) $Q_c = \frac{[SO3]^2}{[SO2]^2[O2]}$; (d) $Q_c = [\mathrm{SO_2}]$; (e) $Q_c = \frac{1}{[P4][O2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br2]}$; (g) $Q_c = \frac{[CO2]}{[CH4][O2]^2}$; (h) $Q_c = [\mathrm{H_2O}]^5$

Q13.2.12

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
b. $4\,\mathrm{NH_3}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 4\,\mathrm{NO}(g) + 6\,\mathrm{H_2O}(g)$
c. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$
d. $\mathrm{CO_2}(g) + \mathrm{H_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2O}(g)$
e. $\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g)$
f. $2\,\mathrm{Pb(NO_3)_2}(s) \rightleftharpoons 2\,\mathrm{PbO}(s) + 4\,\mathrm{NO_2}(g) + \mathrm{O_2}(g)$
g. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{H_2O}(l)$
h. $\mathrm{S_8}(g) \rightleftharpoons 8\,\mathrm{S}(g)$

S13.2.12

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$ $K_c = 17$; $[\mathrm{NH_3}] = 0.20\ M$, $[\mathrm{N_2}] = 1.00\ M$, $[\mathrm{H_2}] = 1.00\ M$
b. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$ $K_P = 6.8 \times 10^4$; initial pressures: $\mathrm{NH_3} = 3.0$ atm, $\mathrm{N_2} = 2.0$ atm, $\mathrm{H_2} = 1.0$ atm
c. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ $K_c = 0.230$; $[\mathrm{SO_3}] = 0.00\ M$, $[\mathrm{SO_2}] = 1.00\ M$, $[\mathrm{O_2}] = 1.00\ M$
d. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ $K_P = 16.5$; initial pressures: $\mathrm{SO_3} = 1.00$ atm, $\mathrm{SO_2} = 1.00$ atm, $\mathrm{O_2} = 1.00$ atm
e. $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g)$ $K_c = 4.6 \times 10^4$; $[\mathrm{NO}] = 1.00\ M$, $[\mathrm{Cl_2}] = 1.00\ M$, $[\mathrm{NOCl}] = 0\ M$
f. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$ $K_P = 0.050$; initial pressures: $\mathrm{NO} = 10.0$ atm, $\mathrm{N_2} = \mathrm{O_2} = 5$ atm

S13.2.13

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

Q13.2.14

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ $K_c = 17$; [NH_3] = 0.50 *M*, [N_2] = 0.15 *M*, [H_2] = 0.12 *M*
b. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ $K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm
c. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_c = 0.230$; [SO_3] = 2.00 *M*, [SO_2] = 2.00 *M*, [O_2] = 2.00 *M*
d. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_P = 6.5$ atm; initial pressures: SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm
e. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$ $K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm
f. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $K_c = 0.050$; [N_2] = 0.100 *M*, [O_2] = 0.200 *M*, [NO] = 1.00 *M*

Q13.2.15

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

\[\ce{N2}(g)+\ce{3H2}(g) \rightleftharpoons \ce{2NH3}(g)\]

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52

S13.2.15

The system will shift toward the reactants to reach equilibrium.

Q13.2.16

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

\(\ce{SO2Cl2}(g) \rightleftharpoons \ce{SO2}(g)+\ce{Cl2}(g)\)

[SO_2Cl_2] = 0.12 *M*, [Cl_2] = 0.16 *M* and [SO_2] = 0.050 *M*. K_c for the reaction is 0.078.

Q13.2.17

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

S13.2.17

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

Q13.2.18

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

S13.2.19

This situation occurs in (a) and (b).

Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

Q13.2.20

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_c = 0.50$ at 400°C
b. $H_2 + I_2 \rightleftharpoons 2\,HI$ $K_c = 50.2$ at 448°C
c. $Na_2SO_4 \cdot 10\,H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10\,H_2O(g)$ $K_P = 4.08 \times 10^{-25}$ at 25°C
d. $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.122$ at 50°C

S13.2.20

(a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

Q13.2.21

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $\mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{BrCl}(g) \quad K_c = 4.7 \times 10^{-2}$ at 25°C
b. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g) \quad K_P = 48.2$ at 500°C
c. $\mathrm{CaCl_2 \cdot 6\,H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s) + 6\,\mathrm{H_2O}(g) \quad K_P = 5.09 \times 10^{-44}$ at 25°C
d. $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad K_P = 0.196$ at 60°C

Q13.2.22

What is the value of the equilibrium constant expression for the change $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g)$ at 30 °C?

S13.2.22

$$K_P = P_{\mathrm{H_2O}} = 0.042. \tag{2.E.1}$$

Q13.2.23

Write the expression of the reaction quotient for the ionization of HOCN in water.

Q13.2.24

Write the reaction quotient expression for the ionization of NH_3 in water.

S13.2.24

$$Q_c = \frac{[NH4+][OH-]}{[HN3]} \tag{2.E.2}$$

Q13.2.25

What is the approximate value of the equilibrium constant K_P for the change $\mathrm{C_2H_5OC_2H_5}(l) \rightleftharpoons \mathrm{C_2H_5OC_2H_5}(g)$ at 25 °C. (Vapor pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

13.3: Shifting Equilbria Exercises

Q13.3.1

The following equation represents a reversible decomposition:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

S13.3.1

The amount of $CaCO_3$ must be so small that $P_{\mathrm{CO_2}}$ is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full $P_{\mathrm{CO_2}}$ required for equilibrium.

Q13.3.2

Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

Q13.3.3

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

S13.3.3

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the

reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

Q13.3.4

What would happen to the color of the solution in part (b) of Figure if a small amount of NaOH were added and Fe(OH)3 precipitated? Explain your answer.

Q13.3.5

The following reaction occurs when a burner on a gas stove is lit:

\(\ce{CH4}(g)+\ce{2O2}(g)\rightleftharpoons\ce{CO2}(g)+\ce{2H2O}(g)\)

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

S13.3.5

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

Q13.3.6

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO3, from sulfur dioxide, SO2, and oxygen, O2, shown here. At high temperatures, the rate of formation of $SO_3$is higher, but the equilibrium amount (concentration or partial pressure) of SO3 is lower than it would be at lower temperatures.

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \tag{2.E.3}$$

a. (a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
b. (b) Is the reaction endothermic or exothermic?

Q13.3.7a

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

\[\ce{N2}(g)+\ce{2H2}(g)\rightleftharpoons\ce{N2H4}(g) \hspace{20px} \Delta H=\ce{95\:kJ}\]

S13.3.7a

Add N_2; add H_2; decrease the container volume; heat the mixture.

Q13.3.7b

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6\,H_2(g) \rightleftharpoons 4\,PH_3(g) \quad \Delta H = 110.5\,kJ \tag{2.E.4}$$

Q13.3.8

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad \Delta H = 92\,kJ$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\,kJ$
c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g) \quad \Delta H = -285\,kJ$
d. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad \Delta H = -176\,kJ$

S13.3.8

(a) ΔT increase = shift right, ΔP increase = shift left; (b) ΔT increase = shift right, ΔP increase = no effect; (c) ΔT increase = shift left, ΔP increase = shift left; (d) ΔT increase = shift left, ΔP increase = shift right.

Q13.3.9

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g) \quad \Delta H = 484\ kJ$
b. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad \Delta H = -92.2\ kJ$
c. $2\,Br(g) \rightleftharpoons Br_2(g) \quad \Delta H = -224\ kJ$
d. $H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g) \quad \Delta H = 53\ kJ$

Q13.3.10

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g). \tag{2.E.5}$$

Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2\,H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90.2\ kJ \tag{2.E.6}$$

b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
c. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?
d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
e. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?
f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

S13.3.10

a. $K_c = \dfrac{[CH3OH]}{[H2]^2[CO]}$;
b. [H_2] increases, [CO] decreases, [CH_3OH] increases;
c. [H_2] increases, [CO] decreases, [CH_3OH] decreases;
d. [H_2] increases, [CO] increases, [CH_3OH] increases;
e. [H_2] increases, [CO] increases, [CH_3OH] decreases;
f. no changes.

Q13.3.11

Nitrogen and oxygen react at high temperatures.

a. Write the expression for the equilibrium constant (Kc) for the reversible reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\ kJ \tag{2.E.7}$$

b. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?
c. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?
d. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?
e. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?
g. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

Q13.3.12

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

a. Write the expression for the equilibrium constant for the reversible reaction

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \quad \Delta H = 131.30\ \mathrm{kJ} \tag{2.E.8}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more C is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if CO is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

S13.3.12

(a) $K_c = \frac{[CO][H2]}{[H2O]}$; (b) [$H_2O$] no change, [CO] no change, [H_2] no change; (c) [H_2O] decreases, [CO] decreases, [H_2] decreases; (d) [H_2O] increases, [CO] increases, [H_2] decreases; (f) [H_2O] decreases, [CO] increases, [H_2] increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

Q13.3.13

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$\mathrm{Fe_2O_3}(s) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{Fe}(s) + 3\,\mathrm{H_2O}(g) \quad \Delta H = 98.7\ \mathrm{kJ} \tag{2.E.9}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Q13.3.14

Ammonia is a weak base that reacts with water according to this equation:

\[\ce{NH3}(aq)+\ce{H2O}(l)\rightleftharpoons\ce{NH4+}(aq)+\ce{OH-}(aq)\]

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water and why?

a. Addition of NaOH
b. Addition of HCl
c. Addition of NH_4Cl

S13.3.14

Only (b)

Q13.3.15

Acetic acid is a weak acid that reacts with water according to this equation:

\[\ce{CH3CO2H}(aq)+\ce{H2O}(aq)\rightleftharpoons\ce{H3O+}(aq)+\ce{CH3CO2-}(aq)\]

Will any of the following increase the percent of acetic acid that reacts and produces $\mathrm{CH_3CO_2^-}$ ion?

a. Addition of HCl
b. Addition of NaOH
c. Addition of $NaCH_3CO_2$

Q13.3.16

Suggest two ways in which the equilibrium concentration of Ag+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and $\mathrm{NO_3^-}$, in contact with solid AgCl.

\(\ce{Na+}(aq)+\ce{Cl-}(aq)+\ce{Ag+}(aq)+\ce{NO3-}(aq)\rightleftharpoons\ce{AgCl}(s)+\ce{Na+}(aq)+\ce{NO3-}(aq)\)

$$\Delta H = -65.9\ \mathrm{kJ}$$

S13.3.16

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

Q13.3.17

How can the pressure of water vapor be increased in the following equilibrium?

\[\ce{H2O}(l)\rightleftharpoons\ce{H2O}(g) \hspace{20px} ΔH=\ce{41\:kJ}\]

Q13.3.18

Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

\[\ce{2Ag+}(aq)+\ce{SO4^2-}(aq)\rightleftharpoons\ce{Ag2SO4}(s)\]

Which of the following will occur?

a. Ag^+ or SO_4^{2-} concentrations will not change.
b. The added silver sulfate will dissolve.
c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine.
d. The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

S13.3.18

(a)

Q13.3.19

The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization ($HX \rightleftharpoons H^+ + X^-$)?

13.4: Equilibrium Calculations Exercises

Q13.4.1

A reaction is represented by this equation: $A(aq) + 2\,B(aq) \rightleftharpoons 2\,C(aq) \quad K_c = 1 \times 10^3$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations ≤1 *M*, make up two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

S13.4.1

$K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

Q13.4.2

A reaction is represented by this equation: $2\,W(aq) \rightleftharpoons X(aq) + 2\,Y(aq) \quad K_c = 5 \times 10^{-4}$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations of ≤1 *M*, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

Q13.4.3

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad (2.E.10)$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

S13.4.3

$K_c = 6.00 \times 10^{-2}$

Q13.4.4

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons 3\,\mathrm{H_2}(g) + \mathrm{CO}(g) \tag{2.E.11}$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

S13.4.4

$K_c = 0.50$

Q13.4.5

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 3.3×10^{-3}% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2\,\mathrm{NO_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \tag{2.E.12}$$

Q13.4.6

Calculate the value of the equilibrium constant K_P for the reaction $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

S13.4.6

The equilibrium equation is $K_P = 1.9 \times 10^3$

Q13.4.7

When heated, iodine vapor dissociates according to this equation:

$$\mathrm{I_2}(g) \rightleftharpoons 2\,\mathrm{I}(g) \tag{2.E.13}$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

Q13.4.8

A sample of ammonium chloride was heated in a closed container.

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g) \tag{2.E.14}$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

S13.4.8

$K_P = 3.06$

Q13.4.9

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the transformation at 60 °C?

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \tag{2.E.15}$$

Q13.4.10

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad (2.E.16)$$

___	___	$+x$	(2.E.17)
___	___	$0.125\ M$	(2.E.18)

(b)

$$4\,NH_3(g) + 3\,O_2(g) \rightleftharpoons 2\,N_2(g) + 6\,H_2O(g) \quad (2.E.19)$$

___	$3x$	___	___	(2.E.20)
___	$0.24\ M$	___	___	(2.E.21)

(c) Change in pressure:

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g) \quad (2.E.22)$$

___	x	___	(2.E.23)
___	25 torr	___	(2.E.24)

(d) Change in pressure:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g) \quad (2.E.25)$$

___	x	___	___	(2.E.26)
___	5 atm	___	___	(2.E.27)

(e)

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \quad (2.E.28)$$

x	___
$1.03 \times 10^{-4}\ M$	___

(2.E.29) (2.E.30)

(f) change in pressure:

$$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g) \quad (2.E.31)$$

$4x$	___
0.40 atm	___

(2.E.32) (2.E.33)

S13.4.10

a. $-2x$, $2x$, $-0.250\ M$, $0.250\ M$;
b. $4x$, $-2x$, $-6x$, $0.32\ M$, $-0.16\ M$, $-0.48\ M$;
c. $-2x$, $3x$, -50 torr, 75 torr;
d. x, $-x$, $-3x$, 5 atm, -5 atm, -15 atm;
e. x, $1.03 \times 10^{-4}\ M$; (f) x, 0.1 atm.

Q13.4.11

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g) \quad (2.E.34)$$

___	___	$+2x$	(2.E.35)
___	___	$1.50\ M$	(2.E.36)

(b)

$$CS_2(g) + 4\,H_2(g) \rightleftharpoons CH_4(g) + 2\,H_2S(g) \quad (2.E.37)$$

x	___	___	___	(2.E.38)
$0.020\ M$	___	___	___	(2.E.39)

(c) Change in pressure:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g) \quad (2.E.40)$$

x	___	___	(2.E.41)
1.50 atm	___	___	(2.E.42)

(d) Change in pressure:

$$2\,NH_3(g) + 2\,O_2(g) \rightleftharpoons N_2O(g) + 3\,H_2O(g) \quad (2.E.43)$$

___	___	___	x	(2.E.44)
___	___	___	60.6 torr	(2.E.45)

(e)

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \quad (2.E.46)$$

x	___
$9.8 \times 10^{-6}\ M$	___

(2.E.47)
(2.E.48)

(f) Change in pressure:

$$Fe(s) + 5\,CO(g) \rightleftharpoons Fe(CO)_4(g) \quad (2.E.49)$$

___	x
___	0.012 atm

(2.E.50)
(2.E.51)

Q13.4.12

Why are there no changes specified for Ni in Exercise, part (f)? What property of Ni does change?

S13.4.12

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

Q13.4.13

Why are there no changes specified for NH_4HS in Exercise, part (e)? What property of NH_4HS does change?

Q13.4.14

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.50 \text{ at } 400\ ^\circ C \quad (2.E.52)$$

Calculate the equilibrium molar concentration of NH_3.

S13.4.14

$[NH_3] = 9.1 \times 10^{-2}\ M$

Q13.4.16

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448\ ^\circ C$$

Q13.4.17

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_P = 4.7 \times 10^{-2} \quad (2.E.53)$$

S13.4.17

$P_{BrCl} = 4.9 \times 10^{-2}$ atm

Q13.4.18

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad K_P = 1.6 \text{ at } 990\ ^\circ C \quad (2.E.54)$$

Q13.4.12

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \quad K_c = 4.90 \times 10^2 \text{ at } 550\ ^\circ C$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

S13.4.12

$[CO] = 2.0 \times 10^{-4}\ M$

Q13.4.13

Carbon reacts with water vapor at elevated temperatures.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad K_c = 0.2 \text{ at } 1000\ ^\circ C$$

What is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500\ M$ at 1000 °C?

Q13.4.14

Sodium sulfate 10−hydrate, $Na_2SO_4 \cdot 10H_2O$, dehydrates according to the equation

$$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \tag{2.E.55}$$

with $K_p = 4.08 \times 10^{-25}$ at 25°C. What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4 \cdot 10H_2O$ and $NaSO_4$?

S13.4.14

$P_{H_2O} = 3.64 \times 10^{-3}$ atm

Q13.4.15

Calcium chloride 6−hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

$$CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \quad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$?

Q13.4.16

A student solved the following problem and found the equilibrium concentrations to be $[SO_2] = 0.590\ M$, $[O_2] = 0.0450\ M$, and $[SO_3] = 0.260\ M$. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3] = 0.500\ M$, $[SO_2] = 0\ M$, and $[O_2] = 0.350\ M$?

S13.4.16

Calculate Q based on the calculated concentrations and see if it is equal to K_c. Because Q does equal 4.32, the system must be at equilibrium.

Q13.4.16

A student solved the following problem and found $[N_2O_4] = 0.16\ M$ at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 M?

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = 160 \tag{2.E.56}$$

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 1.07 \times 10^{-5} \text{ in chloroform}$$

(b) Show that the change is small enough to be neglected.

S13.4.16

(a)

- $[NO_2] = 1.17 \times 10^{-3}\ M$
- $[N_2O_4] = 0.128\ M$

(b) Percent error $= \frac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.

Q13.4.17

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

a. Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

$$\mathrm{COCl_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{Cl_2}(g) \quad K_c = 2.2 \times 10^{-10} \tag{2.E.57}$$

b. Show that the change is small enough to be neglected.

Q13.4.18

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$$2\,\mathrm{H_2S}(g) \rightleftharpoons 2\,\mathrm{H_2}(g) + \mathrm{S_2}(g) \quad K_P = 2.2 \times 10^{-6}$$

(b) Show that the change is small enough to be neglected.

S13.4.18

(a)

- $[H_2S] = 0.810$ atm
- $[H_2] = 0.014$ atm
- $S_2] = 0.0072$ atm

(b) The $2x$ is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring $2x$ is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the "5% test." The error is, indeed, negligible.

Q13.4.19

What are all concentrations after a mixture that contains $[H_2O] = 1.00\ M$ and $[Cl_2O] = 1.00\ M$ comes to equilibrium at 25 °C?

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g) \quad K_c = 0.0900 \tag{2.E.58}$$

Q13.4.20

What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5] = 2.00\ M$?

$$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \quad K_c = 0.0211 \tag{2.E.59}$$

S13.4.20

$[PCl_3] = 1.80\ M$; $[PC_3] = 0.195\ M$; $[PCl_3] = 0.195\ M$.

Q13.4.21

Calculate the pressures of all species at equilibrium in a mixture of NOCl, NO, and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:

$$2\,\mathrm{NOCl}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \quad K_P = 4.0 \times 10^{-4} \tag{2.E.60}$$

Q13.4.22

Calculate the equilibrium concentrations of NO, O_2, and NO_2 in a mixture at 250 °C that results from the reaction of 0.20 *M* NO and 0.10 *M* O_2. (Hint: *K* is large; assume the reaction goes to completion then comes back to equilibrium.)

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = 2.3 \times 10^5 \text{ at } 250\ ^\circ C \tag{2.E.61}$$

S13.4.22

- $[NO_2]$ = 0.19 *M*
- [NO] = 0.0070 *M*
- $[O_2]$ = 0.0035 *M*

Q13.4.23

Calculate the equilibrium concentrations that result when 0.25 *M* O_2 and 1.0 *M* HCl react and come to equilibrium.

$$4\,HCl(g) + O_2(g) \rightleftharpoons 2\,Cl_2(g) + 2\,H_2O(g) \quad K_c = 3.1 \times 10^{13} \tag{2.E.62}$$

Q13.4.24

One of the important reactions in the formation of smog is represented by the equation

$$O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g) \quad K_P = 6.0 \times 10^{34} \tag{2.E.63}$$

What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of 1.2×10^{-8} atm and NO with a pressure of 1.2×10^{-8} atm comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion then comes back to equilibrium.)

S13.4.24

$P_{O_3} = 4.9 \times 10^{-26}$ atm

Q13.4.24

Calculate the pressures of NO, Cl_2, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl_2. (Hint: K_P is small; assume the reverse reaction goes to completion then comes back to equilibrium.)

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_P = 2.5 \times 10^3$$

Q13.4.25

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448\ ^\circ C$$

S13.4.25

507 g

Q13.4.26

Butane exists as two isomers, *n*−butane and isobutane.


Three Lewis structures are shown. The first is labeled, “n dash Butane,” and has a C H subscript 3 single bonded to a C H subscript 2 group. This C H subscript 2 group is single bonded to another C H subscript 2 group which is single bonded to a C H subscript 3 group. The second is labeled, “iso dash Butane,” and is composed of a C H group single bonded to three C H subscript 3 groups. The third structure shows a chain of atoms: “C H subscript 3, C H subscript 2, C H subscript 2, C H subscript 3,” a double-headed arrow, then a carbon atom single bonded to three C H subscript 3 groups as well as a hydrogen atom.

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

Q13.4.27

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of $CaCO_3$ at that temperature?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

S13.4.27

330 g

Q13.4.28

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$\mathrm{H_2}(g) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g) + \mathrm{CO}(g) \tag{2.E.64}$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

Q13.4.29

At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{\mathrm{N_2O_4}} = 0.70\ \mathrm{atm}$ and $P_{\mathrm{NO_2}} = 0.30\ \mathrm{atm}$.

a. Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
b. Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C.

S13.4.29

(a) Both gases must increase in pressure.

(b) $P_{\mathrm{N_2O_4}} = 8.0\ \mathrm{atm}$ and $P_{\mathrm{NO_2}} = 1.0\ \mathrm{atm}$

Q13.4.30

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{2.E.65}$$

a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

Q13.4.31

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

\[\ce{CO}(g)+\ce{H2O}(g) <=> \ce{CO2}(g)+\ce{H2}(g)\)]

a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?
b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

S13.4.31

(a) 0.33 mol.

(b) $[CO]^2 = 0.50\ M$ Added H_2 forms some water to compensate for the removal of water vapor and as a result of a shift to the left after H_2 is added.

Q13.4.32a

Antimony pentachloride decomposes according to this equation:

$$\mathrm{SbCl_5}(g) \rightleftharpoons \mathrm{SbCl_3}(g) + \mathrm{Cl_2}(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

Q13.4.32b

Consider the reaction between H_2 and O_2 at 1000 K

$$\ce{2H2}(g)+\ce{O2}(g)⇌\ce{2H2O}(g) \hspace{20px} K_P=\dfrac{(P_{\ce{H2O}})^2}{(P_{\ce{O2}})(P_{\ce{H2}})^3}=1.33×10^{20}$$

If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components?

S13.4.32b

$P_{H_2} = 8.64 \times 10^{-11}$ atm

$P_{\ce{O2}}=0.250\:\ce{atm}$

$P_{\ce{H2O}}=0.500\:\ce{atm}$

Q13.4.33

An equilibrium is established according to the following equation

$$\begin{aligned} &\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H^+}(aq) \\ &\rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \quad K_c = 4.6 \end{aligned} \tag{2.E.66}$$

What will happen in a solution that is 0.20 *M* each in $\mathrm{Hg_2^{2+}}$, $\mathrm{NO_3^-}$, H^+, Hg^{2+}, and HNO_2?

a. $\mathrm{Hg_2^{2+}}$ will be oxidized and $\mathrm{NO_3^-}$ reduced.
b. $\mathrm{Hg_2^{2+}}$ will be reduced and $\mathrm{NO_3^-}$ oxidized.
c. Hg^{2+} will be oxidized and HNO_2 reduced.
d. Hg^{2+} will be reduced and HNO_2 oxidized.
e. There will be no change because all reactants and products have an activity of 1.

Q13.4.34

Consider the equilibrium

$$4\,\mathrm{NO_2}(g) + 6\,\mathrm{H_2O}(g) \rightleftharpoons 4\,\mathrm{NH_3}(g) + 7\,\mathrm{O_2}(g) \tag{2.E.67}$$

a. What is the expression for the equilibrium constant (K_c) of the reaction?
b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
c. If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2?
d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

S13.4.34

(a) $K_c = \dfrac{[NH3]^4[O2]^7}{[NO2]^4[H2O]^6}$. (b) [$NH_3$] must increase for Q_c to reach K_c. (c) That decrease in pressure would decrease [NO_2]. (d) $P_{O_2} = 49$ torr

Q13.4.35

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$\mathrm{HbO_2}(aq) + \mathrm{H_3O^+}(aq) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2{-}Hb{-}H^+} + \mathrm{O_2}(g) + \mathrm{H_2O}(l)$$

1. (a) Write the equilibrium constant expression for this reaction.

2. (b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

Q13.4.36

The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.

$$\mathrm{C_{12}H_{22}O_{11}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(aq) + \mathrm{C_6H_{12}O_6}(aq)$$

Rate = $k[C_{12}H_{22}O_{11}]$

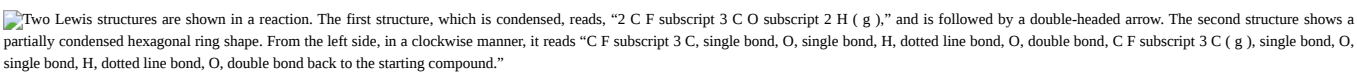
In neutral solution, $k = 2.1 \times 10^{-11}$/s at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $C_6H_{12}O_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27 °C. What are the concentrations of glucose, fructose, and sucrose after a 0.150 *M* aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1.

S13.4.36

[fructose] = 0.15 *M*

Q13.4.37

The density of trifluoroacetic acid vapor was determined at 118.1 °C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid.



Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of $K_P = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

S13.4.37

$$P_{\mathrm{N_2O_3}} = 1.90 \text{ atm and } P_{\mathrm{NO}} = P_{\mathrm{NO_2}} = 1.90 \text{ atm}$$

Q13.4.38

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*?

Q13.4.39

A 0.010 *M* solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25 °C. A 0.010 *M* solution of the weak acid HB has an osmotic pressure of 0.345 atm under the same conditions.

(a) Which acid has the larger equilibrium constant for ionization

$$\text{HA } [\mathrm{HA}(aq) \rightleftharpoons \mathrm{A^-}(aq) + \mathrm{H^+}(aq)] \text{ or HB } [\mathrm{HB}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{B^-}(aq)]?$$

(b) What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.)

S13.4.39

(a) HB ionizes to a greater degree and has the larger K_c.

(b) $K_c(HA) = 5 \times 10^{-4}$

$K_c(\text{HB}) = 3 \times 10^{-3}$

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CHAPTER OVERVIEW

3: Electrochemistry

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

In oxidation–reduction (redox) reactions, electrons are transferred from one species (the reductant) to another (the oxidant). This transfer of electrons provides a means for converting chemical energy to electrical energy or vice versa. The study of the relationship between electricity and chemical reactions is called electrochemistry. In this chapter, we describe electrochemical reactions in more depth and explore some of their applications. We start by describing how they can be used to generate an electrical potential, or *voltage*; and discuss factors that affect the magnitude of the potential. We then explore the relationships among the electrical potential, the change in free energy, and the equilibrium constant for a redox reaction, which are all measures of the thermodynamic driving force for a reaction. Finally, we examine two kinds of applications of electrochemical principles: (1) those in which a spontaneous reaction is used to provide electricity and (2) those in which electrical energy is used to drive a thermodynamically nonspontaneous reaction.

By the end of this chapter, you will understand why different kinds of batteries are used in cars, flashlights, cameras, and portable computers; how rechargeable batteries operate; and why corrosion occurs and how to slow—if not prevent—it. You will also discover how metal objects can be plated with silver or chromium for protection; how silver polish removes tarnish; and how to calculate the amount of electricity needed to produce aluminum, chlorine, copper, and sodium on an industrial scale.

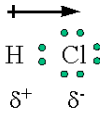
3.0: Oxidation States and Redox Reactions
3.1: Balanced Oxidation-Reduction Equations
3.2: Voltaic Cells
3.3: Cell Potential Under Standard Conditions
3.4: Gibbs Energy and Redox Reactions
3.5: Cell Potential Under Nonstandard Conditions
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3.0: Oxidation States and Redox Reactions

Electron transfer is one of the most basic processes that can happen in chemistry. It simply involves the movement of an electron from one atom to another. Many important biological processes rely on electron transfer, as do key industrial transformations used to make valuable products. In biology, for example, electron transfer plays a central role in respiration and the harvesting of energy from glucose, as well as the storage of energy during photosynthesis. In society, electron transfer has been used to obtain metals from ores since the dawn of civilization.

Oxidation state is a useful tool for keeping track of electron transfers. It is most commonly used in dealing with metals and especially with transition metals. Unlike metals from the first two columns of the periodic table, such as sodium or magnesium, transition metals can often transfer different numbers of electrons, leading to different metal ions (e.g., sodium is generally found as Na^+ and magnesium is almost always Mg^{2+}, but manganese could be Mn^{2+}, Mn^{3+}, and so on, as far as Mn^{7+}). Oxidation state is a number assigned to an element in a compound according to some rules. This number enable us to describe oxidation-reduction reactions, and balancing redox chemical reactions. When a covalent bond forms between two atoms with different electronegativities the shared electrons in the bond lie closer to the more electronegative atom:



The **oxidation number** of an atom is the charge that results when the electrons in a covalent bond are assigned to the more electronegative atom and is the charge an atom would possess ***if*** the bonding were ionic. In HCl (above) the oxidation number for the hydrogen would be +1 and that of the Cl would be -1.

Example 3.0.1

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the Oxidation State of each):

a. $Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$
b. $2\,Al + 3\,Cu^{2+} \longrightarrow 2\,Al^{3+} + 3\,Cu$
c. $CO_3^{2-} + 2\,H^+ \longrightarrow CO_2 + H_2O$

SolutionS

a. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0)
b. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)
c. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

An atom is oxidized if its oxidation number increases, and an atom is reduced if its oxidation number decreases. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation Numbers and Nomenclature

Compounds of the alkali (oxidation number +1) and alkaline earth metals (oxidation number +2) are typically ionic in nature. Compounds of metals with higher oxidation numbers (e.g., tin +4) tend to form molecular compounds

- In ionic and covalent molecular compounds usually the ***less electronegative element is given first***.
- In ionic compounds the names are given which refer to ***the oxidation (ionic) state***
- In molecular compounds the names are given which refer ***to the number of molecules present in the compound***

Figure **3.0.1**: Example of nomenclature based on oxidation states.

Ionic		Molecular	
MgH_2	magnesium hydride	H_2S	dihydrogen sulfide
FeF_2	iron(II) fluoride	OF_2	oxygen difluoride
Mn_2O_3	manganese(III) oxide	Cl_2O_3	dichlorine trioxide

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Oxidation-Reduction Reaction Examples

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG,** meaning "*oxidation is loss*" and "*reduction is gain*," and **LEO says GER,** meaning "*loss of* e^- = *oxidation*" and "*gain of* e^- = *reduced*." There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is called the **oxidizing agent**; by accepting electrons it causes the oxidation of another species. Conversely, the species that donates electrons is called the **reducing agent**; when the reaction occurs, it reduces the other species. In other words, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions).



Figure 3.0.1: A thermite reaction taking place on a cast iron skillet. A thermite reaction, using about 110 g of the mixture, taking place. The cast-iron skillet was destroyed in the process. Image by Schuyler S and used with permission by Wikipedia.

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3 (Figure 20.1.1).

$$Fe_2O_{3(s)} + 2Al_{(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(l)} \tag{3.0.1}$$

Another example of the redox reaction is the reaction between zinc and copper sulfate.

Example 3.0.2: Identifying Oxidized Elements

Using the equations from the previous examples, determine what is oxidized in the following reaction.

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

Solution

The Oxidation State of H changes from +1 to 0, and the Oxidation State of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the reducing agent.

Example 3.0.3: Identifying Reduced Elements

What is reduced species in this reaction?

$$\mathrm{Zn} + \mathrm{2\,H^+} \rightarrow \mathrm{Zn^{2+}} + \mathrm{H_2}$$

Solution

The Oxidation State of H changes from +1 to 0, and the Oxidation State of Zn changes from 0 to +2. Hence, H+ ion is reduced and acts as the oxidizing agent.

Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given below:

$$A + B \rightarrow AB \tag{3.0.2}$$

Example 3.0.4: Combination Reaction

Equation: $H_2 + O_2 \rightarrow H_2O$

Calculation: 0 + 0 → **(2)(+1) + (-2) = 0**

Explanation:

In this equation both H_2 and O_2 are free elements; following Rule #1, their Oxidation States are 0. The product is H_2O, which has a total Oxidation State of 0. According to Rule #6, the Oxidation State of oxygen is usually -2. Therefore, the Oxidation State of H in H_2O must be +1.

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:

$$AB \rightarrow A + B \tag{3.0.3}$$

Example 3.0.5: Decomposition Reaction

Identify the oxidation state of the products and reactant in the decomposition of water:

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{O_2}$$

Calculation

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

In this reaction, water is "decomposed" into hydrogen and oxygen. As in the previous example the H_2O has a total Oxidation State of 0; thus, according to Rule #6 the Oxidation State of oxygen is usually -2, so the Oxidation State of hydrogen in H_2O must be +1.

Single Replacement Reactions

A single replacement reaction involves the "replacing" of an element in the reactants with another element in the products:

$$A + BC \rightarrow AB + C \tag{3.0.4}$$

Example 3.0.6: Single Replacement Reaction

Equation:

$$Cl_2 + NaBr \rightarrow NaCl + Br_2 \tag{3.0.5}$$

Calculation: (0) + ((+1) + (-1) = 0) -> ((+1) + (-1) = 0) + 0
Explanation: In this equation, Br is replaced with Cl, and the Cl atoms in Cl_2 are reduced, while the Br ion in NaBr is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a double replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

$$AB + CD \rightarrow AD + CB \tag{3.0.6}$$

Example 3.0.7: Double Replacement Reaction

The reaction of gasous hydrogen chloride and iron oxide is a double replacement reaction. Write the expected reaction for this chemistry equation.

Solution

$$\mathrm{Fe_2O_3 + 6\,HCl \longrightarrow 2\,FeCl_3 + 3\,H_2O}$$

In this equation, Fe and H trade places, and oxygen and chlorine trade places.

Combustion Reactions

Combustion reactions almost always involve oxygen in the form of O_2, and are almost always exothermic, meaning they produce heat. Chemical reactions that give off light and heat and light are colloquially referred to as "burning."

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{3.0.7}$$

Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals "burn" in other environments. For example, both titanium and magnesium burn in nitrogen as well:

$$2Ti_{(s)} + N_{2(g)} \rightarrow 2TiN_{(s)} \tag{3.0.8}$$

$$3Mg_{(s)} + N_{2(g)} \rightarrow Mg_3N_{2(s)} \tag{3.0.9}$$

Moreover, chemicals can be oxidized by other chemicals than oxygen, such as Cl_2 or F_2; these processes are also considered combustion reactions

Disproportionation Reactions

Disproportionation Reactions: In some redox reactions a single substance can be both oxidized and reduced. These are known as disproportionation reactions, with the following general equation:

$$2A \rightarrow A^{+n} + A^{-n} \tag{3.0.10}$$

Where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

Example 3.0.8: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, H_2O_2 poured over a cut. This a decomposition reaction of hydrogen peroxide, which produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:

$$\mathrm{2\,H_2O_2\,(aq) \rightarrow 2\,H_2O\,(l) + O_2\,(g)}$$

Explanation

On the reactant side, H has an Oxidation State of +1 and O has an Oxidation State of -1, which changes to -2 for the product H_2O (oxygen is reduced), and 0 in the product O_2 (oxygen is oxidized).

Summary

Oxidation signifies a loss of electrons and reduction signifies a gain of electrons. Balancing redox reactions is an important step that changes in neutral, basic, and acidic solutions. Tthe types of redox reactions: Combination and decomposition, Displacement reactions (single and double), Combustion, Disproportionation. The oxidizing agent undergoes reduction and the reducing agent undergoes oxidation.

References

1. Petrucci, et al. *General Chemistry: Principles & Modern Applications*. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.
2. Sadava, et al. *Life: The Science of Biology*. 8th ed. New York, NY. W.H. Freeman and Company, 2007

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3.1: Balanced Oxidation-Reduction Equations

Learning Objectives

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of $Cr^{2+}(aq)$ with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 3.1.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\overset{+2}{Cr}^{2+}(aq) + \overset{+4\ -2}{MnO_2}(aq) + \overset{+1}{H}^{+}(aq) \rightarrow \overset{+3}{Cr}^{3+}(aq) + \overset{+2}{Mn}^{2+}(aq) + \overset{+1\ -2}{H_2O}(l) \tag{3.1.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$Cr^{2+} + Mn^{4+} \rightarrow Cr^{3+} + Mn^{2+} \tag{3.1.2}$$

The oxidation can be written as

$$\underbrace{Cr^{2+} \rightarrow Cr^{3+} + e^-}_{\text{oxidation with 1 electron lost}} \tag{3.1.3}$$

and the reduction as

$$\underbrace{Mn^{4+} + 2e^- \rightarrow Mn^{2+}}_{\text{reduction with 2 electrons gained}} \tag{3.1.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 3.1.3) by 2 to give

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^- \tag{3.1.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 3.1.4):

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$$

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2Cr^{2+} \rightarrow 2Cr^{3+} + \cancel{2e^-}$$

$$Mn^{4+} + \cancel{2e^-} \rightarrow Mn^{2+}$$

to result in the balanced redox reaction (metals only)

$$Mn^{4+} + 2Cr^{2+} \rightarrow 2Cr^{3+} + Mn^{2+} \tag{3.1.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$MnO_{2(aq)} + 2Cr^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + Mn^{2+}_{(aq)} \tag{3.1.7}$$

> *In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 3.1.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add H^+ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding OH^- as necessary to either side of the equation to balance the charges.

In this case, adding four H^+ ions to the left side of Equation 3.1.7 to give

$$MnO_2(s) + 2Cr^{2+}(aq) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq) \tag{3.1.8}$$

Although the charges are now balanced in Equation 3.1.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding H_2O as necessary to either side of the equation. Here, we need to add two H_2O molecules to the right side of Equation 3.1.8:

$$MnO_2(s) + 2Cr^{2+}(aq) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq) + 2H_2O(l) \tag{3.1.9}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example **3.1.1** below.

Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding H_2O molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

Example 3.1.1: Balancing in Acid Solutions

Arsenic acid (H_3AsO_4) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine (AsH_3, a highly toxic and unstable gas) and Zn^{2+}(aq). Balance the equation for this reaction using oxidation states:

$$H_3AsO_4(aq) + Zn(s) \rightarrow AsH_3(g) + Zn^{2+}(aq)$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. **Write a chemical equation showing the reactants and the products.** Because we are given this information, we can skip this step.
2. **Assign oxidation states and determine which atoms change oxidation state.** The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$\overset{+5}{H_3As}O_4(aq) + \overset{0}{Zn}(s) \rightarrow \overset{-3}{As}H_3(g) + \overset{+2}{Zn^{2+}}(aq)$$

3. **Write separate equations for oxidation and reduction.** The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\underbrace{\overset{+5}{As} + 8e^- \rightarrow \overset{-3}{As}}_{\text{Reduction with gain of 8 electrons}}$$

   Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\underbrace{\overset{0}{Zn} \rightarrow \overset{+2}{Zn^{2+}} + 2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. **Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.** The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\begin{aligned} \overset{+5}{As} + 8e^- &\rightarrow \overset{-3}{As} \\ \overset{0}{4Zn} &\rightarrow 4\overset{+2}{Zn^{2+}} + 8e^- \end{aligned}$$

5. **Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.** Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives

$$\begin{aligned} &\textit{Reduction: } H_3AsO_{4(aq)} + 8e^- \rightarrow AsH_{3(g)} \\ &\textit{Oxidation: } 4Zn_{(s)} \rightarrow 4Zn^{2+}_{(aq)} + 8e^- \end{aligned}$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$H_3AsO_{4(aq)} + 4Zn_{(s)} + \cancel{8e^-} \rightarrow AsH_{3(g)} + 4Zn^{2+}_{(aq)} + \cancel{8e^-} \tag{3.1.10}$$

   which then yields after canceling electrons

$$H_3AsO_{4(aq)} + 4Zn_{(s)} \rightarrow AsH_{3(g)} + 4Zn^{2+}_{(aq)}$$

7. *Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$H_3AsO_{4(aq)} + 4Zn_{(s)} + 8H^+_{(aq)} \rightarrow AsH_{3(g)} + 4Zn^{2+}_{(aq)}$$

8. *Balance the oxygen atoms by adding H_2O molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 H_2O molecules to the right side balances the O atoms:

$$H_3AsO_{4(aq)} + 4Zn_{(s)} + 8H^+_{(aq)} \rightarrow AsH_{3(g)} + 4Zn^{2+}_{(aq)} + 4H_2O_{(l)}$$

Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:

$$\begin{aligned} &\textit{Atoms}: 1As + 4Zn + 4O + 11H = 1As + 4Zn + 4O + 11H \\ &\textit{Total charge}: 8(+1) = 4(+2) = +8 \end{aligned}$$

The balanced chemical equation for the reaction is therefore:

$$H_3AsO_{4(aq)} + 4Zn_{(s)} + 8H^+_{(aq)} \rightarrow AsH_{3(g)} + 4Zn^{2+}_{(aq)} + 4H_2O_{(l)}$$

? Exercise 3.1.1: oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$CuS_{(s)} + H^+_{(aq)} + NO^-_{3(aq)} \rightarrow Cu^{2+}_{(aq)} + NO_{(g)} + SO^{2-}_{4(aq)}$$

Answer

$$3CuS_{(s)} + 8H^+_{(aq)} + 8NO^-_{3(aq)} \rightarrow 3Cu^{2+}_{(aq)} + 8NO_{(g)} + 3SO^{2-}_{4(aq)} + 4H_2O_{(l)}$$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example **3.1.2**.

✔ Example 3.1.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$Al_{(s)} + H_2O_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)} + H_{2(g)}$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example **3.1.1**, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[Al(OH)_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in H_2. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}_{(s)} + \overset{+1}{H}_2O_{(aq)} \rightarrow [\overset{+3}{Al}(OH)_4]^-_{(aq)} + \overset{0}{H}_{2(g)}$$

3. Write separate equations for oxidation and reduction.

$$\text{Reduction: } \overset{+1}{H} + e^- \rightarrow \overset{0}{H}\ (in\ H_2)$$
$$\text{Oxidation: } \overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:

$$\text{Reduction: } 3H^+ + 3e^- \rightarrow 3H^0\ (in\ H_2)$$
$$\text{Oxidation: } Al^0 \rightarrow Al^{3+} + 3e^-$$

5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of H_2O contains two protons, in this case, $3H^+$ corresponds to $3/2H_2O$. Similarly, each molecule of hydrogen gas contains two H atoms, so 3H corresponds to $3/2H_2$.

$$\text{Reduction: } \frac{3}{2}H_2O + 3e^- \rightarrow \frac{3}{2}H_2$$
$$\text{Oxidation: } Al \rightarrow [Al(OH)_4]^- + 3e^-$$

6. Adding the equations and canceling the electrons gives

$$Al + \frac{3}{2}H_2O + \cancel{3e^-} \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2 + \cancel{3e^-}$$

$$Al + \frac{3}{2}H_2O \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2$$

To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2Al + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two OH^- ions to the left side:

$$2Al + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three H_2O molecules to the left side:

$$2Al + 2OH^- + 6H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

9. Be sure the equation is balanced:

$$\text{Atoms: } 2Al + 8O + 14H = 2Al + 8O + 14H$$
$$\text{Total charge: } (2)(0) + (2)(-1) + (6)(0) = (2)(-1) + (3)(0)$$

$$-2 = -2$$

The balanced chemical equation is therefore

$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \rightarrow 2[Al(OH)_4]^-_{(aq)} + 3H_{2(g)}$$

Thus 3 mol of H_2 gas are produced for every 2 mol of Al.

? Exercise 3.1.2: Reducing Manganese in permanganate

The permanganate ion reacts with nitrite ion in basic solution to produce manganese(IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer

$$2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$$

As suggested in Examples **3.1.1** and **3.1.2**, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, $\mathrm{MnO_4^-}$, $\mathrm{Cr_2O_7^{2-}}$, and $\mathrm{UF_6}$) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as $\mathrm{CH_4}$, $\mathrm{NH_3}$, $\mathrm{H_2S}$, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> *Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.*

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

Contributors

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3.2: Voltaic Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying REDOX chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)} \tag{3.2.1}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)} \tag{3.2.2}$$

oxidation half-reaction:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-} \tag{3.2.3}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 3.2.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 3.2.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an

electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

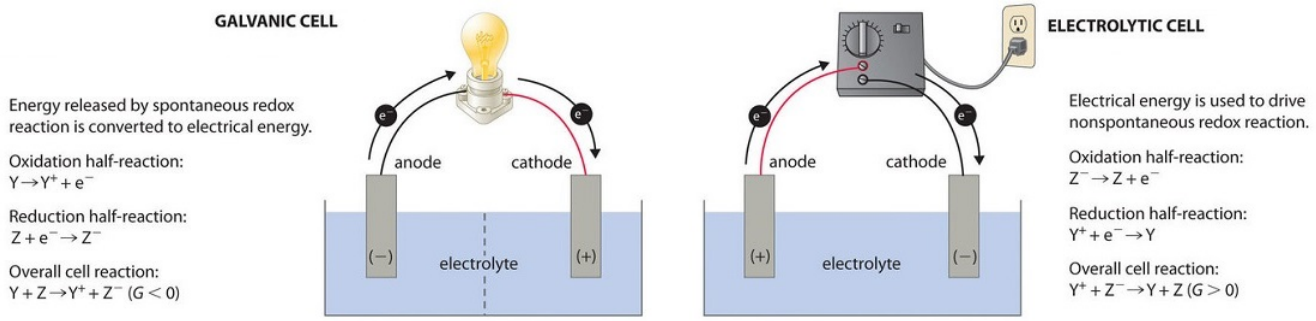


Figure **3.2.1**: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$\mathbf{Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)} \tag{3.2.4}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure **3.2.2**: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give Zn^{2+}(aq) ions, while Cu^{2+}(aq) ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (https://youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure **3.2.3a**. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte.

The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the Zn^{2+} solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the Cu^{2+} solution decreases (Figure **3.2.3***b*). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

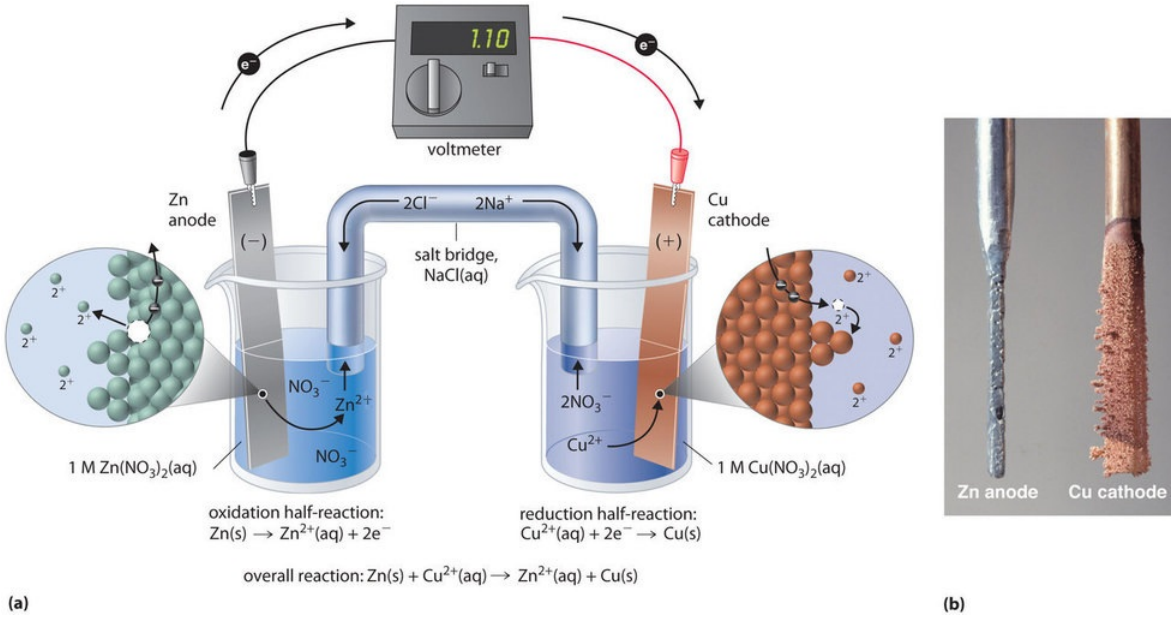


Figure **3.2.3**: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode.

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure **3.2.3***a*). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall

electrochemical reaction. This phenomenon is illustrated in Example **3.2.1**.

> *A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

✔ Example 3.2.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,Sn\,(s) + 2\,NO_3^-\,(aq) + 8\,H^+\,(aq) \rightarrow 3\,Sn^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$NO_3^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \longrightarrow NO\,(g) + 2\,H_2O\,(l)$$

oxidation:

$$Sn\,(s) \longrightarrow Sn^{2+}\,(aq) + 2\,e^-$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

? Exercise 3.2.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt

electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,MnO_4^-(aq) + 5\,Sn^{2+}(aq) + 16\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,Sn^{4+}(aq) + 8\,H_2O(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$
$$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,e^-$$

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in Figure 3.2.3*a* is written as follows:

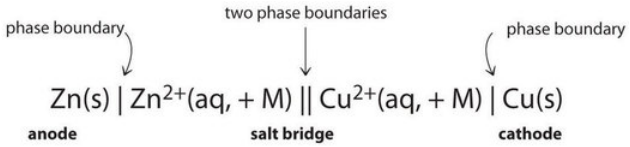


Figure 3.2.4: A cell diagram includes solution concentrations when they are provided.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$Pt(s) \;|\; H_2(g) \;|\; HCl(aq) \;|\; AgCl(s)\;Ag(s) \tag{3.2.5}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq) \tag{3.2.6}$$

anode reaction:

$$\frac{1}{2}\,H_{2(g)} \rightarrow H^+_{(aq)} + e^- \tag{3.2.7}$$

overall:

$$\mathrm{AgCl_{(s)} + \frac{1}{2}H_{2(g)} \rightarrow Ag_{(s)} + Cl^-_{(aq)} + H^+_{(aq)}} \tag{3.2.8}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 3.2.2

Draw a cell diagram for the galvanic cell described in Example **3.2.1**. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn\,(s) + 2\,NO_3^-\,(aq) + 8\,H^+\,(aq) \rightarrow 3\,Sn^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the **Pt** electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4\,(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (**NO**) and the **Pt** electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt\,(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt_{(s)}}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise 3.2.2

Draw the cell diagram for the following reaction, assuming the concentration of $\mathrm{Ag^+}$ and $\mathrm{Mg^{2+}}$ are each 1 M:

$$\mathrm{Mg\,(s) + 2\,Ag^+\,(aq) \rightarrow Mg^{2+}\,(aq) + 2\,Ag\,(s)}$$

Answer

$$\mathrm{Mg\,(s)\,|\,Mg^{2+}(aq,\ 1\ M\ )\,||\,Ag^+(aq,\ 1\ \ M)\,|\,Ag\,(s)}$$

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions,

allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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3.3: Cell Potential Under Standard Conditions

Learning Objectives

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

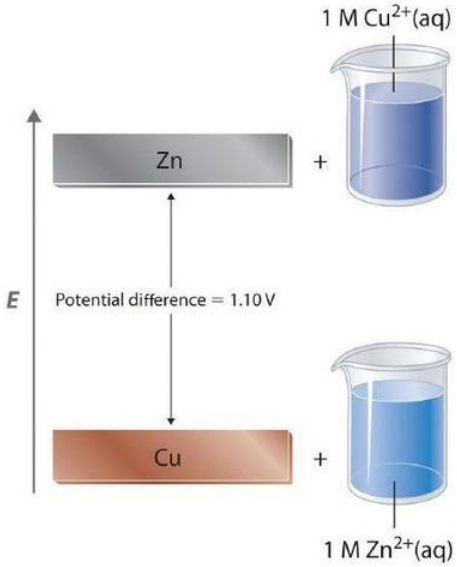


Figure **3.3.1**: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic ***Zn*** and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous ***Zn^{2+}*** *ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.*

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure **3.3.1** but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E° = 0.59\ V \tag{3.3.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{3.3.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 3.3.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{3.3.3}$$

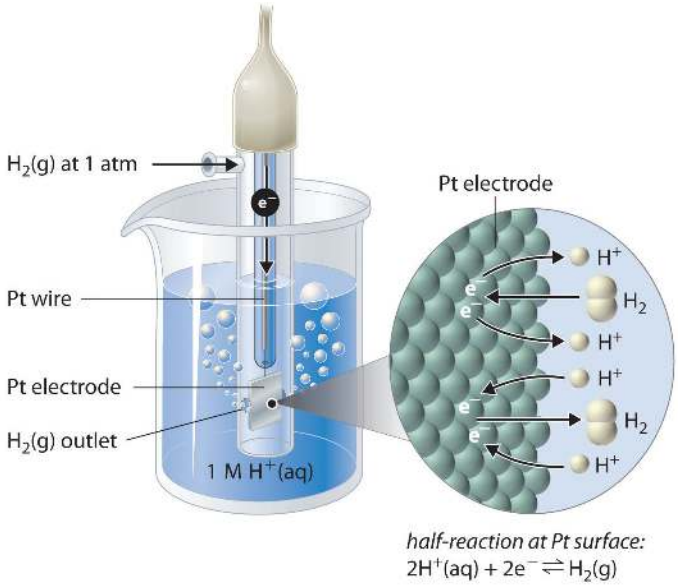


Figure **3.3.2**: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure **3.3.2**). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{3.3.4}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

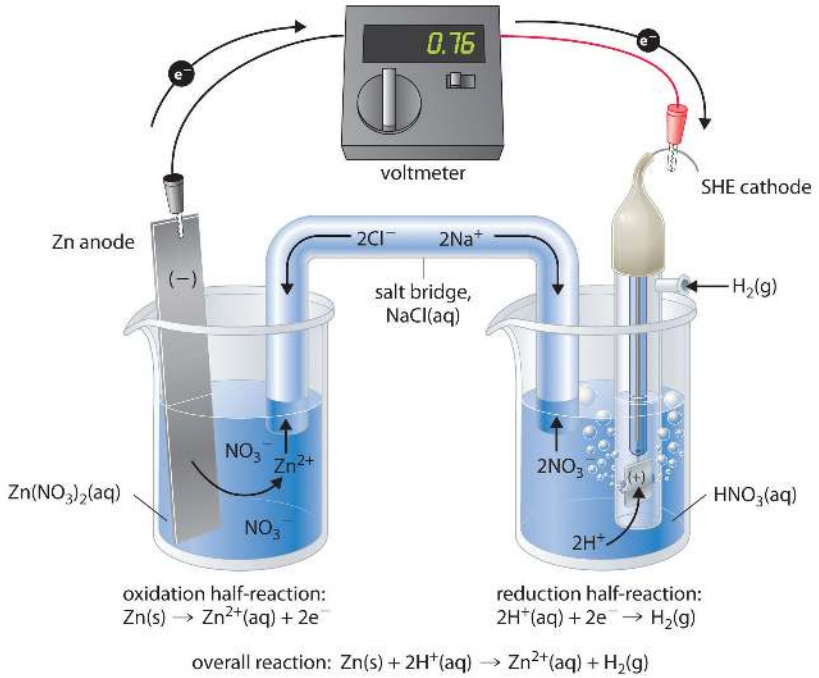


Figure **3.3.3**: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure **3.3.3** shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{3.3.5}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{3.3.6}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{3.3.7}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{3.3.8}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 0.76\ V \tag{3.3.9}$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction.In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E°_{cell} : 0\,V - (-0.76\,V) = 0.76\,V \tag{3.3.10}$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure **3.3.3** but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{3.3.11}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\ V \tag{3.3.12}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\ V \tag{3.3.13}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{3.3.14}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 0.34\ V \tag{3.3.15}$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{3.3.16}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to $H_2$and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{3.3.17}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{3.3.18}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 3.3.17, two H^+ ions gain one electron each in the reduction; in Equation 3.3.18, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 3.3.17) by 3 and the oxidation half-reaction (Equation 3.3.18) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{3.3.19}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{3.3.20}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{3.3.21}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{3.3.22}$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{3.3.23}$$

The atoms also balance, so Equation 3.3.22 is a balanced chemical equation for the redox reaction depicted in Equation 3.3.16.

> *The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 3.3.16, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{3.3.24}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{3.3.25}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{3.3.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{3.3.27}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{3.3.28}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{3.3.29}$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{3.3.30}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{3.3.31}$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 3.3.30 (the reductive half-reaction) by 3 and Equation 3.3.31 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{3.3.32}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{3.3.33}$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{3.3.34}$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{3.3.35}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 3.3.35 is identical to Equation 3.3.22, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 3.3.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O^{2-}_7$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}_{(aq)}$ complex and brown I_2(aq) ions (Figure **3.3.4**):

$$Cr_2O^{2-}_{7(aq)} + I^-_{(aq)} \rightarrow Cr^{3+}_{(aq)} + I_{2(aq)}$$

Balance this equation using half-reactions.

Given: redox reaction and Table P1

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}(_{(aq)} + 7H_2O_{(l)}$$

- oxidation:

$$2I^-_{(aq)} \rightarrow I_{2(aq)} + 2e^-$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$6I^-_{(aq)} \rightarrow 3I_{2(aq)} + 6e^-$$

Adding the two half-reactions and canceling electrons,

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6I^-_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3I_{2(aq)}$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$
$$+6 = +6$$
$$2Cr + 7O + 14H + 6I = 2Cr + 7O + 14H + 6I$$

The charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from Cr^{6+} in $Cr_2O^{2-}_7$ to Cr^{3+}, and I^- ions are oxidized to I_2. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow Cr^{3+}_{(aq)}$$

- oxidation:

$$I^-_{(aq)} \rightarrow I_{2(aq)}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)}$$

- oxidation:

$$2I^-_{(aq)} \rightarrow I_{2(aq)}$$

We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$Cr_2O^{2-}_{7(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

- $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

? Exercise 3.3.1

Copper is found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid (HNO_3), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$\mathrm{CuS\,(s) + HNO_3\,(aq) \rightarrow NO\,(g) + CuSO_4\,(aq)}$$

Balance this equation using the half-reaction method.



Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer

$$3CuS_{(s)} + 8HNO3(aq) \rightarrow 8NO_{(g)} + 3CuSO_{4(aq)} + 4H_2O_{(l)}$$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{3.3.36}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $\boldsymbol{E°_{cell}}$:

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{3.3.37}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{3.3.38}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{3.3.39}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V \tag{3.3.40}$$

This is the same value that is observed experimentally. If the value of $\boldsymbol{E°_{cell}}$ is positive, the reaction will occur spontaneously as written. If the value of $\boldsymbol{E°_{cell}}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example **3.3.2** and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $\boldsymbol{E°_{cell}}$ means that the reaction will occur spontaneously as written. A negative $\boldsymbol{E°_{cell}}$ means that the reaction will proceed spontaneously in the opposite direction.*

Example 3.3.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

cathode: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

anode: $Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B. Use Equation 3.3.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 3.3.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$0.27 \text{ V} = E°_{cathode} - (-0.55 \text{ V})$$
$$E°_{cathode} = -0.28 \text{ V}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28 \text{ V}) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

? Exercise 3.3.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$
- anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

Answer

0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{3.3.41}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)} \tag{3.3.42}$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure **3.3.5**. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{3.3.43}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{3.3.44}$$

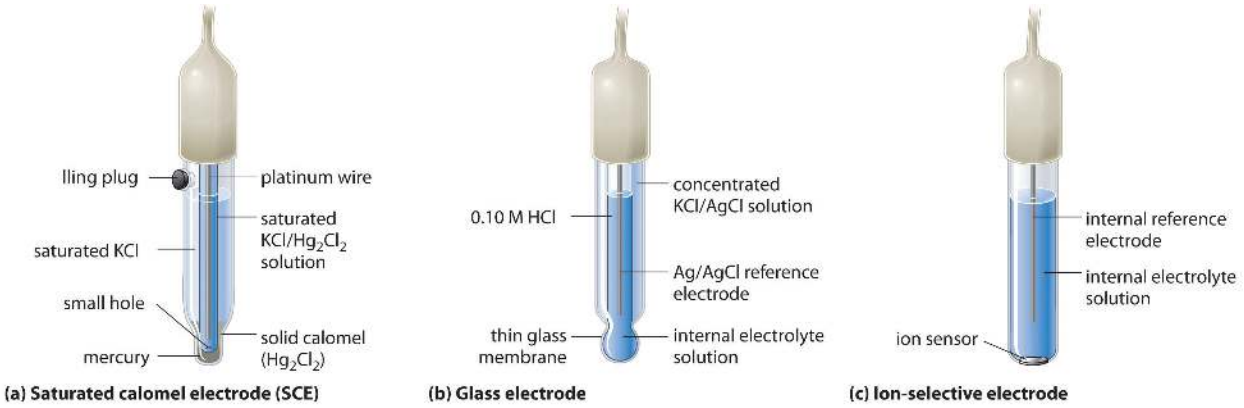


Figure **3.3.5**: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution.

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure **3.3.5**. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that $pH = -\log[H^+]$:

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{3.3.45}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure **3.3.5**). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-

called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table **3.3.1**.

Table **3.3.1**: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} − E°_{anode} \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

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3.4: Gibbs Energy and Redox Reactions

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with Ni^{2+}(aq) to form Ni(s) and Co^{2+}(aq) occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that [Ni^{2+}] is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \text{J}}{1\ \text{V}} = 1\ \text{C} = \text{A} \cdot \text{s} \tag{3.4.1}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$F = (1.60218 \times 10^{-19}\ \text{C}) \left(\frac{6.02214 \times 10^{23}}{1\ \text{mol e}^-} \right) \tag{3.4.2}$$

$$= 9.64855 \times 10^4\ \text{C/mol e}^- \simeq 96,486/(\text{V} \cdot \text{mol e}^-) \tag{3.4.3}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell} \tag{3.4.4}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell} \tag{3.4.5}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{3.4.6}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 3.4.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG° for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E°, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 3.4.6 to calculate ΔG°. If ΔG° is negative, then the reaction is spontaneous.

Solution

A As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E°. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E° values:

$$\text{cathode:} \quad Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\circ_{cathode} = 1.23\ V \tag{3.4.7}$$

$$\text{anode:} \quad 2Br^-(aq) \rightarrow Br_2(aq) + 2e^- \qquad E^\circ_{anode} = 1.09\ V \tag{3.4.8}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E° is not affected:

$$\text{cathode:} \quad Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\circ_{cathode} = 1.23\ V \tag{3.4.9}$$

$$\text{anode:} \quad 6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^- \qquad E^\circ_{anode} = 1.09\ V \tag{3.4.10}$$

$$\text{overall:} \quad Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l) \qquad E^\circ_{cell} = 0.14\ V \tag{3.4.11}$$

B We can now calculate ΔG° using Equation 3.4.6. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\Delta G^\circ = -(n)(F)(E^\circ_{cell}) = -(6\ \text{mole})[96,468\ \text{J}/(\text{V}\cdot\text{mol})(0.14\ \text{V})] \tag{3.4.12}$$

$$= -8.1 \times 10^4\ \text{J} \tag{3.4.13}$$

$$= -81\ \text{kJ/mol}\ Cr_2O_7^{2-} \tag{3.4.14}$$

Thus ΔG° is −81 kJ for the reaction as written, and the reaction is spontaneous.

Exercise 3.4.1

Use the data in Table P2 to calculate ΔG° for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \longrightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

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Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $Fe^{3+}(aq)$ to Fe(s) is not listed in the table, but two related reductions are given:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \quad E^\circ = +0.77V \tag{3.4.15}$$

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(aq) \quad E^\circ = -0.45V \tag{3.4.16}$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E° is not a state function. However, because ΔG° is a state function, the sum of the ΔG° values for the individual reactions gives us ΔG° for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E° for the overall half-reaction, we first must add the values of ΔG° (= −nFE°) for each individual half-reaction to obtain ΔG° for the overall half-reaction:

$$\mathrm{Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)} \quad \Delta G^\circ = -(1)(F)(0.77\ \mathrm{V}) \tag{3.4.17}$$

$$\mathrm{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)} \quad \Delta G^\circ = -(2)(F)(-.045\ \mathrm{V}) \tag{3.4.18}$$

$$\mathrm{Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)} \quad \Delta G^\circ = [-(1)(F)(0.77\ \mathrm{V})] + [-(2)(F)(-0.45\ \mathrm{V})] \tag{3.4.19}$$

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V) \tag{3.4.20}$$

Three electrons (n = 3) are transferred in the overall reaction, so substituting into Equation 3.4.6 and solving for E° gives the following:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} \tag{3.4.21}$$

$$F(0.13\ \mathrm{V}) = -(3)(F)(E^\circ_{\text{cell}}) \tag{3.4.22}$$

$$E^\circ = -\frac{0.13\ \mathrm{V}}{3} = -0.043\ \mathrm{V} \tag{3.4.23}$$

This value of E° is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E° for half-reactions cannot be added to give E° for the sum of the half-reactions; only values of $\Delta G^\circ = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^\circ = -RT \ln K \tag{3.4.24}$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 3.4.6), we can write

$$-nFE^\circ_{cell} = -RT \ln K \tag{3.4.25}$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{3.4.26}$$

For T = 298 K, Equation 3.4.25 can be simplified as follows:

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K = \left[\frac{[8.314\ \mathrm{J/(mol \cdot K)}(298\ \mathrm{K})]}{n[96,486\ \mathrm{J/(V \cdot mol)}]}\right] 2.303 \log K \tag{3.4.27}$$

$$= \left(\frac{0.0591\ \mathrm{V}}{n}\right) \log K$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 3.4.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and $E°_{cell}$.
B. Determine the number of electrons transferred in the overall reaction. Use Equation 3.4.27 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	$E^\circ_{cathode} = 1.69\ V$	(3.4.28)
anode:	$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	$E^\circ_{anode} = -0.36\ V$	(3.4.29)
overall:	$Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$	$E^\circ_{cell} = 2.05\ V$	(3.4.30)

B Two electrons are transferred in the overall reaction, so n = 2. Solving Equation 3.4.27 for log K and inserting the values of n and E°,

$$\log K = \frac{nE^\circ}{0.0591\ V} = \frac{2(2.05\ V)}{0.0591\ V} = 69.37 \quad (3.4.31)$$

$$K = 2.3 \times 10^{69} \quad (3.4.32)$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 3.4.3

Use the data in Table P2 to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightleftharpoons 2Sn^{4+}_{(aq)} + 2H_2O_{(l)} \quad (3.4.33)$$

Answer

1.2×10^{73}

Figure 3.4.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G° < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



Figure **3.4.1**: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, $\Delta G°$, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of $\Delta G°$ and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions.

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

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3.5: Cell Potential Under Nonstandard Conditions

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{3.5.1}$$

We also know that $\Delta G = -nFE_{cell}$ and $\Delta G^\circ = -nFE^\circ_{cell}$. Substituting these expressions into Equation 3.5.1, we obtain

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q \tag{3.5.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{3.5.3}$$

Equation 3.5.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 3.5.3 reduces to Equation 3.5.4 and 3.5.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{3.5.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{3.5.5}$$

Substituting the values of the constants into Equation 3.5.3 with T = 298 K and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential (E°_{cell}), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{3.5.6}$$

The Power of the Nernst Equation

The Nernst Equation (3.5.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 3.5.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 3.5.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 3.5.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2Ce^{4+}(aq) + 2Cl^{-}(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g) \quad E°_{cell} = 0.25\ V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}] = 0.013$ M, $[Ce^{3+}] = 0.60$ M, $[Cl^{-}] = 0.0030$ M, $P_{Cl_2} = 1.0$ atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 3.5.6 instead of Equation 3.5.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^{-} \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^{-}_{(aq)} \rightarrow Cl_{2(g)} + 2e^{-}$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 3.5.6,

$$\begin{aligned} E_{cell} &= E°_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q \\ &= 0.25\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{[Ce^{3+}]^2 P_{Cl_2}}{[Ce^{4+}]^2 [Cl^{-}]^2}\right) \\ &= 0.25\ V - [(0.0296\ V)(8.37)] = 0.00\ V \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture

Exercise 3.5.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4MnO_{2(s)} + 3O_{2(g)} + 4OH^{-}_{(aq)} \rightarrow 4MnO^{-}_{4(aq)} + 2H_2O_{(l)} \quad E°_{cell} = -0.20\ V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2} = 0.20 atm, $[MNO_4^{-}] = 1.0 \times 10^{-4}$ M, and T = 25°C.

Answer

$E_{cell} = -0.22$ V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{3.5.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 3.5.6:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{3.5.8}$$

$$= 1.10\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ V \tag{3.5.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so $Q = 1$ and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0×10^{-6} M Cu^{2+}), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V.

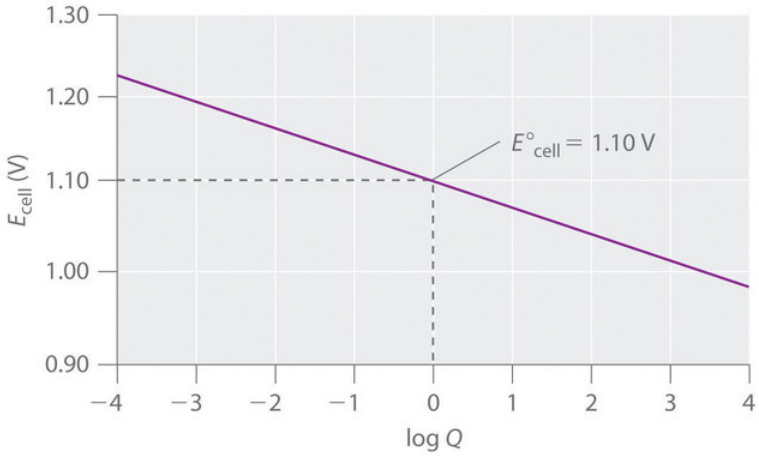


Figure 3.5.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell} = 1.10$ V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure 3.5.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when $E_{cell} = 0$ is calculated as follows:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q = 0 \tag{3.5.10}$$

$$E^\circ = \left(\frac{0.0591\ V}{n}\right) \log Q \tag{3.5.11}$$

$$\log Q = \frac{E°n}{0.0591\ V} = \frac{(1.10\ V)(2)}{0.0591\ V} = 37.23 \tag{3.5.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{3.5.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$Ag(s)\ |\ Ag^+(aq, 0.010\ M)\ ||\ Ag+(aq, 1.0\ M)\ |\ Ag(s) \tag{3.5.14}$$

cathode:

$$Ag^+(aq, 1.0\ M) + e^- \rightarrow Ag(s) \tag{3.5.15}$$

anode:

$$Ag(s) \rightarrow Ag^+(aq, 0.010\ M) + e^- \tag{3.5.16}$$

Overall

$$Ag^+(aq, 1.0\ M) \rightarrow Ag^+(aq, 0.010\ M) \tag{3.5.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$E_{cell} = E°_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q \tag{3.5.18}$$

$$= 0 - \left(\frac{0.0591\ V}{1}\right) \log\left(\frac{0.010}{1.0}\right) \tag{3.5.19}$$

$$= 0.12\ V \tag{3.5.20}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

Example 3.5.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.
B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}_{(aq,2.0M)} \rightarrow Mn^{2+}_{(aq,5.2\times10^{-2}M)}$$

B For the reduction of $Mn^{2+}(aq)$ to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 3.5.6:

$$E_{cell} = E°_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q = 0\ V - \left(\frac{0.0591\ V}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) = 0.047\ V$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 3.5.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure **3.5.1**, which is designed to measure the solubility product of silver chloride: $K_{sp} = [Ag^+][Cl^-]$. In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting: $[Ag^+] = K_{sp}/[Cl^-] = K_{sp}/1.0 = K_{sp}$. The overall cell reaction is as follows:

$$Ag^+(aq, \text{concentrated}) \rightarrow Ag^+(aq, \text{dilute})$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$E_{cell} = 0\ V - \left(\frac{0.0591\ V}{1}\right) \log\left(\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}\right) = \tag{3.5.21}$$

$$-0.0591\ V\ \log\left(\frac{K_{sp}}{1.0}\right) = -0.0591\ V\ \log K_{sp} \tag{3.5.22}$$

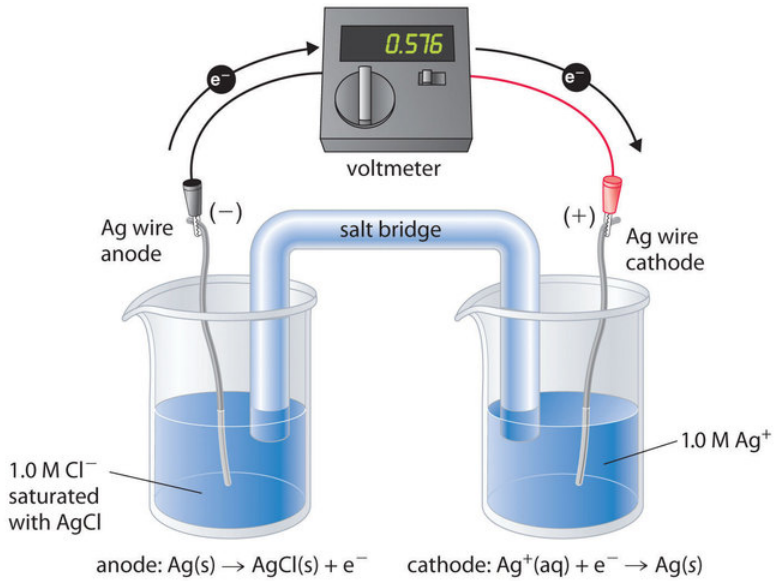


Figure **3.5.1**: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}.

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 3.5.12 for Ksp,

$$\log K_{sp} = \frac{-E_{cell}}{0.0591\ \text{V}} = \frac{-0.580\ \text{V}}{0.0591\ \text{V}} = -9.81 \tag{3.5.23}$$

$$K_{sp} = 1.5 \times 10^{-10} \tag{3.5.24}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.+

Example 3.5.3

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure **3.5.1**, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.
B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation 3.5.12 and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb2+ and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ \text{M}} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, \text{concentrated}) \rightarrow Pb^{2+}(aq, \text{dilute})$$

so

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$

$$0.230\ \text{V} = 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log \left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ \text{V} \log \left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = \log K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

? Exercise 3.5.3

A concentration cell similar to the one described in Example **3.5.3** contains a 1.0 M solution of lanthanum nitrate $[La(NO_3)_3]$ in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example **3.5.3**, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated in Example 20.5.6.

✓ Example 3.5.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$Zn(s)\,|\,Zn^{2+}(aq, 1.0\ M)\,\|\,H^+(aq, ?\ M)\,|\,H_2(g, 1.0\ atm)\,|\,Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 3.5.6), we can calculate $[H^+]$ under nonstandard conditions:

$$E_{cell} = E^{\circ}_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right) \log\left(\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}\right) \tag{3.5.25}$$

$$0.26\ \text{V} = 0.76\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log\left(\frac{(1.0)(1.0)}{[H^+]^2}\right) \tag{3.5.26}$$

$$16.9 = \log\left(\frac{1}{[H^+]^2}\right) = \log[H^+]^{-2} = (-2)\log[H^+] \tag{3.5.27}$$

$$8.46 = -\log[H^+] \tag{3.5.28}$$

$$8.5 = \text{pH} \tag{3.5.29}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 3.5.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E^{\circ}_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because ΔG = 0 at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

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3.6: Batteries and Fuel Cells

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure **3.6.1**). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

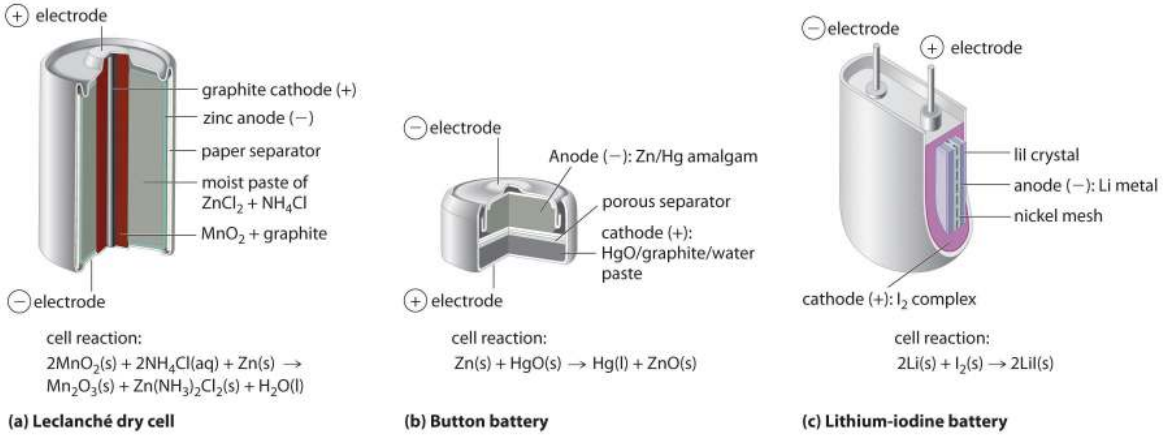


Figure **3.6.1**: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure **3.6.1**). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2MnO_{2(s)} + 2NH^+_{4(aq)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} \tag{3.6.1}$$

- anode (oxidation):

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \tag{3.6.2}$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall:

$$2MnO_{2(s)} + 2NH_4Cl_{(aq)} + Zn_{(s)} \rightarrow Mn_2O_{3(s)} + Zn(NH_3)_2Cl_{2(s)} + H_2O_{(l)} \tag{3.6.3}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.



Source: Photo courtesy of Mitchclanky2008, http://www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)} \tag{3.6.4}$$

- anode (oxidation):

$$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^- \tag{3.6.5}$$

- overall:

$$Zn_{(s)} + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)} \tag{3.6.6}$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 (part (b) in Figure 3.6.1).



Button batteries. Photo courtesy of Gerhard H Wrodnigg, Images used with permission from Wikipedia

The cathode and overall reactions and cell output for these two types of button batteries are as follows:

- cathode (Hg):

$$HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)} \tag{3.6.7}$$

- overall (Hg):

$$Zn_{(s)} + 2HgO_{(s)} \rightarrow Hg_{(l)} + ZnO_{(s)} \tag{3.6.8}$$

with $E_{cell} = 1.35\,V$

- cathode (Ag):

$$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)} \tag{3.6.9}$$

- overall (Ag):

$$Zn_{(s)} + 2Ag_2O_{(s)} \rightarrow 2Ag_{(s)} + ZnO_{(s)} \tag{3.6.10}$$

with $E_{cell} = 1.6\,V$

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-_{(LiI)} \tag{3.6.11}$$

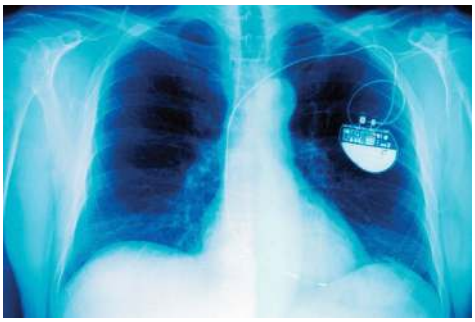
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{3.6.12}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{3.6.13}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure **3.6.1**, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure **3.6.2**, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

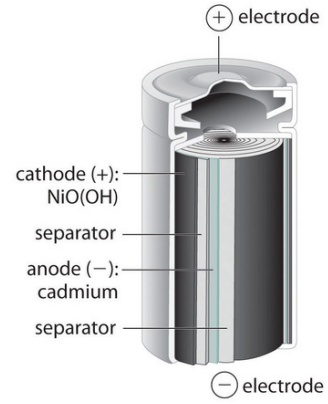


Figure 3.6.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a ***NiCad*** battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{3.6.14}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{3.6.15}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{3.6.16}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

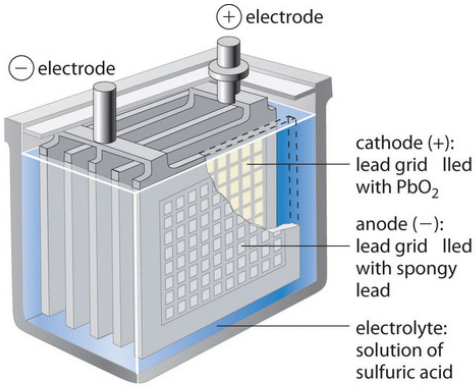
$$NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \tag{3.6.17}$$

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.



cell reaction:

$Pb(s) + PbO_2(s) + 2HSO_4^-(aq) + 2H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Figure **3.6.3**: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure **3.6.3**, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

$$PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \tag{3.6.18}$$

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{3.6.19}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{3.6.20}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (https://www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{3.6.21}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

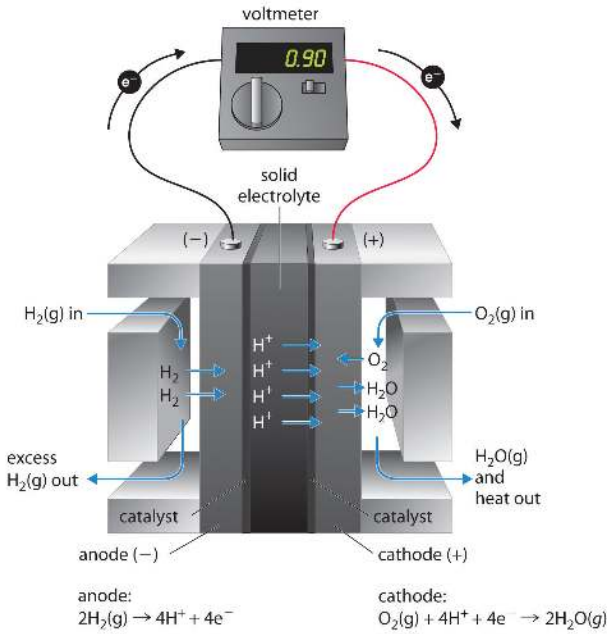


Figure **3.6.4**: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure **3.6.4**. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{3.6.22}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{3.6.23}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{3.6.24}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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3.7: Corrosion

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3 \cdot xH_2O$), commonly known as rust, that does not provide a tight protective film (Figure **3.7.1**). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

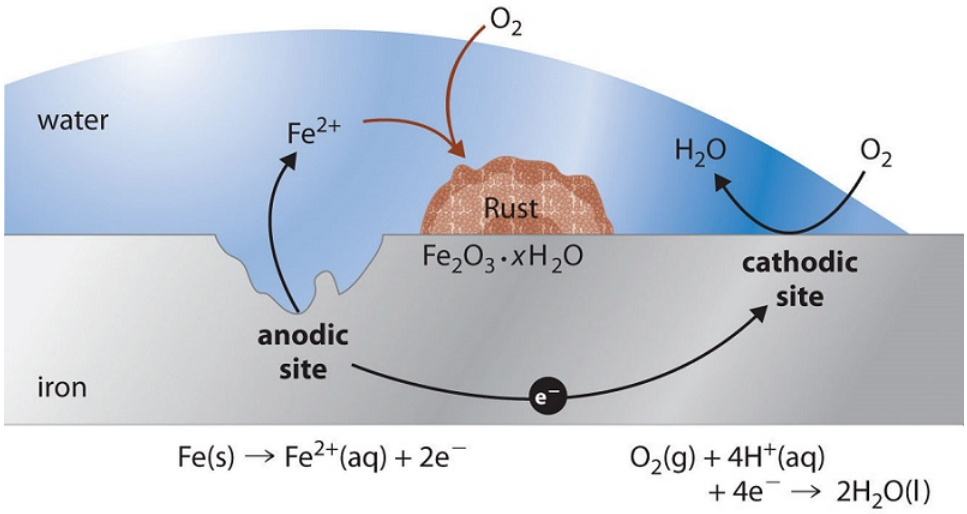


Figure **3.7.1**: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \cdot xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)} \quad E° = 1.23\ V \tag{3.7.1}$$

- at anode:

$$Fe(s) \rightarrow Fe^{2+}_{(aq)} + 2e^- \qquad E° = -0.45\ V \tag{3.7.2}$$

- overall:

$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad E° = 1.68\ V \tag{3.7.3}$$

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + (2 + 4x)H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+_{(aq)} \tag{3.7.4}$$

The sign and magnitude of E° for the corrosion process (Equation 3.7.3) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 3.7.2).

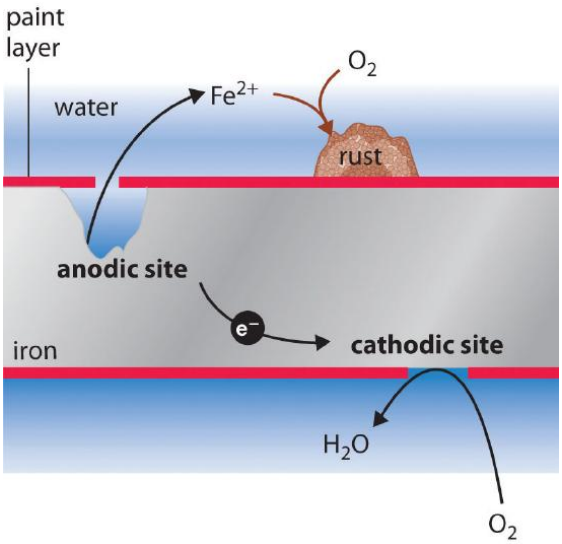


Figure 3.7.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings.

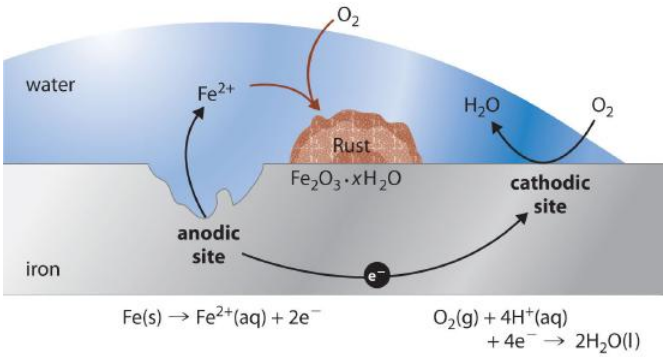


Figure **3.7.3**: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} ($E° = -0.14$ V) and Fe^{2+} ($E° = -0.45$ V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure **3.7.3**). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn ($E° = -0.76$ V for $Zn^{2+} + 2e^- \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{3.7.5}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{3.7.6}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{3.7.7}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure **3.7.4**). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

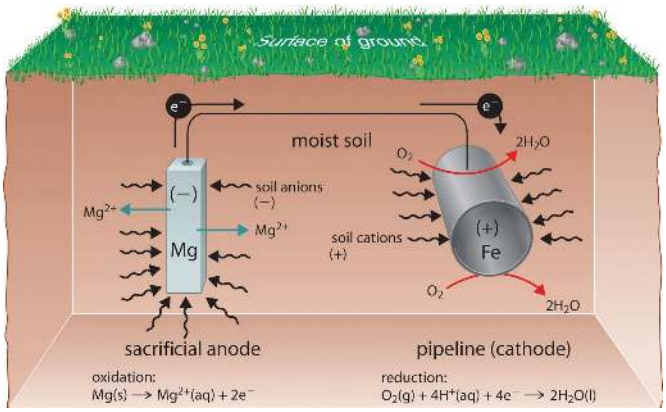


Figure **3.7.4**: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E° = -2.37$ V) is much more easily oxidized than iron ($E° = -0.45$ V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 3.7.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of E° than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

cathode:	$O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$E°_{cathode} = 1.23$ V	(3.7.8)
anode:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$E°_{anode} = -0.45$ V	(3.7.9)
overall:	$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$E°_{overall} = 1.68$ V	(3.7.10)

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 3.7.7).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 3.7.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

Answer a

Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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3.8: Electrolysis

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure **3.8.1***a*).

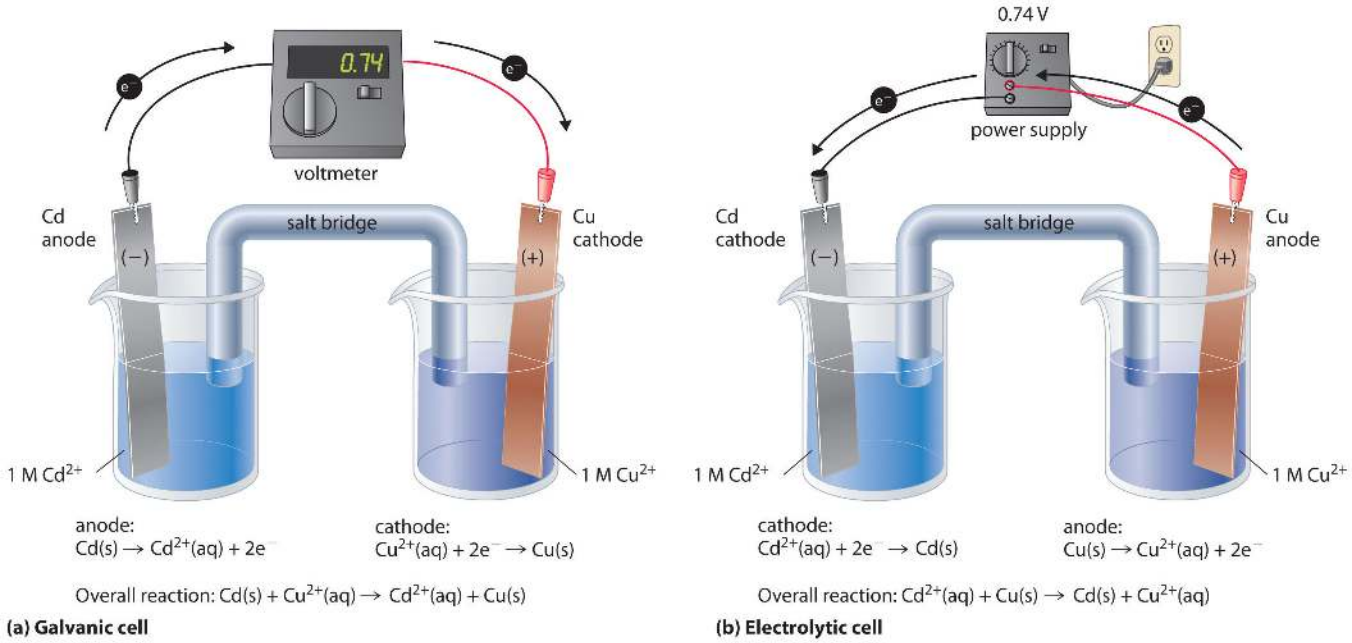


Figure **3.8.1**: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it.

The overall reaction is as follows:

$$\mathrm{Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cd^{2+}\,(aq) + Cu\,(s)} \tag{3.8.1}$$

with $E°_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G° < 0$):

$$\Delta G° = -nFE°_{\mathrm{cell}} \tag{3.8.2}$$

$$= -(2\ \mathrm{mol\ e^-})[96,486\ \mathrm{J/(V \cdot mol)}](0.74\ \mathrm{V}) \tag{3.8.3}$$

$$= -140\ \mathrm{kJ\ (per\ mole\ Cd)} \tag{3.8.4}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure **3.8.1***b*). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{3.8.5}$$

with $E^\circ_{cathode} = -0.40\,V$

- anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{3.8.6}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{3.8.7}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table **3.8.1**.

Table **3.8.1**: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten $NaCl$, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{3.8.8}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of $NaCl$ (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten $NaCl$ in a Downs cell (Figure **3.8.2**). In this

specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the $NaCl$ to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

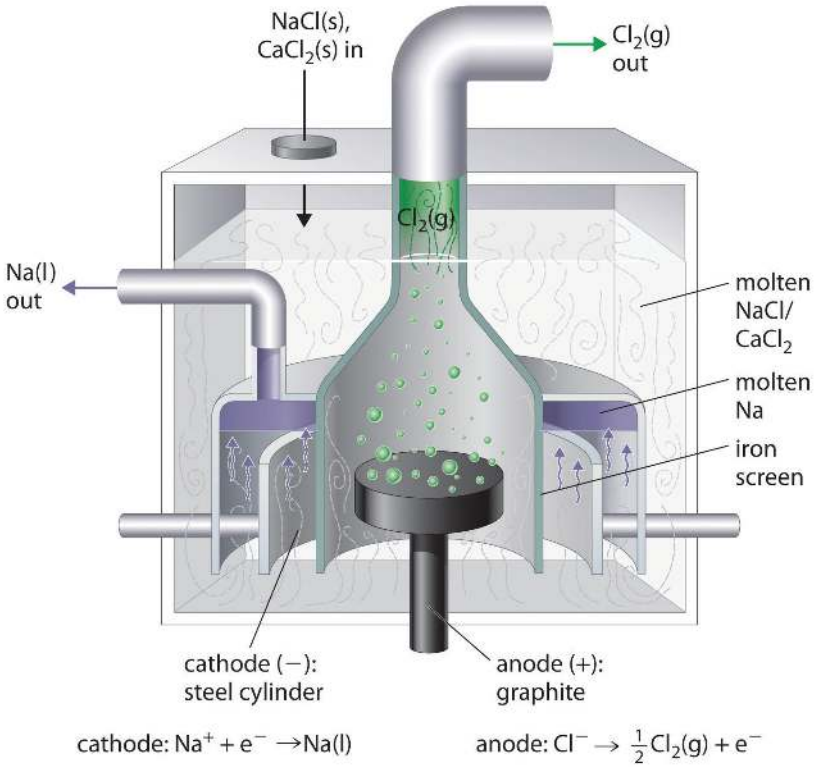


Figure 3.8.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2Al_2O_{3(l)} + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)} \tag{3.8.9}$$

Oxide ions react with oxidized carbon at the anode, producing $CO_2(g)$.

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Example 3.8.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

Exercise 3.8.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure **3.8.3**).

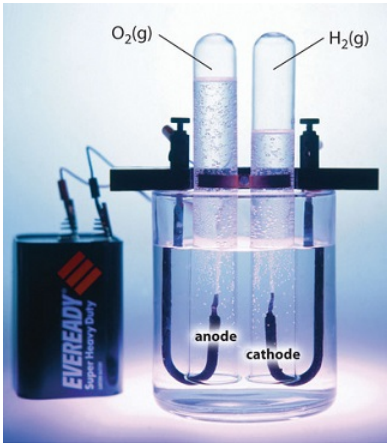


Figure **3.8.3**: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode.

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{3.8.10}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H +_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{3.8.11}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{3.8.12}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right) \log(P_{O_2} P^2_{H_2}) \tag{3.8.13}$$

$$E_{cell} = -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right) \log(1) = -1.23\ \text{V} \tag{3.8.14}$$

Thus E_{cell} is −1.23 V, which is the value of E°_{cell} if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure **3.8.4**.

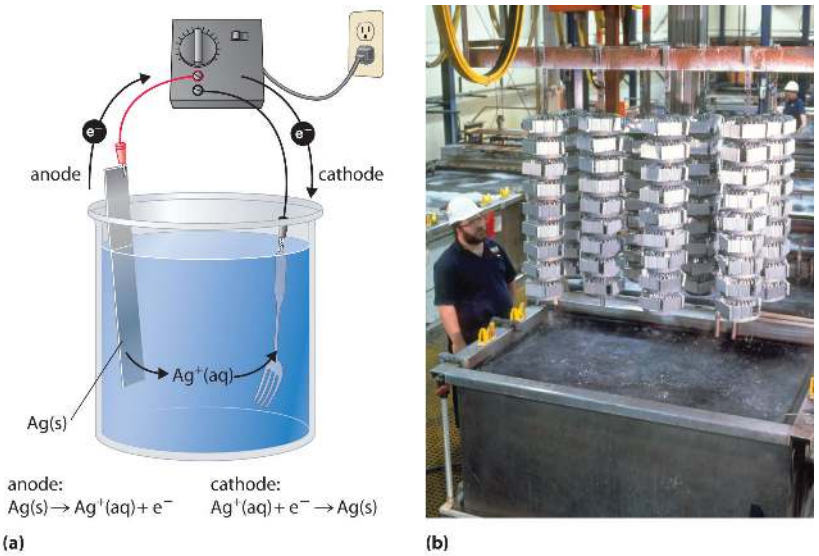


Figure **3.8.3**: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag+ solution and applying the correct potential.

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$Ag^{+}_{(aq)} + e- \rightarrow Ag_{(s)} \qquad E°_{cathode} = 0.80V \tag{3.8.15}$$

- anode (silver bar):

$$Ag_{(s)} \rightarrow Ag^{+}_{(aq)} \qquad E°_{anode} = 0.80V \tag{3.8.16}$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell} = 0$ V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of Ag^{+} to Ag metal. In contrast, in the reaction $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,486 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (C) transferred is the product of the current (A) and the time (t, in seconds):

$$C = A \times t \tag{3.8.17}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\text{charge} = (0.60\ \text{A})(6.0\ \text{min})(60\ \text{s/min}) = 220\ \text{A} \cdot \text{s} = 220\ \text{C}$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$\text{moles e}^- = \frac{220\ \text{C}}{96{,}486\ \text{C/mol}} = 2.3 \times 10^{-3}\ \text{mol e}^-$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 3.8.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}486\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\text{amperes} = \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \tag{3.8.18}$$

$$= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A} \tag{3.8.19}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise 3.8.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$C = A \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

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3.E: Electrochemistry (Exercises)

Questions moved to ADAPT.

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CHAPTER OVERVIEW

4: Chemical Kinetics

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

This chapter will present a quantitative description of when the chemical composition of a system is *not* constant with time. Chemical kinetics is the study of reaction rates, the changes in the concentrations of reactants and products with time. With a discussion of chemical kinetics, the reaction rates or the changes in the concentrations of reactants and products with time are studied. The techniques you are about to learn will enable you to describe the speed of many such changes and predict how the composition of each system will change in response to changing conditions. As you learn about the factors that affect reaction rates, the methods chemists use for reporting and calculating those rates, and the clues that reaction rates provide about events at the molecular level.

- 4.0: Factors that Affect Reaction Rates
- 4.1: Reaction Rates
- 4.2: Concentration and Rates (Differential Rate Laws)
- 4.3: The Change of Concentration with Time (Integrated Rate Laws)
- 4.4: Temperature and Rate
- 4.5: Reaction Mechanisms
- 4.6: Catalysis
- 4.E: Exercises
- 4.S: Chemical Kinetics (Summary)

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4.0: Factors that Affect Reaction Rates

Learning Objectives

- To gain a general overview of some of the important factors that manipulate chemical reaction rates.

There are many factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants and their dispersion, the solvent, and the presence of a catalyst.

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either are present. By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

Concentration Effects

Two substances cannot possibly react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more reactant particles that collide per unit time, the more often a reaction between them can occur. Consequently, the reaction rate usually increases as the concentration of the reactants increases.

Temperature Effects

Increasing the temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate of virtually all reactions decreases with decreasing temperature. For example, refrigeration retards the rate of growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce.

In systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100°C, ethanol is converted to diethyl ether:

$$2CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O \tag{4.0.1}$$

At 180°C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$CH_3CH_2OH \xrightarrow{H_2SO_4} C_2H_4 + H_2O \tag{4.0.2}$$

Phase and Surface Area Effects

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

Automobile engines use surface area effects to increase reaction rates. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction.

Solvent Effects

The nature of the solvent can also affect the reaction rates of solute particles. For example, a sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide.

$$CH_3CO_2Na_{(soln)} + CH_3I_{(l)} \rightarrow CH_3CO_2CH_{3\ (soln)} + NaI_{(soln)} \tag{4.0.3}$$

This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide [DMF; $(CH_3)_2NCHO$] than it does in methanol (CH_3OH). Although both are organic solvents with similar dielectric constants (36.7 for DMF versus 32.6 for methanol), methanol is able to hydrogen bond with acetate ions, whereas DMF cannot. Hydrogen bonding reduces the reactivity of the oxygen atoms in the acetate ion.

Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus the reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

Catalyst Effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Consider, for example, the decomposition of hydrogen peroxide in the presence and absence of different catalysts. Because most catalysts are highly selective, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.

Most of the bulk chemicals produced in industry are formed with catalyzed reactions. Recent estimates indicate that about 30% of the gross national product of the United States and other industrialized nations relies either directly or indirectly on the use of catalysts.

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4.1: Reaction Rates

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

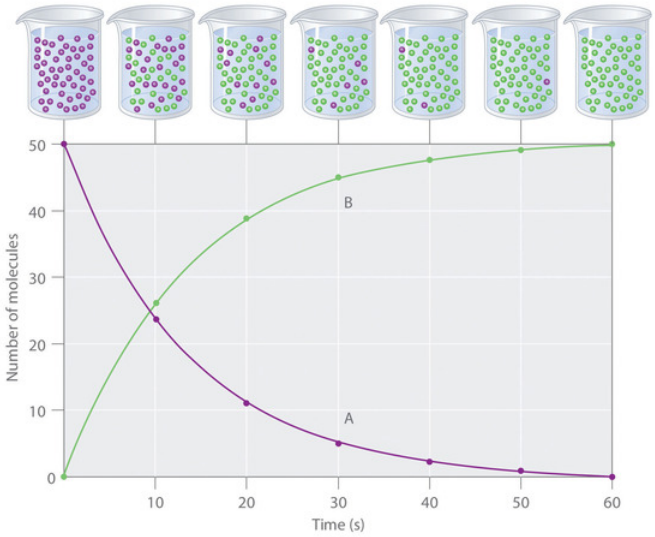


Figure **4.1.1**: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure **4.1.1**; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure **4.1.1**. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{4.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 4.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 4.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure **4.1.2**.

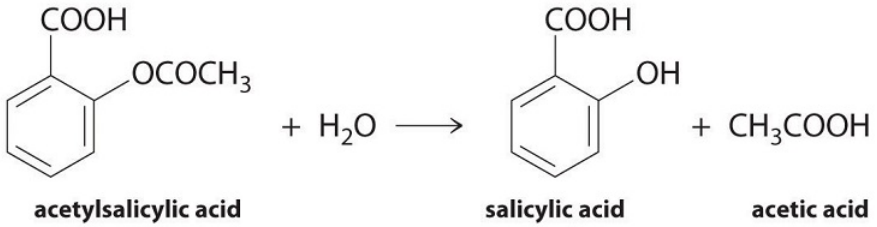


Figure 4.1.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 4.1.1 and are shown in the graph in Figure 4.1.3.

Table 4.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 4.1.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

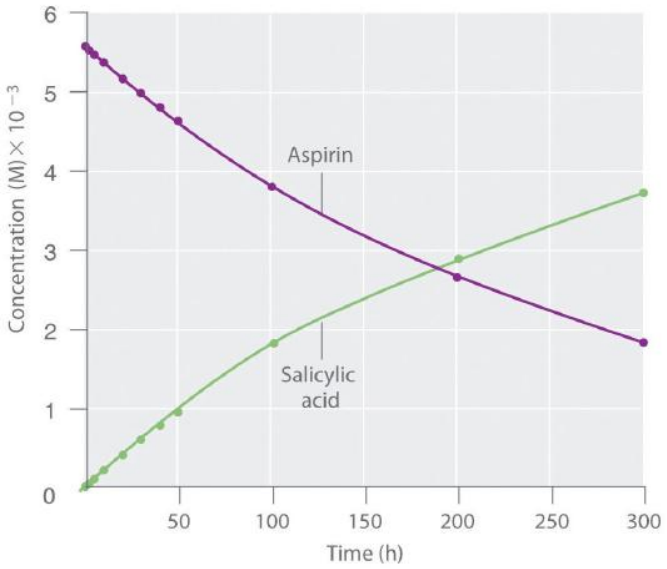


Figure **4.1.3**: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\text{rate}_{(t=0-2.0\ \text{h})} = \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\ \text{h} - 0\ \text{h}} \tag{4.1.2}$$

$$= \frac{0.040 \times 10^{-3}\ \text{M} - 0\ \text{M}}{2.0\ \text{h}} = 2.0 \times 10^{-5}\ \text{M/h} \tag{4.1.3}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\text{rate}_{(t=0-2.0\ \text{h})} = -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\,\text{h} - 0\,\text{h}} \tag{4.1.4}$$

$$= -\frac{(5.51 \times 10^{-3}\ \text{M}) - (5.55 \times 10^{-3}\ \text{M})}{2.0\ \text{h}} \tag{4.1.5}$$

$$= 2 \times 10^{-5}\ \text{M/h} \tag{4.1.6}$$

If the reaction rate is calculated during the last interval given in Table **4.1.1**(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\text{rate}_{(t=200-300\text{h})} = \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\,\text{h} - 200\,\text{h}} \tag{4.1.7}$$

$$= -\frac{(3.73 \times 10^{-3}\ \text{M}) - (2.91 \times 10^{-3}\ \text{M})}{100\ \text{h}} \tag{4.1.8}$$

$$= 8.2 \times 10^{-6}\ \text{M/h} \tag{4.1.9}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{4.1.10}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or

product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{4.1.11}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 4.1.11 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 4.1.10) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{4.1.12}$$

✔ Example 4.1.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

? Exercise 4.1.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[SO_2]}{2\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*

Example 4.1.2: Decomposition Reaction II

Using the reaction shown in Example **4.1.1**, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example **4.1.1**, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example **4.1.1**, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600\ \text{s} - 240\ \text{s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\ \text{M} - 0.0388\ \text{M}}{2(360\ \text{s})} = 2.65 \times 10^{-5}\ \text{M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600\ \text{s} - 240\ \text{s})} = \frac{0.0699\ \text{M} - 0.0314\ \text{M}}{4(360\ \text{s})} = 2.67 \times 10^{-5}\ \text{M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600\ \text{s} - 240\ \text{s}} = \frac{0.0175\ \text{M} - 0.00792\ \text{M}}{360\ \text{s}} = 2.66 \times 10^{-5}\ \text{M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 4.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

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4.2: Concentration and Rates (Differential Rate Laws)

Learning Objectives

- To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{4.2.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{4.2.2}$$

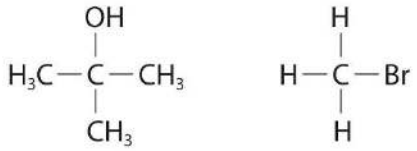
The proportionality constant (k) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of k, however, does not change as the reaction progresses under a given set of conditions.

> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers m and n, respectively. The values of m and n are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; m and n need not be integers. For example, Equation 4.2.2 tells us that Equation 4.2.1 is m^{th} order in reactant A and n^{th} order in reactant B. It is important to remember that n and m are not related to the stoichiometric coefficients a and b in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: $m + n$.

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



t-butanol methyl bromide

This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{4.2.3}$$

Combining the rate expression in Equation 4.2.2 with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{4.2.4}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{4.2.5}$$

Inserting the identities of the reactants into Equation 4.2.5 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{4.2.6}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 4.2.5 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{4.2.7}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{4.2.8}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 4.2.8 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-] \tag{4.2.9}$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

Example 4.2.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g) \tag{4.2.10}$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n \tag{4.2.11}$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\mathrm{NO_2}]^2[\mathrm{CO}]^0 = k[\mathrm{NO_2}]^2 \tag{4.2.12}$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 4.2.1A

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g) \tag{4.2.13}$$

has been experimentally determined to be $rate = k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2
- order in H_2 = 1
- overall order = 3

Exercise 4.2.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH} \tag{4.2.14}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\mathrm{CH_3OH}] \tag{4.2.15}$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1
- order in $CH_3CH_2OCOCH_3$ = 0
- overall order = 1

Example 4.2.2: Differential Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

a.
$$2\text{HI(g)} \xrightarrow{\text{Pt}} \text{H}_2\text{(g)} + \text{I}_2\text{(g)} \tag{4.2.16}$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\text{HI}]}{\Delta t}\right) = k[\text{HI}]^2$$

b.
$$2\text{N}_2\text{O(g)} \xrightarrow{\Delta} 2\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \tag{4.2.17}$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\text{N}_2\text{O}]}{\Delta t}\right) = k$$

c.
$$\text{cyclopropane(g)} \rightarrow \text{propane(g)} \tag{4.2.18}$$
$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$

Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A. Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

B. Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Add all exponents to obtain the overall reaction order.

C. Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution

1. **A** $[\text{HI}]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$k\text{M}^2 = \frac{\text{M}}{\text{s}}k = \frac{\text{M/s}}{\text{M}^2} = \frac{1}{\text{M}\cdot\text{s}} = \text{M}^{-1}\cdot\text{s}^{-1} \tag{4.2.19}$$

B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

C If the concentration of HI is doubled, the reaction rate will increase from $k[\text{HI}]_0^2$ to $k(2[\text{HI}])_0^2 = 4k[\text{HI}]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M\cdot s^{-1}$ = M/s.

B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

? Exercise 4.2.2

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

a. $\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)} \quad \text{rate} = -\dfrac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t}$ (4.2.20)

$= k[\mathrm{CH_3N{=}NCH_3}]$ (4.2.21)

b. $\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)} \quad \text{rate} = -\dfrac{\Delta[\mathrm{F_2}]}{\Delta t} = -\dfrac{1}{2}\left(\dfrac{\Delta[\mathrm{NO_2}]}{\Delta t}\right)$ (4.2.22)

$= k[\mathrm{NO_2}][\mathrm{F_2}]$ (4.2.23)

Answer a

s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.

Answer b

$M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow \textit{products}$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{4.2.24}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow \textit{products}$ are given in Table 4.2.1.

Table 4.2.1: Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow \textit{products}$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

The general rate law for the reaction is given in Equation 4.2.24. We can obtain m or n directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 4.2.3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\mathrm{A_1}]^m[\mathrm{B_1}]^n}{k[\mathrm{A_3}]^m[\mathrm{B_3}]^n} \tag{4.2.25}$$

Inserting the appropriate values from Table **4.2.3**,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n} \tag{4.2.26}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m = 1.00\ \text{M}$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for m.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for n.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table **4.2.3**,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n} \tag{4.2.27}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $\boldsymbol{n = 0}$; that is, the reaction is zeroth order in $\boldsymbol{B}$. The experimentally determined rate law is therefore

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table **4.2.3** into the experimentally determined rate law and solving for $\boldsymbol{k}$. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table **4.2.1** gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 4.2.3

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with $\boldsymbol{O_2}$ to give $\boldsymbol{NO_2}$, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_2 + \text{HNO}_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Determine the rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.

B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1} \tag{4.2.28}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1} \tag{4.2.29}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m + n) = 3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

? Exercise 4.2.3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O_{8(aq)}^{2-} + 3I_{(aq)}^{-} \rightarrow 2SO_{4(aq)}^{2-} + I_{3(aq)}^{-}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer:

rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ \text{M}^{-1}\cdot\text{s}^{-1}$

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant (*k*) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

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4.3: The Change of Concentration with Time (Integrated Rate Laws)

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

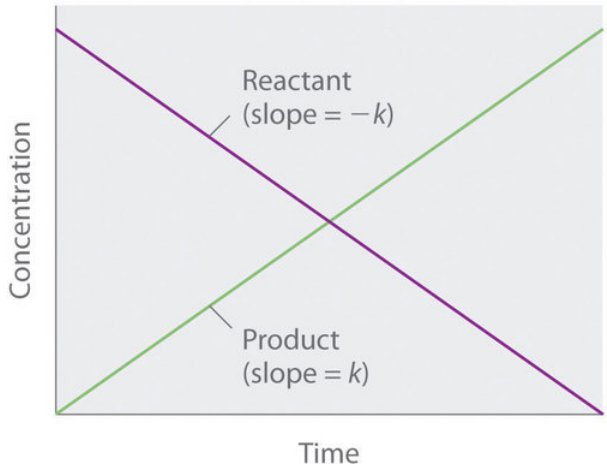
A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k. \tag{4.3.1}$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{4.3.2}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.



The graph of a zeroth-order reaction. *The change in concentration of reactant and product with time produces a straight line.*

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{4.3.3}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 4.3.3 has the form of the algebraic equation for a straight line,

$$y = mx + b, \tag{4.3.4}$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{4.3.5}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{4.3.6}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure **4.3.1**, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

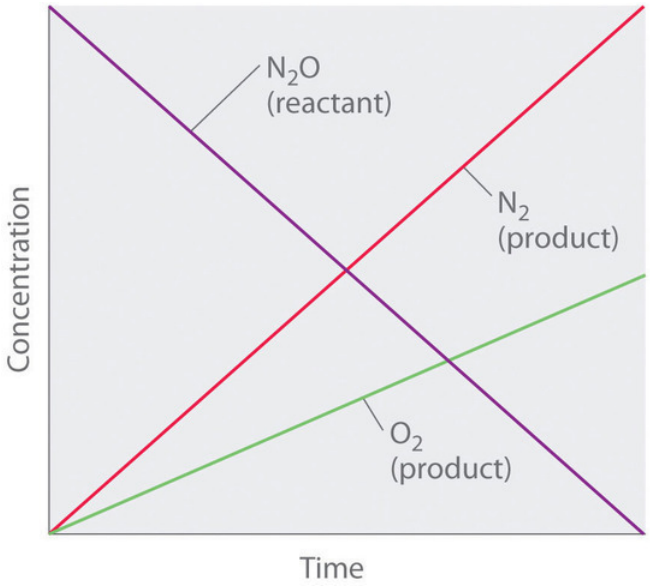


Figure **4.3.1**: *A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.*

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is



Figure **4.3.2**

where NAD^+ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (part (a) in Figure **4.3.3**). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure **4.3.3**).

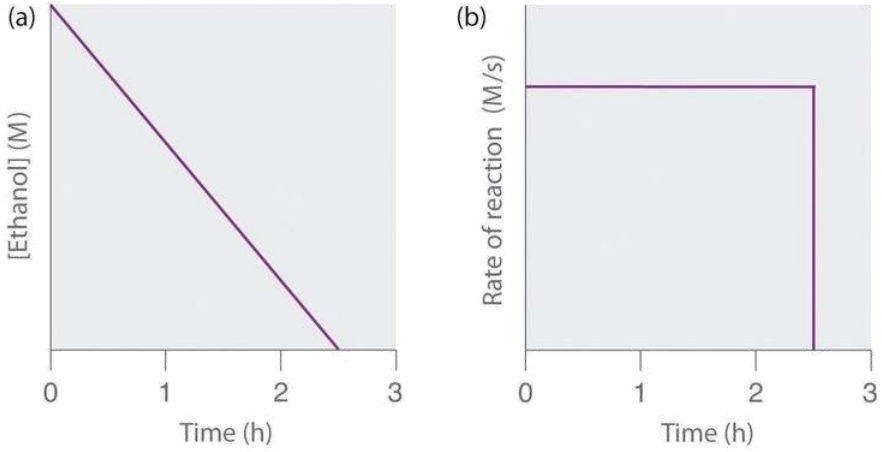


Figure **4.3.3**: The Catalyzed Oxidation of Ethanol *(a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.*

These examples illustrate two important points:

1. *In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.*
2. *A linear change in concentration with time is a clear indication of a zeroth-order reaction.*

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{4.3.7}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{4.3.8}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 4.3.8 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 4.3.8 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln [A]_0 - kt \tag{4.3.9}$$

Because Equation 4.3.9 has the form of the algebraic equation for a straight line,

$$y = mx + b, \tag{4.3.10}$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 4.3.7) or the integrated rate law (Equation 4.3.9) can be used to determine whether a particular reaction is first order.

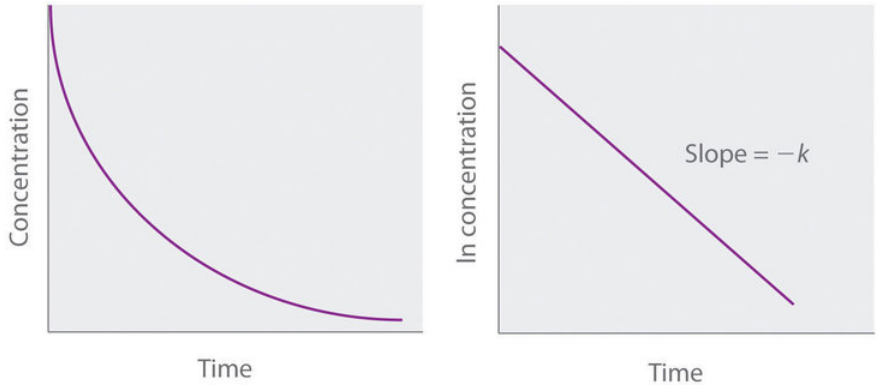


Figure 4.3.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. We have already encountered two examples of first-order reactions: the hydrolysis of aspirin (Figure 4.3.4) and the reaction of *t*-butyl bromide with water to give *t*-butanol (Equation ???). Another reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

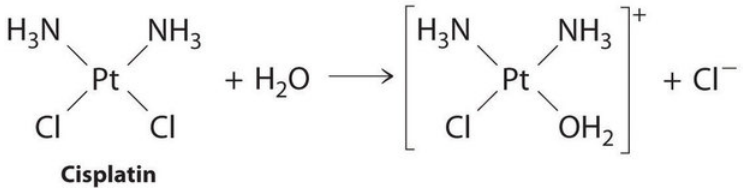


Figure 4.3.5: ***Cis*-platin reaction with water.**

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 4.3.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 4.3.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> *If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.*

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 4.3.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 4.3.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table **4.3.1** shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = k[cisplatin]^1. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table **4.3.1**. For example, substituting the values for Experiment 3 into Equation **4.3.7**,

$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$

$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 4.3.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$\mathrm{CH_3CH_2Cl(g) \xrightarrow{\Delta} HCl(g) + C_2H_4(g)}$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

Experiment	$[\mathrm{CH_3CH_2Cl}]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

Exercise 4.3.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5}\ \text{s}^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure **4.3.6***a* shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

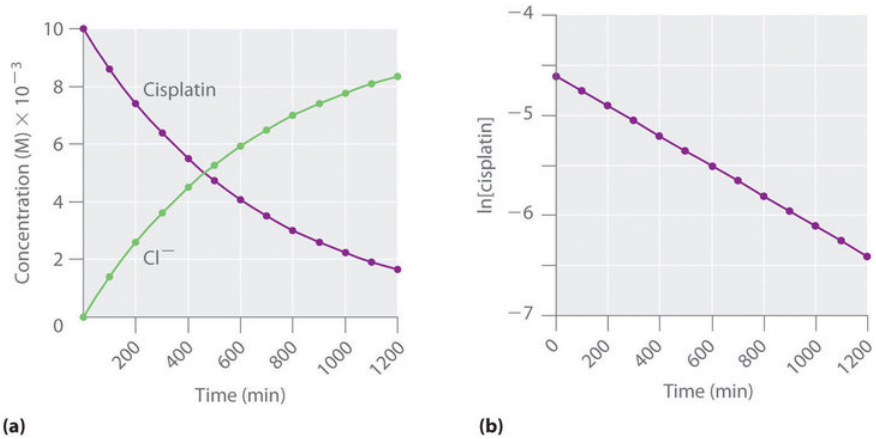


Figure **4.3.6**: *The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.*

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure **4.3.6**. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure **4.3.6** for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}} \tag{4.3.11}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1} \tag{4.3.12}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1} \tag{4.3.13}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure **4.3.6** are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

Example 4.3.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M (k = 1.6 × 10^{-6} s^{-1}) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.

B. Given a concentration [A], solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 4.3.8) is $[A] = [A]_0e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of k = 1.6 × 10^{-6} s^{-1}, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$\begin{aligned}[\text{CH}_3\text{CH}_2\text{Cl}]_{10\ \text{h}} &= [\text{CH}_3\text{CH}_2\text{Cl}]_0e^{-kt} \\ &= 0.0200\ \text{M}(e^{-(1.6\times10^{-6}\ \text{s}^{-1})[(10\ \text{h})(60\ \text{min/h})(60\ \text{s/min})]}) \\ &= 0.0189\ \text{M}\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 4.3.9):

$$\begin{aligned}\ln[\text{CH}_3\text{CH}_2\text{Cl}]_{10\ \text{h}} &= \ln[\text{CH}_3\text{CH}_2\text{Cl}]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6}\ \text{s}^{-1})[(10\ \text{h})(60\ \text{min/h})(60\ \text{s/min})] \\ &= -3.912 - 0.0576 = -3.970 \\ [\text{CH}_3\text{CH}_2\text{Cl}]_{10\ \text{h}} &= e^{-3.970}\ \text{M} \\ &= 0.0189\ \text{M}\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 4.3.9 gives the following:

$$\ln [CH_3CH_2Cl]_t = \ln [CH_3CH_2Cl]_0 - kt$$

$$kt = \ln [CH_3CH_2Cl]_0 - \ln [CH_3CH_2Cl]_t = \ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\left(\ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6 \times 10^{-6}\ \text{s}^{-1}}\left(\ln \frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right)$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6}\ \text{s}^{-1}} = 8.7 \times 10^5\ \text{s} = 240\ \text{h} = 2.4 \times 10^2\ \text{h}$$

? Exercise 4.3.2

In the exercise in Example **4.3.1**, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form 2A → products. A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2 \tag{4.3.14}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \tag{4.3.15}$$

Because Equation 4.3.15 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

> *Second-order reactions generally have the form 2A → products or A + B → products.*

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

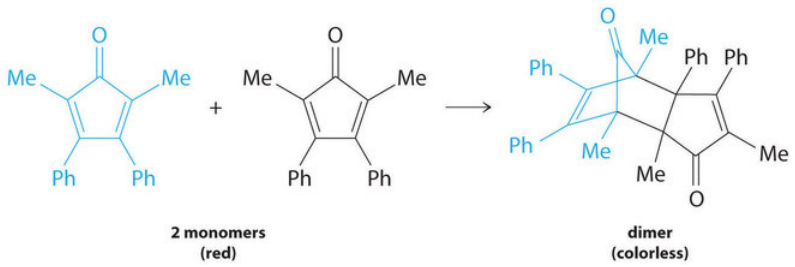


Figure **4.3.7**

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 4.3.14) or the integrated rate law (Equation 4.3.15).

Table **4.3.2**: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table **4.3.2**. From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7 \tag{4.3.16}$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 4.3.14 and the data from any row in Table **4.3.2**, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{4.3.17}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{4.3.18}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{4.3.19}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure **4.3.8***a*. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in Figure **4.3.8***b*. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ \text{M}^{-1}\cdot\text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation.

Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

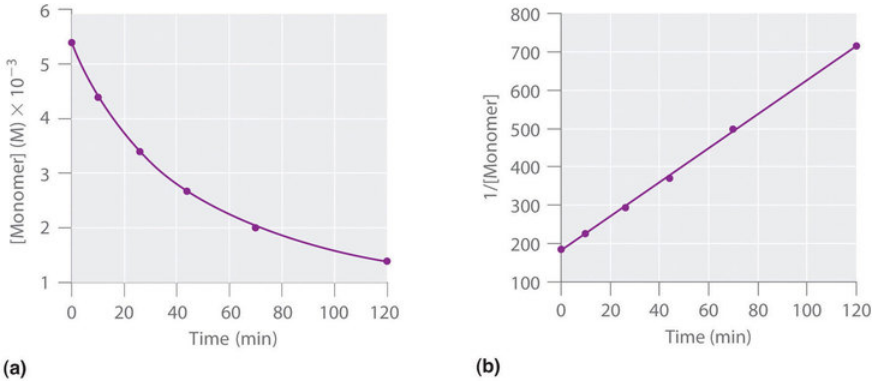


Figure **4.3.8**: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

Example 4.3.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2NO_2(g) \xrightarrow{\Delta} 2NO(g) + O_2(g)$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.
B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\text{rate} = k[NO_2]^2$$
$$5.40 \times 10^{-5}\ \text{M/s} = k(0.010\ \text{M})^2$$
$$0.54\ \text{M}^{-1} \cdot \text{s}^{-1} = k$$

Exercise 4.3.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO_2; $k = 1.4 \times 10^9\ \text{M}^{-1}\cdot\text{s}^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/reaction concentration versus time is linear, then the reaction is second order.

Example 4.3.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 4.3.15) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].
B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 14.4.9,

$$\frac{1}{[NO_2]_{3600}} = \frac{1}{[NO_2]_0} + kt = \frac{1}{0.056\ \text{M}} + [(0.54\ \text{M}^{-1} \cdot \text{s}^{-1})(3600\ \text{s})] \tag{4.3.20}$$
$$= 2.0 \times 10^3\ \text{M}^{-1} \tag{4.3.21}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056\ M$. To do this, we solve Equation 4.3.15 for t, using the concentrations given.

$$t = \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} = \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1} \cdot s^{-1}} = 3.0 \times 10^2\ s = 5.0\ min$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

? Exercise 4.3.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1} \cdot s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 4.3.15) and the rate constant calculated in the exercise in Example 4.3.3.

Answer

2.0×10^{-13} M; 6.4×10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = k[A][B] \tag{4.3.22}$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k$$

$$[A] = [A]_0 - kt$$

- **first-order reaction**:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

$$[A] = [A]_0 e^{-kt} \tag{4.3.23}$$

$$\ln[A] = \ln[A]_0 - kt$$

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

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4.4: Temperature and Rate

Learning Objectives

The Learning Objective of this Module is to understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. According to the collision model, a chemical reaction can occur only when the reactant molecules, atoms, or ions collide with more than a certain amount of kinetic energy and in the proper orientation. The collision model explains why, for example, most collisions between molecules do not result in a chemical reaction. Nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO_2 a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide. The collision model also explains why such chemical reactions occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates.

Activation Energy

Previously, we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy (E_a)**. We will define this concept using the reaction of ***NO*** with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \tag{4.4.1}$$

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

The reaction rate, not the rate constant, will vary with concentration. The rate constant, however, does vary with temperature. Figure ***Table* 4.4.1** shows a plot of the rate constant of the reaction of NO with O_3 at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature. In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

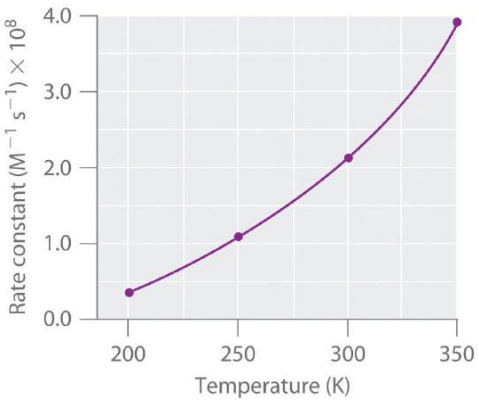


Figure **4.4.1:** *Rate Constant versus Temperature for the Reaction of* ***NO*** *with* O_3*The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases.*

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the activation energy, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> *Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.*

Graphing Energy Changes during a Reaction

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure **4.4.2** shows a plot for the NO–O_3 system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

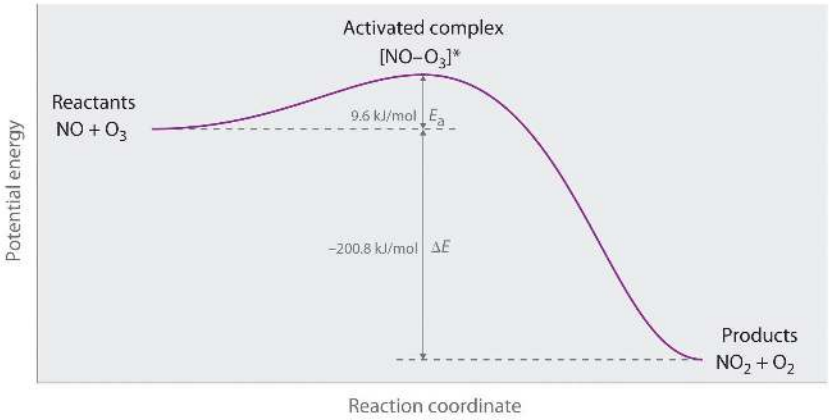


Figure **4.4.2**: *Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex.*

Part (a) in Figure **4.4.3** illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, part (b) in Figure **4.4.3** illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta E > 0$. Although the energy changes that result from a reaction can be positive, negative, or even zero, in all cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is always positive.

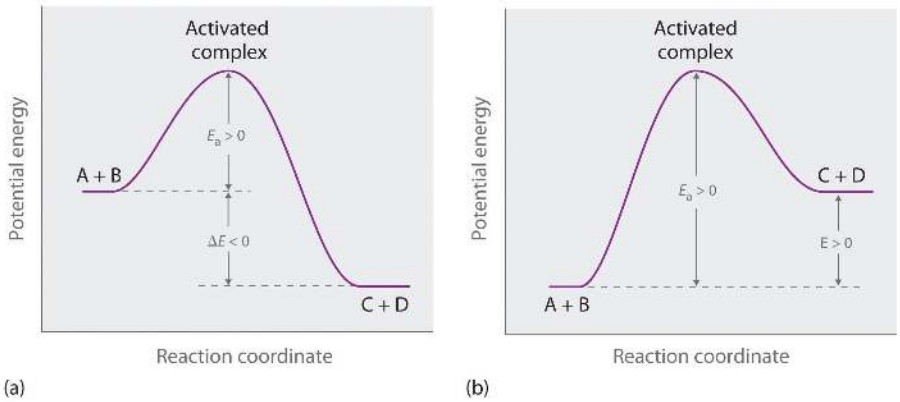


Figure **4.4.3**: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) ΔE < 0 and (b) ΔE > 0 illustrate the change in the potential energy of the system as reactants are converted to products. E_a is always positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE.

> *For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.*

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.

Even when the energy of collisions between two reactant species is greater than E_a, however, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure **4.4.4**). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a, most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the **steric factor (*p*)**, and, in general, its value can range from 0 (no orientations of molecules result in reaction) to 1 (all orientations result in reaction).

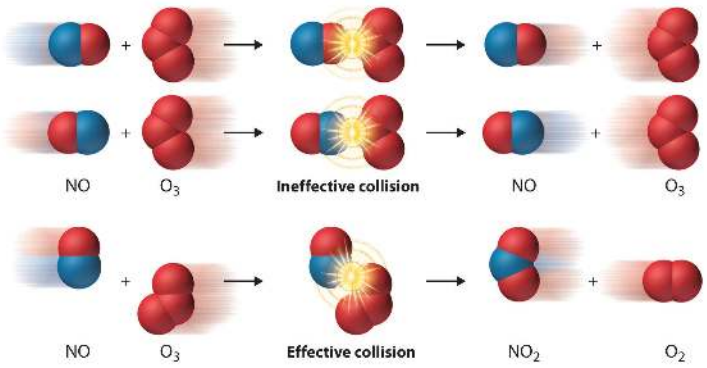


Figure **4.4.4**: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$.

The Arrhenius Equation

Figure 14.5.5 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

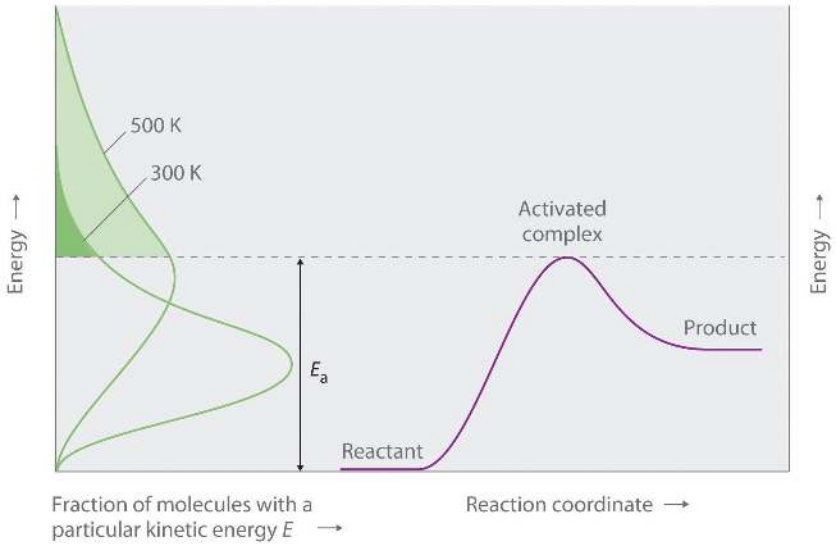


Figure **4.4.5**: *Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have $E > E_a$ and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K.*

For an A + B elementary reaction, all the factors that affect the reaction rate can be summarized in a single series of relationships:

$$\text{rate} = (\text{collision frequency})(\text{steric factor})(\text{fraction of collisions with } E > E_a)$$

where

$$rate = k[A][B] \tag{4.4.2}$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A, called the **frequency factor**:

$$k = Ae^{-E_a/RT} \tag{4.4.3}$$

The frequency factor is used to convert concentrations to collisions per second. Because the frequency of collisions depends on the temperature, A is actually not constant. Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time. Equation 4.4.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. $\boldsymbol{E_a}$ indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller $\boldsymbol{E_a}$ increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 4.4.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) = \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{4.4.4}$$

Equation 4.4.4 is the equation of a straight line, $y = mx + b$, where $y = \ln k$ and $x = 1/T$. This means that a plot of ln k versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of ln A. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the $\boldsymbol{E_a}$ at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining $\boldsymbol{E_a}$ from reaction rates measured at several temperatures is illustrated in Example **4.4.1**.

Example 4.4.1

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of ln[chirping rate] versus $1/T$ in Figure 14.5.6, to calculate $\boldsymbol{E_a}$ for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Frequency (f; chirps/min)	ln f	T (K)	1/T (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

A. From the plot of ln f versus $1/T$ in Figure 14.5.6, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
B. Express Equation 14.5.4 in terms of k_1 and T_1 and then in terms of k_2 and T_2.
C. Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1.

D. Using measured data from the table, solve the equation to obtain the ratio k_2/k_1. Using the value listed in the table for k_1, solve for k_2.

Solution

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of ln f versus $1/T$ should give a straight line (Figure **4.4.5**).

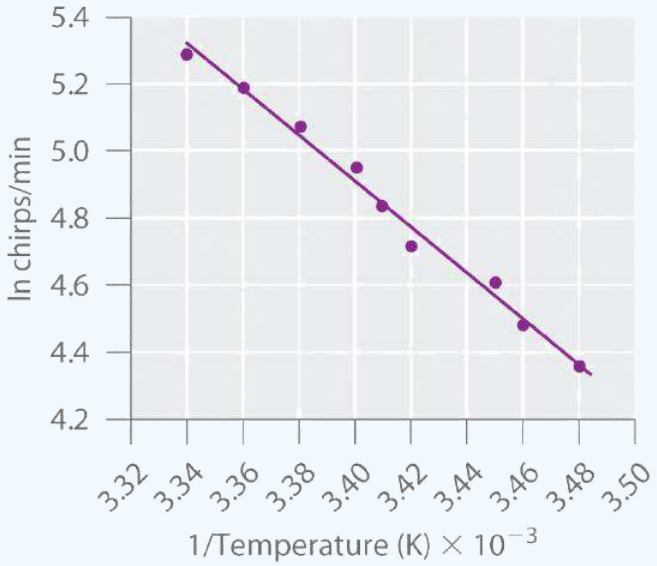


Figure **4.4.6**: Graphical Determination of E_a for Tree Cricket Chirping. *When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol.*

Also, the slope of the plot of ln f versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure **4.4.5** to estimate the slope:

$$\text{slope} = \frac{\Delta \ln f}{\Delta(1/T)} = \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ \text{K}^{-1} - 3.48 \times 10^{-3}\ \text{K}^{-1}} \tag{4.4.5}$$

$$= \frac{0.93}{-.014 \times 10^{-3}\ \text{K}^{-1}} = -6.6 \times 10^{3}\ \text{K} \tag{4.4.6}$$

A computer best-fit line through all the points has a slope of -6.67×10^3 K, so our estimate is very close. We now use it to solve for the activation energy:

$$E_a = -(\text{slope})(R) = -(-6.6 \times 10^{3}\ \text{K})\left(\frac{8.314\ \text{J}}{\text{K} \cdot \text{mol}}\right)\left(\frac{1\ \text{KJ}}{1000\ \text{J}}\right) = \frac{55\ \text{kJ}}{\text{mol}}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 14.5.4 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

C These two equations contain four known quantities (E_a, T_1, T_2, and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\ln k_2 - \ln k_1 = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

Then

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for T_1 = 296 K, where f = 158, and using the E_a calculated previously,

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{55\ \text{kJ/mol}}{8.314\ \text{J/(K·mol)}}\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right)\left(\frac{1}{296\ \text{K}} - \frac{1}{308\ \text{K}}\right) = 0.87$$

Thus k_{308}/k_{296} = 2.4 and k_{308} = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

? Exercise 4.4.1*A*

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

T (K)	k ($M^{-1}·s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}·s^{-1}$ = 1.86 × 10^4 $M^{-1}·s^{-1}$.

? Exercise 4.4.1*B*

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer

1. about 51 kJ/mol

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The **Arrhenius equation is** $k = Ae^{-E_a/RT}$. A minimum energy (activation energy,E_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

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4.5: Reaction Mechanisms

Learning Objectives

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2C_8H_{18\,(l)} + 25O_{2\,(g)} \rightarrow 16CO_{2\,(g)} + 18H_2O_{(g)} \tag{4.5.1}$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the mechanism of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> *The overall sequence of elementary reactions is the mechanism of the reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_{2\,(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2\,(g)} \tag{4.5.2}$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[NO_2]^2 \tag{4.5.3}$$

The fact that the reaction is second order in $[NO_2]$ and independent of $[CO]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[NO_2][CO]. \tag{4.5.4}$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

step 1	$NO_2 + NO_2 \xrightarrow{slow} NO_3 + NO$	elementary reaction
step 2	$NO_3 + CO \rightarrow NO_2 + CO_2$	elementary reaction
sum	$NO_2 + CO \rightarrow NO + CO_2$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

> *The sum of the elementary reactions in a reaction mechanism **must** give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as unimolecular; if there are two reactant molecules, it is bimolecular; and if there are three reactant molecules (a relatively rare situation), it is termolecular. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

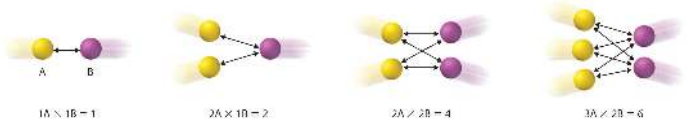


Figure **4.5.1***: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step.*

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table **4.5.1**). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is rate = k[A]. For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure **4.5.1**. For a bimolecular elementary reaction of the form A + B → products, the general rate law is rate = k[A][B].

Table **4.5.1***: Common Types of Elementary Reactions and Their Rate Laws*

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = k[A]^2	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = k[A]^2[B]	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow.

Look at the rate laws for each elementary reaction in our example as well as for for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	rate $= k_1[NO_2]^2$ (predicted)
step 2	$\underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$	rate $= k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	rate $= k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 4.5.1: A Reaction with an Intermediate

In an alternative mechanism for the reaction of NO_2 with CO, N_2O_4 appears as an intermediate.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$
step 2	$\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$
sum	$NO_2 + CO \rightarrow NO + CO_2$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A. Determine the rate law for each elementary reaction in the reaction.
B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

Exercise 4.5.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2ICl(l) + H_2(g) \rightarrow 2HCl(g) + I_2(s)$$

The experimentally determined rate law is rate = k[ICl][H_2]. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	rate $= k_1[ICl][H_2]$ (slow)
step 2	$\underline{HI + ICl \xrightarrow{k_2} HCl + I_2}$	rate $= k_2[HI][ICl]$ (fast)
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

Example 4.5.2 : NO with H_2

Assume the reaction between NO and H_2 occurs via a three-step process:

step 1	$\mathrm{NO + NO \xrightarrow{k_1} N_2O_2}$
step 2	$\mathrm{N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O}$
step 3	$\mathrm{N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O}$

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: rate = $k[NO]^2[H^2]$?

Answer:

- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$
- Step 3: $rate = k_3[N_2O][H_2]$

The overall reaction is then

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g) \tag{4.5.5}$$

- Rate Determining Step : #2
- Yes, because the rate of formation of $[N_2O_2] = k_1[NO]^2$. Substituting $k_1[NO]^2$ for $[N_2O_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

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4.6: Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure **4.6.1**). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

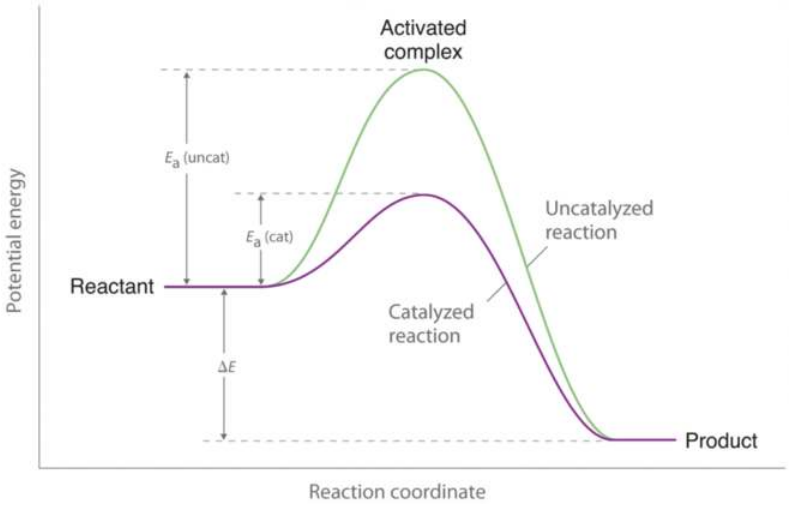


Figure **4.6.1**: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE).

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure **4.6.2**, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

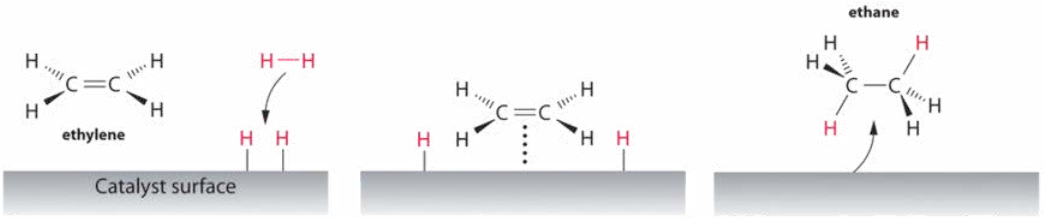


Figure **4.6.2**: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released.

Figure **4.6.2** shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table **4.6.1**. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

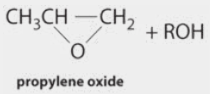
Table **4.6.1**: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$ acrylonitrile
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table **4.6.2**), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table **4.6.2**: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	 propylene oxide
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$-(CH_2CH_2-)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure **4.6.3**).



Figure **4.6.3**: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In

homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

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4.E: Exercises

14.1: Factors that Affect Reaction Rates

Q14.1.1

What information can you obtain by studying the chemical kinetics of a reaction? Does a balanced chemical equation provide the same information? Why or why not?

S14.1.1

Kinetics gives information on the reaction rate and reaction mechanism; the balanced chemical equation gives only the stoichiometry of the reaction.

Q14.1.2

If you were tasked with determining whether to proceed with a particular reaction in an industrial facility, why would studying the chemical kinetics of the reaction be important to you?

S14.1.2

Studying chemical kinetics determines whether to proceed with a reaction as it measures the rate of a reaction. Reactions conducted in an industrial facility mix compounds together, heating and stirring them for a while, before moving to the next process. When the compounds are then moved to the next phase of the process it is important to know how long to hold the reaction at one stage before continuing, to make sure a reaction has finished before starting the next one

Q14.1.3

What is the relationship between each of the following factors and the reaction rate: reactant concentration, temperature of the reaction, physical properties of the reactants, physical and chemical properties of the solvent, and the presence of a catalyst?

S14.1.3

Reactant concentration:

Reaction rate and the concentration of reactants have a direct relationship; as concentration goes up, so does reaction rate. This is because a higher concentration causes the reactants to have a higher probability to collide with a another reactant particle, possibly inducing the chemical reaction. This comes from the Collision theory.

Reaction temperature:

Reaction rate and the reaction temperature also have a direct relationship; as temperature goes up, so does reaction rate. A higher temperature makes the particles move at a faster speed so when two or more reactant particles collide, they collide with more energy and are more likely to reach the activation energy threshold, starting a chemical reaction.

Physical properties of the reactants:

If the reactants have the same physical properties, they are more likely to react, increasing the reaction rate, because the reactants mix and are more likely to collide another one of the reactants.

Physical and chemical properties of the solvent:

The properties of the solvent also affect the rates of a reaction. High viscosity means that particles more slowly than in low viscosity solvents, so reaction rates are slower in high viscosity solvents than in low viscosity solvents. This indicates an inverse relationship between viscosity and reaction rate.

Presence of a catalyst:

The chemical definition of a catalyst in a substance that increases the rate of a reaction without being used up in the reaction. Therefore, if a catalyst is present, reaction rate increases.

Q14.1.4

A slurry is a mixture of a finely divided solid with a liquid in which it is only sparingly soluble. As you prepare a reaction, you notice that one of your reactants forms a slurry with the solvent, rather than a solution. What effect will this have on the reaction rate? What steps can you take to try to solve the problem?

Q14.1.5

Why does the reaction rate of virtually all reactions increase with an increase in temperature? If you were to make a glass of sweetened iced tea the old-fashioned way, by adding sugar and ice cubes to a glass of hot tea, which would you add first?

S14.1.5

Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. First dissolve sugar in the hot tea, and then add the ice.

Q14.1.6

In a typical laboratory setting, a reaction is carried out in a ventilated hood with air circulation provided by outside air. A student noticed that a reaction that gave a high yield of a product in the winter gave a low yield of that same product in the summer, even though his technique did not change and the reagents and concentrations used were identical. What is a plausible explanation for the different yields?

Q14.1.7

A very active area of chemical research involves the development of solubilized catalysts that are not made inactive during the reaction process. Such catalysts are expected to increase reaction rates significantly relative to the same reaction run in the presence of a heterogeneous catalyst. What is the reason for anticipating that the relative rate will increase?

Q14.1.8

Water has a dielectric constant more than two times greater than that of methanol (80.1 for H_2O and 33.0 for CH_3OH). Which would be your solvent of choice for a substitution reaction between an ionic compound and a polar reagent, both of which are soluble in either methanol or water? Why?

14.2: Reaction Rates

Q14.2.1

Explain why the reaction rate is generally fastest at early time intervals. For the second-order A + B → C, what would the plot of the concentration of C versus time look like during the course of the reaction?

S14.2.1

Reactant concentrations are highest at the beginning of a reaction. The plot of [C] versus t is a curve with a slope that becomes steadily less positive.

Q14.2.2

Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?

Q14.2.3

Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of 10^{10} L/(mol·s). Are the reactions expected to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $H_3O^+ + OH^- \rightarrow 2H_2O$ and $H_3O^+ + N(CH_3)_3 \rightarrow H_2O + HN(CH_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?

S14.2.3

Faster in a less viscous solvent because the rate of diffusion is higher; the H_3O^+/OH^- reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.

Q14.2.4

What information can be obtained from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?

Q14.2.5

During the hydrolysis reaction A + H_2O → B + C, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How would this effect be reflected in the overall reaction order?

Q14.2.6

The reaction rate of a particular reaction in which A and B react to make C is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{2}\left(\frac{\Delta[\text{C}]}{\Delta t}\right)$$

Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

Q14.2.7

While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?

Q14.2.8

Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

Time (s)	[A] (M)
120	0.158
240	0.089
360	0.062

Q14.2.9

Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.

a. C_2H_5I → C_2H_4 + HI: rate = $k[C_2H_5I]$
b. SO + O_2 → SO_2 + O: rate = k[SO][O_2]
c. $2CH_3$ → C_2H_6: rate = $k[CH_3]^2$
d. ClOO → Cl + O_2: rate = k

Q14.2.10

Cleavage of C_2H_6 to produce two CH_3· radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with k = 5.46×10^{-4} s^{-1}. How long will it take for the reaction to go to 15% completion? to 50% completion?

S14.2.10

298 s; 1270 s

Q14.2.11

Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.

$$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+ \tag{4.E.1}$$

$$O_2^+ + O \xrightarrow{k_2} O_2 + O^+ \tag{4.E.2}$$

$$(O^+ + N_2 \xrightarrow{k_3} NO^+ + N \tag{4.E.3}$$

Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[N_2^+][O_2]$, which one of the steps is rate limiting?

Q14.2.12

The oxidation of aqueous iodide by arsenic acid to give I_3^- and arsenous acid proceeds via the following reaction:

$$H_3AsO_4(aq) + 3I^-(aq) + 2H^+(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_3AsO_3(aq) + I_3^-(aq) + H_2O(l)$$

Write an expression for the initial rate of decrease of $[I_3^-]$, $\Delta[I_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [H_3AsO_3][I_3^-]/[H_3AsO_4][I^-]^3[H^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

14.3: Concentration and Rate

14.4: The Change of Concentration with Time

Q14.4.1

What are the characteristics of a zeroth-order reaction? Experimentally, how would you determine whether a reaction is zeroth order?

Q14.4.2

Predict whether the following reactions are zeroth order and explain your reasoning.

a. a substitution reaction of an alcohol with HCl to form an alkyl halide and water
b. catalytic hydrogenation of an alkene
c. hydrolysis of an alkyl halide to an alcohol
d. enzymatic conversion of nitrate to nitrite in a soil bacterium

Q14.4.3

In a first-order reaction, what is the advantage of using the integrated rate law expressed in natural logarithms over the rate law expressed in exponential form?

Q14.4.4

If the reaction rate is directly proportional to the concentration of a reactant, what does this tell you about (a) the reaction order with respect to the reactant and (b) the overall reaction order?

Q14.4.5

The reaction of NO with O_2 is found to be second order with respect to NO and first order with respect to O_2. What is the overall reaction order? What is the effect of doubling the concentration of each reagent on the reaction rate?

Q14.4.6

Iodide reduces Fe(III) according to the following reaction:

$$2Fe^{3+}(soln) + 2I^-(soln) \rightarrow 2Fe^{2+}(soln) + I_2(soln) \tag{4.E.4}$$

Experimentally, it was found that doubling the concentration of Fe(III) doubled the reaction rate, and doubling the iodide concentration increased the reaction rate by a factor of 4. What is the reaction order with respect to each species? What is the overall rate law? What is the overall reaction order?

S14.4.6

First order in Fe^{3+}; second order in I^-; third order overall; rate = $k[Fe^{3+}][I^-]^2$.

Q14.4.7

Benzoyl peroxide is a medication used to treat acne. Its rate of thermal decomposition at several concentrations was determined experimentally, and the data were tabulated as follows:

Experiment	[Benzoyl Peroxide]$_0$ (M)	Initial Rate (M/s)
1	1.00	2.22×10^{-4}
2	0.70	1.64×10^{-4}
3	0.50	1.12×10^{-4}
4	0.25	0.59×10^{-4}

What is the reaction order with respect to benzoyl peroxide? What is the rate law for this reaction?

S14.4.7

The general rate law is: rate = k [Benzoyl Peroxide]^m. In order to find the reaction order with respect to benzoyl peroxide, divide two rate laws and solve for m:

$$\frac{rate_2}{rate_1} = \frac{k_2}{k_1}\left(\frac{[Benzoyl Peroxide]_2}{[Benzoyl Peroxide]_1}\right)^m$$

$$\frac{1.64 \times 10^{-4}\frac{M}{s}}{2.22 \times 10^{-4}\frac{M}{s}} = \left(\frac{0.070M}{1.00M}\right)^m$$

$$0.738 = (0.7)^m$$

$$m = 0.85$$

rate law: rate = k [Benzoyl Peroxide]$^{0.85}$

Q14.4.8

1-Bromopropane is a colorless liquid that reacts with $S_2O_3^{2-}$ according to the following reaction:

$$C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^- + Br^- \tag{4.E.5}$$

The reaction is first order in 1-bromopropane and first order in $S_2O_3^{2-}$, with a rate constant of 8.05×10^{-4} $M^{-1}{\cdot}s^{-1}$. If you began a reaction with 40 mmol/100 mL of C_3H_7Br and an equivalent concentration of $S_2O_3^{2-}$, what would the initial reaction rate be? If you were to decrease the concentration of each reactant to 20 mmol/100 mL, what would the initial reaction rate be?

S14.4.8

1.29×10^{-4} M/s; 3.22×10^{-5} M/s

Q14.4.9

The experimental rate law for the reaction 3A + 2B → C + D was found to be $\Delta[C]/\Delta t = k[A]^2[B]$ for an overall reaction that is third order. Because graphical analysis is difficult beyond second-order reactions, explain the procedure for determining the rate law experimentally.

14.5: Temperature and Rate

Q14.5.1

Although an increase in temperature results in an increase in kinetic energy, this increase in kinetic energy is not sufficient to explain the relationship between temperature and reaction rates. How does the activation energy relate to the chemical kinetics of a reaction? Why does an increase in temperature increase the reaction rate despite the fact that the average kinetic energy is still less than the activation energy?

S14.5.1

Activation energy is required for a collision between molecules to result in a chemical reaction, as well it is related to the rate due to the Arrhenius equation

Activation energy is the threshold of energy needed in order for a reaction to occur. Reactant particles must collide with enough energy to be able to break chemical bonds, that will then allow the creation of new bonds. If the particles do not have enough energy, when they collide they will simply bounce off one another.

$k=Ae^{(-Ea/RT)}$. The increase in temperature increases the rate of reaction despite the fact the average kinetic is less than the activation energy since it increase the rate of collision between molecules.

With an increase in temperature, there is a greater distribution of kinetic energy among reactant particles. This increase of temperature allows the rate in which particles collide with one another to increase. Although the average kinetic energy is still lower than the activation energy, the increase of collisions among particles increases the chance of particles that contain enough energy to overcome the energy barrier to collide. Thus, the reaction rate increases due to this increased rate of collisions.

Additionally, there is a higher amount of molecules that have sufficient kinetic energy to overcome the energy barrier, despite the average energy of all these molecules still being lower than the activation energy.

Q14.5.2

For any given reaction, what is the relationship between the activation energy and each of the following?

a. electrostatic repulsions
b. bond formation in the activated complex
c. the nature of the activated complex

S14.5.2

1.) Electrostatic repulsion: Electrostatic repulsion is the unfavorable interaction between two species of like charge. Activation energy is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed.

2.) Bond formation in the activated complex: An activated complex is an intermediate state that is formed during the conversion of reactants into products. Bond breaking can increase activation energy as breaking bonds requires energy.

3.) Nature of the activated complex: The activation energy of a chemical reaction is the difference between the energy of the activated complex and the energy of the reactants. If the structure has a high steric hindrance the activation energy will be higher.

Q14.5.3

If you are concerned with whether a reaction will occur rapidly, why would you be more interested in knowing the magnitude of the activation energy than the change in potential energy for the reaction?

Q14.5.4

The product C in the reaction A + B → C + D can be separated easily from the reaction mixture. You have been given pure A and pure B and are told to determine the activation energy for this reaction to determine whether the reaction is suitable for the industrial synthesis of C. How would you do this? Why do you need to know the magnitude of the activation energy to make a decision about feasibility?

Q14.5.5

Above E_a, molecules collide with enough energy to overcome the energy barrier for a reaction. Is it possible for a reaction to occur at a temperature less than that needed to reach E_a? Explain your answer.

Q14.5.6

What is the relationship between A, E_a, and T? How does an increase in A affect the reaction rate?

Q14.5.7

Of two highly exothermic reactions with different values of E_a, which would need to be monitored more carefully: the one with the smaller value or the one with the higher value? Why?

Q14.5.8

What happens to the approximate rate of a reaction when the temperature of the reaction is increased from 20°C to 30°C? What happens to the reaction rate when the temperature is raised to 70°C? For a given reaction at room temperature (20°C), what is the shape of a plot of reaction rate versus temperature as the temperature is increased to 70°C?

S14.5.8

The reaction rate will approximately double: 20°C to 30°C, the reaction rate increases by about $2^1 = 2$; 20°C to 70°C, the reaction rate increases by about $2^5 = 32$-fold. A plot of reaction rate versus temperature will give an exponential increase: rate $\propto 2^{\Delta T/10}$.

Q14.5.9

Acetaldehyde, used in silvering mirrors and some perfumes, undergoes a second-order decomposition between 700 and 840 K. From the data in the following table, would you say that acetaldehyde follows the general rule that each 10 K increase in temperature doubles the reaction rate?

T (K)	k ($M^{-1}·s^{-1}$)
720	0.024
740	0.051
760	0.105
800	0.519

Q14.5.10

Bromoethane reacts with hydroxide ion in water to produce ethanol. The activation energy for this reaction is 90 kJ/mol. If the reaction rate is 3.6×10^{-5} M/s at 25°C, what would the reaction rate be at the following temperatures?

a. 15°C
b. 30°C
c. 45°C

Q14.5.11

An enzyme-catalyzed reaction has an activation energy of 15 kcal/mol. How would the value of the rate constant differ between 20°C and 30°C? If the enzyme reduced the E_a from 25 kcal/mol to 15 kcal/mol, by what factor has the enzyme increased the reaction rate at each temperature?

S14.5.11

a. 1.0×10^{-5} M/s
b. 6.6×10^{-5} M/s
c. 3.5×10^{-4} M/s

Q14.5.12

The data in the following table are the rate constants as a function of temperature for the dimerization of 1,3-butadiene. What is the activation energy for this reaction?

T (K)	k ($M^{-1}·min^{-1}$)
529	1.4
560	3.7
600	25
645	82

S14.5.12

100 kJ/mol

Q14.5.13

The reaction rate at 25°C is 1.0×10^{-4} M/s. Increasing the temperature to 75°C causes the reaction rate to increase to 7.0×10^{-2} M/s. Estimate E_a for this process. If E_a were 25 kJ/mol and the reaction rate at 25°C is 1.0×10^{-4} M/s, what would be the reaction rate at 75°C?

14.6: Reaction Mechanisms

Q14.6.1

How does the term molecularity relate to elementary reactions? How does it relate to the overall balanced chemical equation?

Q14.6.2

What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?

Q14.6.3

When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?

Q14.6.3

If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?

Q14.6.4

Give the rate-determining step for each case.

a. Traffic is backed up on a highway because two lanes merge into one.
b. Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
c. A document containing text and graphics is downloaded from the Internet.

Q14.6.5

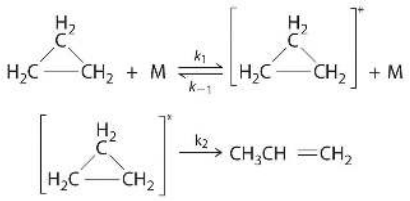
Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

S14.6.5

Free radicals are uncharged molecules with an unpaired valence electron. The reason these are so dangerous is because they like to grab electrons from other atoms to fill their own outer shell. This allows them to impair protein function because free radicals readily oxidize proteins and cell membrane which could lead to a loss of function. It was important to purge James Bond of radicals because radicals set off chain reactions of continuously pulling electrons from molecules, which in turn, can damage cells in the body.

Q14.6.6

Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



where M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

S14.6.6

When we are trying to decide which step is a rate-determining step, you have to look at which step is the slowest of them all, since we have no knowledge of the time scale for either of these steps we have to look elsewhere to determine the rate-determining step.

In our specific problem, we do not know what exact molecules we have however we do see that the first step is an equilibrium since it has a double-headed arrow with two k values one that is the reciprocal of the other. Since it is an equilibrium we can reasonably assume that energized propane is rapidly created which would lead us to the conclusion that the second step is the slower of the two steps and is, therefore, the rate-determining step. So, the second step (with k_2) determines the rate constant of the overall reaction.

Q14.6.7

Above approximately 500 K, the reaction between NO_2 and CO to produce CO_2 and NO follows the second-order rate law $\Delta[CO_2]/\Delta t = k[NO_2][CO]$. At lower temperatures, however, the rate law is $\Delta[CO_2]/\Delta t = k'[NO_2]^2$, for which it is known that NO_3 is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?

S14.6.7

Given that NO_3 is an intermediate in the low temperature reaction mechanism, we automatically know two things: 1) *NO_3 won't show up in the final overall reaction*, and thus, 2) *NO_3 will be in the products of the first reaction of the mechanism and in the reactants of the second reaction*. We can also assume that since we're given an intermediate from the problem, this is the only intermediate (so we won't have to dream up any other compounds that might exist in the series of reactions.) These things being said, the **lower temperature reaction mechanism** will look like this:

$$2NO_2(g) \rightarrow NO_3(g) + NO(g) \quad (1)$$

$$CO(g) + NO_3(g) \rightarrow CO_2(g) + NO_2(g) \quad (2)$$

And the overall reaction will look like this (notice how NO_3 is not present):

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g) \quad \textbf{(overall reaction)}$$

Now that we have the reaction mechanism written out, we can go about determining which step is the slowest. It would be pretty tricky to do this if we weren't given any further information, however, we know two more things: 1) *the high-temperature mechanism's rate = $k[NO_2][CO]$ meaning that it took place in one step* (given that the overall reaction is also equal to this rate) and 2) *the low-temperature mechanism's rate = $k'[NO_2]^2$*. These two things being said, we've both confirmed that our proposed low-temperature reaction mechanism is in fact two steps, and that *we have a means to find which step is slower*.

By using the "guess-and-check" method we can label each step reaction one at a time as the **"slow reaction"** and see if the rate matches up with the rate given to us.

Let's first try the 2nd reaction. (see above)

By using rate laws we can determine that the rate of the reaction must be in terms of its reactants, which follows:

$$k[CO][NO_3] \tag{4.E.6}$$

... *But wait!* We can't have the overall reaction rate in terms of an intermediate.

By looking at the 1st reaction, we can determine that we can sub in "$[NO_2]$ /[NO]" for "$[NO_3]$" since by writing the full reaction rate of the first step and solving for $[NO_3]$ this is equivalent. So, we now have the overall rate of the mechanism as the following given the 2nd reaction is the "slow reaction:"

$$k\frac{[CO][NO_2]^2}{[NO]} \tag{4.E.7}$$

Note that NO_2 is raised to the second power to account for the stoichiometry of the balanced reaction.

So clearly the 2nd reaction isn't the slow reaction since the rate is not equivalent to what we were given!

Let's check the rate of the 1st reaction now...

$$k[NO_2]^2 \tag{4.E.8}$$

What do you know... the rates are equal!

We have now confirmed that the 1st reaction is the slow reaction equation, since its rate is equivalent to the overall reaction rate.

Q14.6.8

Nitramide (O_2NNH_2) decomposes in aqueous solution to N_2O and H_2O. What is the experimental rate law ($\Delta[N_2O]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?

$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+$	(fast)
$O_2NNH^- \xrightarrow{k_2} N_2O + OH^-$	(slow)
$H^+ + OH^- \xrightarrow{k_3} H_2O$	(fast)

Assume that the rates of the forward and reverse reactions in the first equation are equal.

S14.6.8

We know that the slowest step of the reaction is the rate determining step, since it usually has the highest activation energy requirement. As a result, the slowest step of the reaction is the experimental rate law we are looking for.

Note: since the slowest step is the rate determining step, that usually means there is some intermediate in between. Intermediates should NEVER be a part of the rate law mechanism.

$$rate = rate_2 = k_2[O_2NNH^-] \tag{4.E.9}$$

Since Nitramide is an intermediate, we must find some way to substitute it. To solve that problem, we look for where Nitramide is produced and consumed. We see that

$$rate_1 = k_1[O_2NNH_2] \tag{4.E.10}$$

$$rate_{-1} = k_{-1}[O_2NNH^-][H^+] \tag{4.E.11}$$

Since these two rates produce and consume the same amount of O_2NNH^- over the same time period, we can set them equal to each other and solve for the intermediate

$$rate_1 = rate_{-1} \tag{4.E.12}$$

$$k_1[O_2NNH_2] = k_{-1}[O_2NNH^-][H^+] \tag{4.E.13}$$

$$[O_2NNH^-] = \frac{k_1[O_2NNH_2]}{k_{-1}[H^+]} \tag{4.E.14}$$

Substituting this equation back into our original equation gives us

$$rate = rate_2 = k_2\frac{k_1[O_2NNH_2]}{k_{-1}[H^+]} \tag{4.E.15}$$

With all of the rate constants (k), we can clean up our equation a little bit by saying

$$k = \frac{k_2k_1}{k_{-1}} \tag{4.E.16}$$

Leaving us with

$$rate = \frac{k[O_2NNH_2]}{[H^+]} \tag{4.E.17}$$

A14.6.8

$$\text{rate} = k_2\frac{k_1[\text{O}_2\text{NNH}_2]}{k_{-1}[\text{H}^+]} = k\frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^+]}$$

Q14.6.9

The following reactions are given:

$$\text{A} + \text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{C} + \text{D} \tag{4.E.18}$$

$$\text{D} + \text{E} \xrightarrow{k_2} \text{F} \tag{4.E.19}$$

What is the relationship between the relative magnitudes of k_{-1} and k_2 if these reactions have the following rate law?

$$\frac{\Delta[F]}{\Delta t} = k\frac{[A][B][E]}{[C]} \tag{4.E.20}$$

How does the magnitude of k_1 compare to that of k_2? Under what conditions would you expect the rate law to be

$$\frac{\Delta[F]}{\Delta t} = k'[A][B]? \tag{4.E.21}$$

Assume that the rates of the forward and reverse reactions in the first equation are equal.

S14.6.9

First, because we have broken the equations down into elementary steps we can write the rate laws for each step.

Step1:

$$A + B \xrightarrow{k_1} C + D \tag{4.E.22}$$

$$rate = k_1[A][B] \tag{4.E.23}$$

Step 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{4.E.24}$$

$$rate = k_{-1}[C][D] \tag{4.E.25}$$

Step 3:

$$D + E \xrightarrow{k_2} F \tag{4.E.26}$$

$$rate = k_2[D][E] \tag{4.E.27}$$

If we add a these steps together we see that we get overall reaction

$$A + B + E \rightarrow C + F \tag{4.E.28}$$

we can see that [D] is an intermediate and

$$k_1 = k_{-1} \tag{4.E.29}$$

.

Since we are not told which steps are fast or slow we need to use Steady State Approximation.

If the second step is the slower step ($k_{-1} >> k_2$) then our rate determining step would be

$$rate = k_2[D][E] \tag{4.E.30}$$

Since we can only write rate laws in terms of products and reactants we have to rewrite this so that we are not including an intermediate.

Assume: rate of [D] formation = rate of its disappearance

$$k_1[A][B] = k_{-1}[C][D] + k_2[D][E] \tag{4.E.31}$$

$$k_1[A][B] = [D](k_{-1}[C] + k_2[E]) \tag{4.E.32}$$

Solving for [D] we find that

$$[D] = \frac{k_1[A][B]}{(k_{-1}[C] + k_2[E])} \tag{4.E.33}$$

now we can use this to substitute the intermediate [D] in the rate law to get an appropriate rate law.

$$rate = \frac{k_2 k_1[A][B][E]}{(k_{-1}[C] + k_2[E])} \tag{4.E.34}$$

because we had already established $k_{-1} >> k_2$ *we can assume that*

$$k_{-1}[C] + k_2[E] \approx k_{-1}[C] \tag{4.E.35}$$

this would give us the observed rate law

$$\frac{\Delta[F]}{\Delta t} = \frac{k_2 k_1[A][B][E]}{k_{-1}[C]} \tag{4.E.36}$$

to make this clearer we can set

$$k = \frac{(k_2)(k_1)}{(k_{-1})} \tag{4.E.37}$$

and we can then simplify it down to

$$\frac{\Delta[F]}{\Delta t} = k\frac{[A][B][E]}{[C]} \tag{4.E.38}$$

we can see that all of these rate constants are related by this ratio k_2k_1/k_{-1}. Since k_2 is our rate determining step $k_{-1} >> k_2$ *and since* $k_1 = k_{-1}$ then we can see that $k_1 >> k_2$.

We would expect the rate law to be

$$\frac{\Delta[F]}{\Delta t} = k'[A][B]? \tag{4.E.39}$$

if the rate determining step aka the slowest step is that corresponding to (step 1) since the rate law for this step is k_1[A][B] and this is the exact the same as the rate law that we were given.

14.7: Catalysis

Q14.7.1

What effect does a catalyst have on the activation energy of a reaction? What effect does it have on the frequency factor (*A*)? What effect does it have on the change in potential energy for the reaction?

S14.7.1

A catalyst lowers the activation energy of a reaction. Some catalysts can also orient the reactants and thereby increase the frequency factor. Catalysts have no effect on the change in potential energy for a reaction.

Q14.7.2

How is it possible to affect the product distribution of a reaction by using a catalyst?

Q14.7.3

A heterogeneous catalyst works by interacting with a reactant in a process called *adsorption*. What occurs during this process? Explain how this can lower the activation energy.

S14.7.3

In adsorption, a reactant binds tightly to a surface. Because intermolecular interactions between the surface and the reactant weaken or break bonds in the reactant, its reactivity is increased, and the activation energy for a reaction is often decreased.

Q14.7.4

What effect does increasing the surface area of a heterogeneous catalyst have on a reaction? Does increasing the surface area affect the activation energy? Explain your answer.

Q14.7.5

Identify the differences between a heterogeneous catalyst and a homogeneous catalyst in terms of the following.

a. ease of recovery
b. collision frequency
c. temperature sensitivity
d. cost

S14.7.4

a. Heterogeneous catalysts are easier to recover.
b. Collision frequency is greater for homogeneous catalysts.
c. Homogeneous catalysts are often more sensitive to temperature.
d. Homogeneous catalysts are often more expensive.

Q14.7.6

An area of intensive chemical research involves the development of homogeneous catalysts, even though homogeneous catalysts generally have a number of operational difficulties. Propose one or two reasons why a homogenous catalyst may be preferred.

S14.7.6

Catalysts are compounds that, when added to chemical reactions, reduce the activation energy and increase the reaction rate. The amount of a catalyst does not change during a reaction, as it is not consumed as part of the reaction process. Catalysts lower the energy required to reach the transition state of the reaction, allowing more molecular interactions to achieve that state. However, catalysts do not affect the degree to which a reaction progresses. In other words, though catalysts affect reaction kinetics, the equilibrium state remains unaffected.

Catalysts can be classified into two types: homogenous and heterogeneous. Homogenous catalysts are those which exist in the same phase (gas or liquid) as the reactants, while heterogeneous catalysts are not in the same phase as the reactants. Typically, heterogeneous catalysis involves the use of solid catalysts placed in a liquid reaction mixture. For this question, we will be discussing homogenous catalysts.

Most of the times, homogeneous catalysis involves the introduction of an aqueous phase catalyst into an aqueous solution of reactants. One reason why homogeneous catalysts are preferred over heterogeneous catalysts because homogeneous catalysts mix well in chemical reactions in comparison to heterogeneous catalysts. However, homogeneous catalyst is often irrecoverable after the reaction has run to completion.

Q14.7.7

Consider the following reaction between cerium(IV) and thallium(I) ions:

$$2\,Ce^{4+} + Tl^{+} \longrightarrow 2\,Ce^{3+} + Tl^{3+} \tag{4.E.40}$$

This reaction is slow, but Mn^{2+} catalyzes it, as shown in the following mechanism:

$$Ce^{4+} + Mn^{2+} \longrightarrow Ce^{3+} + Mn^{3+} \tag{4.E.41}$$

$$Ce^{4+} + Mn^{3+} \longrightarrow Ce^{3+} + Mn^{4+} \tag{4.E.42}$$

$$Mn^{4+} + Tl^{+} \longrightarrow Tl^{3+} + Mn^{2+} \tag{4.E.43}$$

In what way does Mn^{2+} increase the reaction rate?

S14.7.7

The Mn^{2+} ion donates two electrons to Ce^{4+}, one at a time, and then accepts two electrons from Tl^{+}. Because Mn can exist in three oxidation states separated by one electron, it is able to couple one-electron and two-electron transfer reactions.

Q14.7.8

The text identifies several factors that limit the industrial applications of enzymes. Still, there is keen interest in understanding how enzymes work for designing catalysts for industrial applications. Why?

S14.7.8

Enzymes are expensive to make, denature and fail at certain temperatures, are not that stable in a solution, and are very specific to the reaction it was made for. However, scientists can use the observations from enzymes to create catalysts that are more effective in aiding the reaction and cost less to produce. Overall, catalysts still play a large part in lowering the activation energy for reactions. Creating new catalysts can help in the improvement of areas such as medical, ecological, and even commercial products.

Q14.7.9

Most enzymes have an optimal pH range; however, care must be taken when determining pH effects on enzyme activity. A decrease in activity could be due to the effects of changes in pH on groups at the catalytic center or to the effects on groups located elsewhere in the enzyme. Both examples are observed in chymotrypsin, a digestive enzyme that is a protease that hydrolyzes polypeptide chains. Explain how a change in pH could affect the catalytic activity due to (a) effects at the catalytic center and (b) effects elsewhere in the enzyme. (*Hint*: remember that enzymes are composed of functional amino acids.)

Q14.7.10

At some point during an enzymatic reaction, the concentration of the activated complex, called an enzyme–substrate complex (***ES***), and other intermediates involved in the reaction is nearly constant. When a single substrate is involved, the reaction can be represented by the following sequence of equations:

$$\begin{aligned}\text{enzyme (E)} + \text{substrate (S)} &\rightleftharpoons \text{enzyme-substrate complex (ES)} \\ &\rightleftharpoons \text{enzyme (E)} + \text{product (P)}\end{aligned} \tag{4.E.44}$$

This can also be shown as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \tag{4.E.45}$$

Using molar concentrations and rate constants, write an expression for the rate of disappearance of the enzyme–substrate complex. Typically, enzyme concentrations are small, and substrate concentrations are high. If you were determining the rate law by varying the substrate concentrations under these conditions, what would be your apparent reaction order?

S14.7.10

$\frac{\Delta[ES]}{\Delta t} = -(k_2 + k_{-1})[ES] + k_1[E][S] + k_{-2}[E][P] \approx 0$; zeroth order in substrate.

Q14.7.11

A particular reaction was found to proceed via the following mechanism:

- $A + B \rightarrow C + D$ (slow)
- $2C \rightarrow E$ (fast)
- $E + A \rightarrow B + F$ (fast)

What is the overall reaction? Is this reaction catalytic, and if so, what species is the catalyst? Identify the intermediates

Q14.7.12

A particular reaction has two accessible pathways (A and B), each of which favors conversion of *X* to a different product (*Y* and *Z*, respectively). Under uncatalyzed conditions pathway A is favored, but in the presence of a catalyst pathway B is favored. Pathway B is reversible, whereas pathway A is not. Which product is favored in the presence of a catalyst? without a catalyst? Draw a diagram illustrating what is occurring with and without the catalyst.

S14.7.12

In both cases, the product of pathway A is favored. All of the *Z* produced in the catalyzed reversible pathway B will eventually be converted to *X* as *X* is converted irreversibly to *Y* by pathway A.

Q14.7.13

The kinetics of an enzyme-catalyzed reaction can be analyzed by plotting the reaction rate versus the substrate concentration. This type of analysis is referred to as a Michaelis–Menten treatment. At low substrate concentrations, the plot shows behavior characteristic of first-order kinetics, but at very high substrate concentrations, the behavior shows zeroth-order kinetics. Explain this phenomenon.

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4.S: Chemical Kinetics (Summary)

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

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These is a summary of key concepts of the chapter in the Textmap created for "Chemistry: The Central Science" by Brown et al.

14.1: Factors that Affect Reaction Rates

chemical kinetics – area of chemistry dealing with speeds/rates of reactions

- rates of reactions affected by four factors
  1. concentrations of reactants
  2. temperature at which reaction occurs
  3. presence of a catalyst
  4. surface area of solid or liquid reactants and/or catalysts

14.2: Reaction Rates

- **reaction rate** – speed of a chemical reaction

Misplaced '#'

$$\Delta moles\ B = moles\ B\ at\ final\ time - moles\ B\ at\ initial\ time \tag{4.S.1}$$

$$average\ rate = -\frac{\Delta moles\ A}{\Delta t}\ \ if\ A \rightarrow B \tag{4.S.2}$$

14.2.1 Rates in Terms of Concentrations

- rate calculated in units of M/s
- brackets around a substance indicate the concentration
- **instantaneous rate** – rate at a particular time
- instantaneous rate obtained from the straight line tangent that touches the curve at a specific point
- slopes give instantaneous rates
- instantaneous rate also referred to as the rate

14.2.2 Reaction Rates and Stoichiometry

- for the irreversible reaction $aA + bB \rightarrow cC + dD$

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \tag{4.S.3}$$

14.3: Concentration and Rate

- equation used only if C and D only substances formed
- Rate = k[A][B]
- **Rate law** – expression that shows that rate depends on concentrations of reactants
- k = rate constant

14.3.1 Reaction Order

- Rate = k[reactant 1]^m[reactant 2]^n
- m, n are called reaction orders

- m+n, overall reaction order
- reaction orders do not have to correspond with coefficients in balanced equation
- values of reaction order determined experimentally
- reaction order can be fractional or negative

14.3.2 Units of Rates Constants

- units of rate constant depend on overall reaction order of rate law
- for reaction of second order overall
- units of rate = (units of rate constant)(units of concentration)^2
- units of rate constant = $M^{-1}s^{-1}$

14.3.3 Using Initial Rates to Determine Rate Laws

- **zero order** – no change in rate when concentration changed
- **first order** – change in concentration gives proportional changes in rate
- **second order** – change in concentration changes rate by the square of the concentration change, such as 2^2 or 3^2, etc…
- rate constant does not depend on concentration

14.4: The Change of Concentration with Time

- rate laws can be converted into equations that give concentrations of reactants or products

14.4.1 First-Order Reactions

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A] \tag{4.S.4}$$

and in integral form:

$$\ln[A]_t - \ln[A]_0 = -kt \tag{4.S.5}$$

or

$$\ln\frac{[A]_t}{[A]_0} = -kt \tag{4.S.6}$$

$$\ln[A]_t = -kt + \ln[A]_0 \tag{4.S.7}$$

- corresponds to a straight line with $y = mx + b$
- equations used to determine:
  1. concentration of reactant remaining at any time
  2. time required for given fraction of sample to react
  3. time required for reactant concentration to reach a certain level

14.3.2 Half-Life

- half-life of first order reaction

$$t_{\frac{1}{2}} = -\frac{\ln\frac{1}{2}}{k} = \frac{0.693}{k} \tag{4.S.8}$$

- **half-life** – time required for concentration of reactant to drop to one-half of initial value
- $t_{1/2}$ of first order independent of initial concentrations
- half-life same at any given time of reaction
- in first order reaction – concentrations of reactant decreases by ½ in each series of regularly spaced time intervals

14.3.3 Second-Order Reactions

- rate depends on reactant concentration raised to second power or concentrations of two different reactants each raised to first power

$$\text{Rate} = k[A]^2 \tag{4.S.9}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \tag{4.S.10}$$

$$half\ life = t_{\frac{1}{2}} = \frac{1}{k[A]_0} \tag{4.S.11}$$

- half life dependent on initial concentration of reactant

14.5: Temperature and Rate

- rate constant must increase with increasing temperature, thus increasing the rate of reaction

14.5.1 The Collision Model

- **collision model** – molecules must collide to react
- greater frequency of collisions the greater the reaction rate
- for most reactions only a small fraction of collisions leads to a reaction

14.5.2 Activation Energy

- Svante August Arrhenius
- Molecules must have a minimum amount of energy to react
- Energy comes from kinetic energy of collisions
- Kinetic energy used to break bonds
- Activation energy, E_a – minimum energy required to initiate a chemical reaction
- Activated complex or transition state – atoms at the top of the energy barrier
- Rate depends on temperature and E_a
- Lower E_a means faster reaction
- Reactions occur when collisions between molecules occur with enough energy and proper orientation

14.5.3 The Arrhenius Equation

- reaction rate data:
- theArrhenius Equation:

$$k = Ae^{\frac{-E_a}{RT}} \tag{4.S.12}$$

- k = rate constant, E_a = activation energy, R = gas constant (8.314 J/(mol K)), T = absolute temperature, A = frequency factor
- A relates to frequency of collisions, favorable orientations

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{4.S.13}$$

- the $\ln k$ vs. $1/t$ graph (also known as an Arrhenius plot) has a slope $-E_a/R$ and the y-intercept $\ln A$
- for two temperatures:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.S.14}$$

- used to calculate rate constant, k_1 and T_1

14.6: Reaction Mechanisms

- **reaction mechanism** – process by which a reaction occurs

14.6.1 Elementary Steps

- **elementary steps** – each step in a reaction
- **molecularity** – if only one molecule involved in step
- **unimolecular** – if only one molecule involved in step

- **bimolecular** – elementary step involving collision of two reactant molecules
- **termolecular** – elementary step involving simultaneous collision of three molecules
- elementary steps in multi-step mechanism must always add to give chemical equation of overall process
- **intermediate** – product formed in one step and consumed in a later step

14.6.2 Rate Laws of Elementary Steps

- if reaction is known to be an elementary step then the rate law is known
- rate of unimolecular step is first order (Rate = k[A])
- rate of bimolecular steps is second order (Rate = k[A][B])
- first order in [A] and [B]
- if double [A] than number of collisions of A and B will double

14.6.3 Rate Laws of Multi-step Mechanisms

- **rate-determining step** – slowest elementary step
- determines rate law of overall reaction

14.6.4 Mechanisms with an Initial Slow Step vs. Mechanisms with an Initial Fast Step

- intermediates are usually unstable, in low concentration, and difficult to isolate
- when a fast step precedes a slow one, solve for concentration of intermediate by assuming that equilibrium is established in fast step

14.7: Catalysis

- **catalyst** – substance that changes speed of chemical reaction without undergoing a permanent chemical change

14.7.1 Homogeneous Catalysis

- **homogeneous catalyst** – catalyst that is present in same phase as reacting molecule
- catalysts alter E_a or A
- generally catalysts lowers overall E_a for chemical reaction
- catalysts provides a different mechanism for reaction

14.7.2 Heterogeneous Catalysis

- exists in different phase from reactants
- initial step in heterogeneous catalyst is adsorption
- **adsorption** – binding of molecules to surface
- adsorption occurs because ions/atoms at surface of solid extremely reactive

14.7.3 Enzymes

- biological catalysts
- large protein molecules with molecular weights 10,000 – 1 million amu
- **catalase** – enzyme in blood and liver that decomposes hydrogen peroxide into water and oxygen
- **substrates** – substances that undergo reaction at the active site
- **lock-and-key model** – substrate molecules bind specifically to the active site
- **enzyme-substrate complex** – combination of enzyme and substrate
- binding between enzyme and substrate involves intermolecular forces (dipole-dipole, hydrogen bonding, and London dispersion forces)
- product from reaction leaves enzyme allowing for another substrate to enter enzyme
- **enzyme inhibitors** – molecules that bind strongly to enzymes
- **turnover number** – number of catalyzed reactions occurring at a particular active site
- large turnover numbers = low activation energies

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CHAPTER OVERVIEW

5: Transition Metals and Coordination Chemistry

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

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Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. These include the *d*-block (groups 3–11) and f-block element elements. The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

5.0: Properties of Transition Metals and Their Compounds
5.1: Metal Complexes
5.2: Ligands with more than one Donor Atom
5.3: Nomenclature of Coordination Chemistry
5.4: Isomerization
5.5: Color and Magnetism
5.6: Crystal Field Theory
5.E: Chemistry of Coordination Chemistry (Exercises)

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5.0: Properties of Transition Metals and Their Compounds

Learning Objectives

- Outline the general approach for the isolation of transition metals from natural sources
- Describe typical physical and chemical properties of the transition metals
- Identify simple compound classes for transition metals and describe their chemical properties

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure **5.0.2**, the *d*-block elements in groups 3–11 are transition elements. The *f*-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.



Figure **5.0.1**: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The *d*-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.

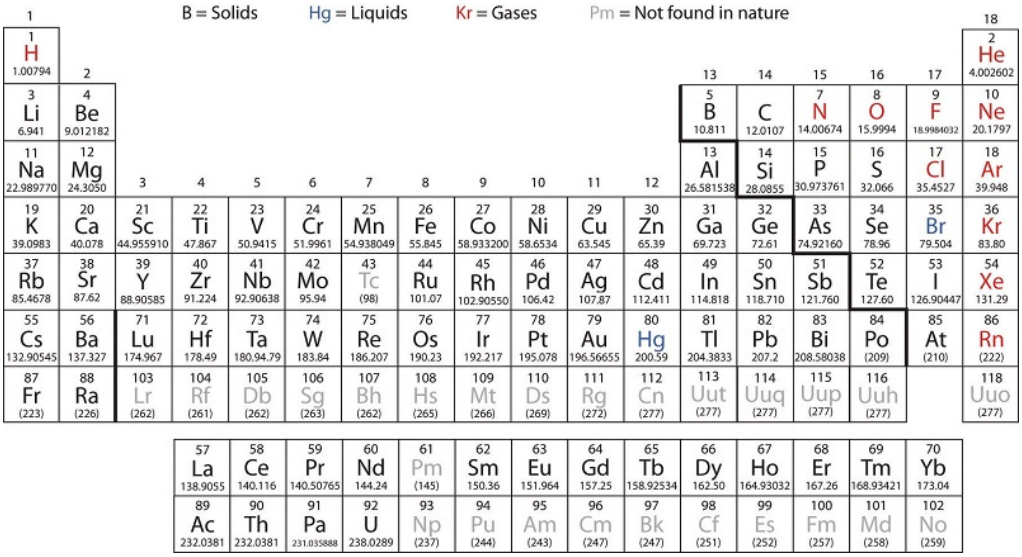


Figure **5.0.2**: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *f*-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third

transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

Example 5.0.1: Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

a. cerium(III)
b. lead(II)
c. Ti^{2+}
d. Am^{3+}
e. Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

a. $Ce^{3+}[Xe]4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.
b. $Pb^{2+}[Xe]6s^25d^{10}4f^{14}$; the electrons are lost from the *p* orbital. This is a main group element.
c. titanium(II) $[Ar]3d^2$; first transition series
d. americium(III) $[Rn]5f^6$; actinide
e. palladium(II) $[Kr]4d^8$; second transition series

Exercise 5.0.1

Check Your Learning Give an example of an ion from the first transition series with no *d* electrons.

Answer

V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

Uses of Lanthanides in Devices

Lanthanides (elements 57–71) are fairly abundant in the earth's crust, despite their historic characterization as rare earth elements. Thulium, the rarest naturally occurring lanthanoid, is more common in the earth's crust than silver (4.5×10^{-5}% versus 0.79×10^{-5}% by mass). There are 17 rare earth elements, consisting of the 15 lanthanoids plus scandium and yttrium. They are called rare because they were once difficult to extract economically, so it was rare to have a pure sample; due to similar chemical properties, it is difficult to separate any one lanthanide from the others. However, newer separation methods, such as ion exchange resins similar to those found in home water softeners, make the separation of these elements easier and more economical. Most ores that contain these elements have low concentrations of all the rare earth elements mixed together.

The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline (Figure **5.0.3**). Holmium is found in dental and medical equipment. In addition, many alternative energy technologies rely heavily on lanthanoids. Neodymium and dysprosium are key components of hybrid vehicle engines and the magnets used in wind turbines.

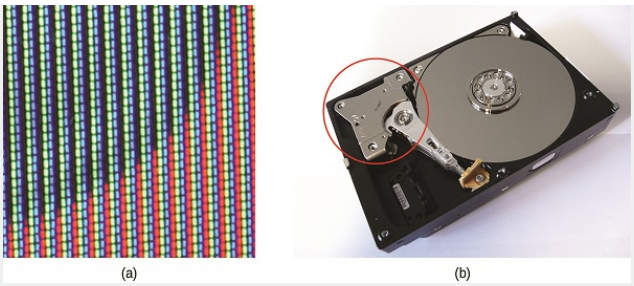


Figure 5.0.3: (a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by "KUERT Datenrettung"/Flickr)

As the demand for lanthanide materials has increased faster than supply, prices have also increased. In 2008, dysprosium cost $110/kg; by 2014, the price had increased to $470/kg. Increasing the supply of lanthanoid elements is one of the most significant challenges facing the industries that rely on the optical and magnetic properties of these materials.

The transition elements have many properties in common with other metals. They are almost all hard, high-melting solids that conduct heat and electricity well. They readily form alloys and lose electrons to form stable cations. In addition, transition metals form a wide variety of stable coordination compounds, in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons. Many different molecules and ions can donate lone pairs to the metal center, serving as Lewis bases. In this chapter, we shall focus primarily on the chemical behavior of the elements of the first transition series.

Properties of the Transition Elements

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (Table P1), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as MoO_4^{2-} and ReO_4^-.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the platinum metals. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure 5.0.4. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure 5.0.4: Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

✔ Example 5.0.2: Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (Table P1) for each oxide in the specified oxidation state:

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad +1.33\ V} \tag{5.0.1}$$

$$\mathrm{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + H_2O \quad +1.51\ V} \tag{5.0.2}$$

$$\mathrm{TiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ti^{2+} + 2\,H_2O \quad -0.50\ V} \tag{5.0.3}$$

A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

? Exercise 5.0.2

Predict what reaction (if any) will occur between HCl and Co(*s*), and between HBr and Pt(*s*). You will need to use the standard reduction potentials from (Table P1).

Answer

$\mathrm{Co}(s) + 2\,\mathrm{HCl} \longrightarrow \mathrm{H_2} + \mathrm{CoCl_2}(aq)$; no reaction because Pt(*s*) will not be oxidized by H^+

Preparation of the Transition Elements

Ancient civilizations knew about iron, copper, silver, and gold. The time periods in human history known as the Bronze Age and Iron Age mark the advancements in which societies learned to isolate certain metals and use them to make tools and goods. Naturally occurring ores of copper, silver, and gold can contain high concentrations of these metals in elemental form (Figure 5.0.5). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe_2O_3). The earliest known iron implements were made from iron meteorites. Surviving iron artifacts dating from approximately 4000 to 2500 BC are rare, but all known examples contain specific alloys of iron and nickel that occur only in extraterrestrial objects, not on earth. It took thousands of years of technological advances before civilizations developed iron smelting, the ability to extract a pure element from its naturally occurring ores and for iron tools to become common.

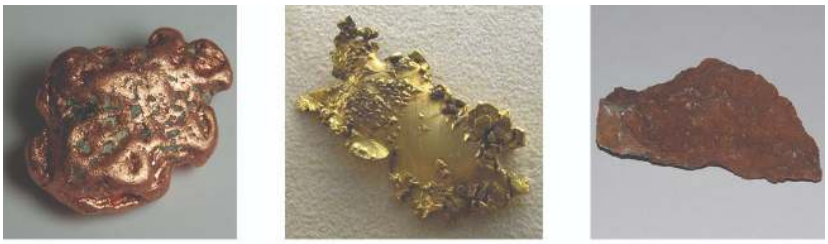


Figure **5.0.5**: Transition metals occur in nature in various forms. Examples include (a) a nugget of copper, (b) a deposit of gold, and (c) an ore containing oxidized iron. (credit a: modification of work by http://images-of-elements.com/copper-2.jpg; credit c: modification of work by http://images-of-elements.com/iron-ore.jpg)

Generally, the transition elements are extracted from minerals found in a variety of ores. However, the ease of their recovery varies widely, depending on the concentration of the element in the ore, the identity of the other elements present, and the difficulty of reducing the element to the free metal.

In general, it is not difficult to reduce ions of the *d*-block elements to the free element. Carbon is a sufficiently strong reducing agent in most cases. However, like the ions of the more active main group metals, ions of the *f*-block elements must be isolated by electrolysis or by reduction with an active metal such as calcium.

We shall discuss the processes used for the isolation of iron, copper, and silver because these three processes illustrate the principal means of isolating most of the *d*-block metals. In general, each of these processes involves three principal steps: preliminary treatment, smelting, and refining.

1. Preliminary treatment. In general, there is an initial treatment of the ores to make them suitable for the extraction of the metals. This usually involves crushing or grinding the ore, concentrating the metal-bearing components, and sometimes treating these substances chemically to convert them into compounds that are easier to reduce to the metal.
2. Smelting. The next step is the extraction of the metal in the molten state, a process called smelting, which includes reduction of the metallic compound to the metal. Impurities may be removed by the addition of a compound that forms a slag—a substance with a low melting point that can be readily separated from the molten metal.
3. Refining. The final step in the recovery of a metal is refining the metal. Low boiling metals such as zinc and mercury can be refined by distillation. When fused on an inclined table, low melting metals like tin flow away from higher-melting impurities. Electrolysis is another common method for refining metals.

Isolation of Iron

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. For a long time, charcoal was the form of carbon used in the reduction process. The production and use of iron became much more widespread about 1620, when coke was introduced as the reducing agent. Coke is a form of carbon formed by heating coal in the absence of air to remove impurities.

The first step in the metallurgy of iron is usually roasting the ore (heating the ore in air) to remove water, decomposing carbonates into oxides, and converting sulfides into oxides. The oxides are then reduced in a blast furnace that is 80–100 feet high and about 25 feet in diameter (Figure **5.0.6**) in which the roasted ore, coke, and limestone (impure $CaCO_3$) are introduced continuously into the top. Molten iron and slag are withdrawn at the bottom. The entire stock in a furnace may weigh several hundred tons.

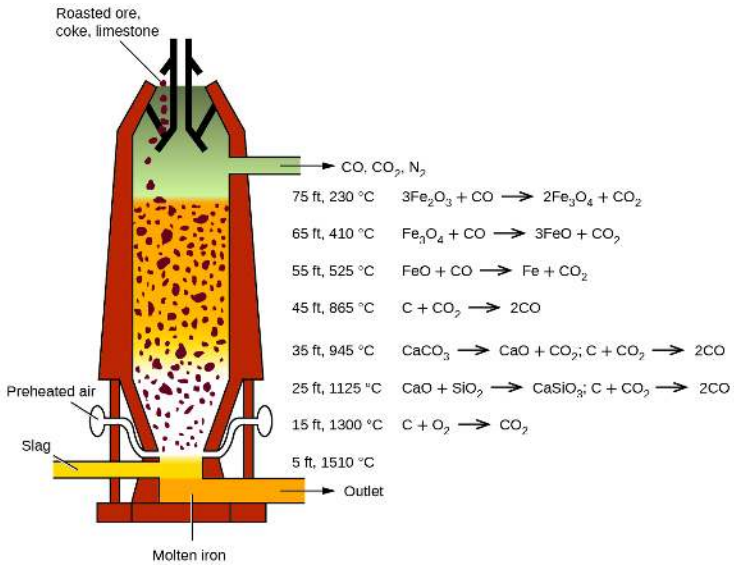


Figure 5.0.6:Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.

Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer of white-hot coke, where it is reduced to carbon monoxide:

$$\mathrm{CO_2}(g) + \mathrm{C}(s) \longrightarrow 2\,\mathrm{CO}(g) \tag{5.0.4}$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 5.0.6.

The iron oxides are reduced in the upper region of the furnace. In the middle region, limestone (calcium carbonate) decomposes, and the resulting calcium oxide combines with silica and silicates in the ore to form slag. The slag is mostly calcium silicate and contains most of the commercially unimportant components of the ore:

$$\mathrm{CaO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l) \tag{5.0.5}$$

Just below the middle of the furnace, the temperature is high enough to melt both the iron and the slag. They collect in layers at the bottom of the furnace; the less dense slag floats on the iron and protects it from oxidation. Several times a day, the slag and molten iron are withdrawn from the furnace. The iron is transferred to casting machines or to a steelmaking plant (Figure 5.0.7).



Figure 5.0.7:Molten iron is shown being cast as steel. (credit: Clint Budd)

Much of the iron produced is refined and converted into steel. Steel is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle.

Isolation of Copper

The most important ores of copper contain copper sulfides (such as covellite, CuS), although copper oxides (such as tenorite, CuO) and copper hydroxycarbonates [such as malachite, $Cu_2(OH)_2CO_3$] are sometimes found. In the production of copper metal, the concentrated sulfide ore is roasted to remove part of the sulfur as sulfur dioxide. The remaining mixture, which consists of Cu_2S, FeS, FeO, and SiO_2, is mixed with limestone, which serves as a flux (a material that aids in the removal of impurities), and heated. Molten slag forms as the iron and silica are removed by Lewis acid-base reactions:

$$\mathrm{CaCO_3}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l) + \mathrm{CO_2}(g) \tag{5.0.6}$$

$$\mathrm{FeO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{FeSiO_3}(l) \tag{5.0.7}$$

In these reactions, the silicon dioxide behaves as a Lewis acid, which accepts a pair of electrons from the Lewis base (the oxide ion).

Reduction of the Cu_2S that remains after smelting is accomplished by blowing air through the molten material. The air converts part of the Cu_2S into Cu_2O. As soon as copper(I) oxide is formed, it is reduced by the remaining copper(I) sulfide to metallic copper:

$$2\,\mathrm{Cu_2S}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Cu_2O}(l) + 2\,\mathrm{SO_2}(g) \tag{5.0.8}$$

$$2\,\mathrm{Cu_2O}(l) + \mathrm{Cu_2S}(l) \longrightarrow 6\,\mathrm{Cu}(l) + \mathrm{SO_2}(g) \tag{5.0.9}$$

The copper obtained in this way is called blister copper because of its characteristic appearance, which is due to the air blisters it contains (Figure 5.0.8). This impure copper is cast into large plates, which are used as anodes in the electrolytic refining of the metal (which is described in the chapter on electrochemistry).



Figure 5.0.8: Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: “Tortie tude”/Wikimedia Commons)

Isolation of Silver

Silver sometimes occurs in large nuggets (Figure 5.0.9) but more frequently in veins and related deposits. At one time, panning was an effective method of isolating both silver and gold nuggets. Due to their low reactivity, these metals, and a few others, occur in deposits as nuggets. The discovery of platinum was due to Spanish explorers in Central America mistaking platinum nuggets for silver. When the metal is not in the form of nuggets, it often useful to employ a process called hydrometallurgy to separate silver from its ores.



Figure 5.0.9: Naturally occurring free silver may be found as nuggets (a) or in veins (b). (credit a: modification of work by "Teravolt"/Wikimedia Commons; credit b: modification of work by James St. John)

Hydrology involves the separation of a metal from a mixture by first converting it into soluble ions and then extracting and reducing them to precipitate the pure metal. In the presence of air, alkali metal cyanides readily form the soluble dicyanoargentate(I) ion, $[Ag(CN)_2]^-$, from silver metal or silver-containing compounds such as Ag_2S and AgCl. Representative equations are:

$$4\,Ag(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Ag(CN)_2]^-(aq) + 4\,OH^-(aq) \tag{5.0.10}$$

$$2\,Ag_2S(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Ag(CN)_2]^-(aq) + 2\,S(s) + 4\,OH^-(aq) \tag{5.0.11}$$

$$AgCl(s) + 2\,CN^-(aq) \longrightarrow [Ag(CN)_2]^-(aq) + Cl^-(aq) \tag{5.0.12}$$

The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:

$$2\,[Ag(CN)_2]^-(aq) + Zn(s) \longrightarrow 2\,Ag(s) + [Zn(CN)_4]^{2-}(aq) \tag{5.0.13}$$

Example 5.0.3: Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargenate(I) ions:

$$4\,Ag(s) + 8\,CN^-(aq) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,[Ag(CN)_2]^-(aq) + 4\,OH^-(aq) \tag{5.0.14}$$

Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:

$$4\,Ag(s) + 8\,CN^-(aq) \longrightarrow 4\,[Ag(CN)_2]^-(aq)? \tag{5.0.15}$$

Solution

The charges, as well as the atoms, must balance in reactions. The silver atom is being oxidized from the 0 oxidation state to the 1+ state. Whenever something loses electrons, something must also gain electrons (be reduced) to balance the equation. Oxygen is a good oxidizing agent for these reactions because it can gain electrons to go from the 0 oxidation state to the 2− state.

Exercise 5.0.3

During the refining of iron, carbon must be present in the blast furnace. Why is carbon necessary to convert iron oxide into iron?

Answer

The carbon is converted into CO, which is the reducing agent that accepts electrons so that iron(III) can be reduced to iron(0).

Transition Metal Compounds

The bonding in the simple compounds of the transition elements ranges from ionic to covalent. In their lower oxidation states, the transition elements form ionic compounds; in their higher oxidation states, they form covalent compounds or polyatomic ions. The variation in oxidation states exhibited by the transition elements gives these compounds a metal-based, oxidation-reduction chemistry. The chemistry of several classes of compounds containing elements of the transition series follows.

Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:

$$2\,Fe(s) + 3\,Cl_2(g) \longrightarrow 2\,FeCl_3(s) \tag{5.0.16}$$

Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:

$$Fe(s) + 2\,FeCl_3(s) \longrightarrow 3\,FeCl_2(s) \tag{5.0.17}$$

The stoichiometry of the metal halide that results from the reaction of the metal with a halogen is determined by the relative amounts of metal and halogen and by the strength of the halogen as an oxidizing agent. Generally, fluorine forms fluoride-containing metals in their highest oxidation states. The other halogens may not form analogous compounds.

In general, the preparation of stable water solutions of the halides of the metals of the first transition series is by the addition of a hydrohalic acid to carbonates, hydroxides, oxides, or other compounds that contain basic anions. Sample reactions are:

$$NiCO_3(s) + 2\,HF(aq) \longrightarrow NiF_2(aq) + H_2O(l) + CO_2(g) \tag{5.0.18}$$

$$Co(OH)_2(s) + 2\,HBr(aq) \longrightarrow CoBr_2(aq) + 2\,H_2O(l) \tag{5.0.19}$$

Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:

$$Cr(s) + 2\,HCl(aq) \longrightarrow CrCl_2(aq) + H_2(g) \tag{5.0.20}$$

The polarity of bonds with transition metals varies based not only upon the electronegativities of the atoms involved but also upon the oxidation state of the transition metal. Remember that bond polarity is a continuous spectrum with electrons being shared evenly (covalent bonds) at one extreme and electrons being transferred completely (ionic bonds) at the other. No bond is ever 100% ionic, and the degree to which the electrons are evenly distributed determines many properties of the compound. Transition metal halides with low oxidation numbers form more ionic bonds. For example, titanium(II) chloride and titanium(III) chloride ($TiCl_2$ and $TiCl_3$) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride ($TiCl_4$) is a volatile liquid, consistent with having covalent titanium-chlorine bonds. All halides of the heavier *d*-block elements have significant covalent characteristics.

The covalent behavior of the transition metals with higher oxidation states is exemplified by the reaction of the metal tetrahalides with water. Like covalent silicon tetrachloride, both the titanium and vanadium tetrahalides react with water to give solutions containing the corresponding hydrohalic acids and the metal oxides:

$$SiCl_4(l) + 2\,H_2O(l) \longrightarrow SiO_2(s) + 4\,HCl(aq) \tag{5.0.21}$$

$$TiCl_4(l) + 2\,H_2O(l) \longrightarrow TiO_2(s) + 4\,HCl(aq) \tag{5.0.22}$$

Oxides

As with the halides, the nature of bonding in oxides of the transition elements is determined by the oxidation state of the metal. Oxides with low oxidation states tend to be more ionic, whereas those with higher oxidation states are more covalent. These variations in bonding are because the electronegativities of the elements are not fixed values. The electronegativity of an element increases with increasing oxidation state. Transition metals in low oxidation states have lower electronegativity values than oxygen; therefore, these metal oxides are ionic. Transition metals in very high oxidation states have electronegativity values close to that of oxygen, which leads to these oxides being covalent.

The oxides of the first transition series can be prepared by heating the metals in air. These oxides are Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, and CuO.

Alternatively, these oxides and other oxides (with the metals in different oxidation states) can be produced by heating the corresponding hydroxides, carbonates, or oxalates in an inert atmosphere. Iron(II) oxide can be prepared by heating iron(II) oxalate, and cobalt(II) oxide is produced by heating cobalt(II) hydroxide:

$$FeC_2O_4(s) \longrightarrow FeO(s) + CO(g) + CO_2(g) \tag{5.0.23}$$

$$Co(OH)_2(s) \longrightarrow CoO(s) + H_2O(g) \tag{5.0.24}$$

With the exception of CrO_3 and Mn_2O_7, transition metal oxides are not soluble in water. They can react with acids and, in a few cases, with bases. Overall, oxides of transition metals with the lowest oxidation states are basic (and react with acids), the intermediate ones are amphoteric, and the highest oxidation states are primarily acidic. Basic metal oxides at a low oxidation state react with aqueous acids to form solutions of salts and water. Examples include the reaction of cobalt(II) oxide accepting protons from nitric acid, and scandium(III) oxide accepting protons from hydrochloric acid:

$$\mathrm{CoO}(s) + 2\,\mathrm{HNO_3}(aq) \longrightarrow \mathrm{Co(NO_3)_2}(aq) + \mathrm{H_2O}(l) \tag{5.0.25}$$

$$\mathrm{Sc_2O_3}(s) + 6\,\mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{ScCl_3}(aq) + 3\,\mathrm{H_2O}(l) \tag{5.0.26}$$

The oxides of metals with oxidation states of 4+ are amphoteric, and most are not soluble in either acids or bases. Vanadium(V) oxide, chromium(VI) oxide, and manganese(VII) oxide are acidic. They react with solutions of hydroxides to form salts of the oxyanions $\mathrm{VO_4^{3-}}$, $\mathrm{CrO_4^{2-}}$, and $\mathrm{MnO_4^-}$. For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:

$$\mathrm{CrO_3}(s) + 2\,\mathrm{Na^+}(aq) + 2\,\mathrm{OH^-}(aq) \longrightarrow 2\,\mathrm{Na^+}(aq) + \mathrm{CrO_4^{2-}}(aq) + \mathrm{H_2O}(l) \tag{5.0.27}$$

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and $HMnO_4$, respectively.

Hydroxides

When a soluble hydroxide is added to an aqueous solution of a salt of a transition metal of the first transition series, a gelatinous precipitate forms. For example, adding a solution of sodium hydroxide to a solution of cobalt sulfate produces a gelatinous pink or blue precipitate of cobalt(II) hydroxide. The net ionic equation is:

$$\mathrm{Co^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Co(OH)_2}(s) \tag{5.0.28}$$

In this and many other cases, these precipitates are hydroxides containing the transition metal ion, hydroxide ions, and water coordinated to the transition metal. In other cases, the precipitates are hydrated oxides composed of the metal ion, oxide ions, and water of hydration:

$$4\,\mathrm{Fe^{3+}}(aq) + 6\,\mathrm{OH^-}(aq) + n\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{Fe_2O_3 \cdot (n+3)H_2O}(s) \tag{5.0.29}$$

These substances do not contain hydroxide ions. However, both the hydroxides and the hydrated oxides react with acids to form salts and water. When precipitating a metal from solution, it is necessary to avoid an excess of hydroxide ion, as this may lead to complex ion formation as discussed later in this chapter. The precipitated metal hydroxides can be separated for further processing or for waste disposal.

Carbonates

Many of the elements of the first transition series form insoluble carbonates. It is possible to prepare these carbonates by the addition of a soluble carbonate salt to a solution of a transition metal salt. For example, nickel carbonate can be prepared from solutions of nickel nitrate and sodium carbonate according to the following net ionic equation:

$$\mathrm{Ni^{2+}}(aq) + \mathrm{CO_3^{2-}} \longrightarrow \mathrm{NiCO_3}(s) \tag{5.0.30}$$

The reactions of the transition metal carbonates are similar to those of the active metal carbonates. They react with acids to form metals salts, carbon dioxide, and water. Upon heating, they decompose, forming the transition metal oxides.

Other Salts

In many respects, the chemical behavior of the elements of the first transition series is very similar to that of the main group metals. In particular, the same types of reactions that are used to prepare salts of the main group metals can be used to prepare simple ionic salts of these elements.

A variety of salts can be prepared from metals that are more active than hydrogen by reaction with the corresponding acids: Scandium metal reacts with hydrobromic acid to form a solution of scandium bromide:

$$2\,\mathrm{Sc}(s) + 6\,\mathrm{HBr}(aq) \longrightarrow 2\,\mathrm{ScBr_3}(aq) + 3\,\mathrm{H_2}(g) \tag{5.0.31}$$

The common compounds that we have just discussed can also be used to prepare salts. The reactions involved include the reactions of oxides, hydroxides, or carbonates with acids. For example:

$$\mathrm{Ni(OH)_2}(s) + 2\,\mathrm{H_3O^+}(aq) + 2\,\mathrm{ClO_4^-}(aq) \longrightarrow \mathrm{Ni^{2+}}(aq) + 2\,\mathrm{ClO_4^-}(aq) + 4\,\mathrm{H_2O}(l) \tag{5.0.32}$$

Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

$$\begin{aligned}\mathrm{Ba^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{K^+}(aq) + \mathrm{CrO_4^{2-}}(aq) \\ \longrightarrow \mathrm{BaCrO_4}(s) + 2\,\mathrm{K^+}(aq) + 2\,\mathrm{Cl^-}(aq)\end{aligned} \tag{5.0.33}$$

In our discussion of oxides in this section, we have seen that reactions of the covalent oxides of the transition elements with hydroxides form salts that contain oxyanions of the transition elements.

High Temperature Superconductors

A superconductor is a substance that conducts electricity with no resistance. This lack of resistance means that there is no energy loss during the transmission of electricity. This would lead to a significant reduction in the cost of electricity.

Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium has deterred the widespread application of superconductors.

One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is $YBa_2Cu_3O_7$.

The new materials become superconducting at temperatures close to 90 K (Figure **5.0.10**), temperatures that can be reached by cooling with liquid nitrogen (boiling temperature of 77 K). Not only are liquid nitrogen-cooled materials easier to handle, but the cooling costs are also about 1000 times lower than for liquid helium.

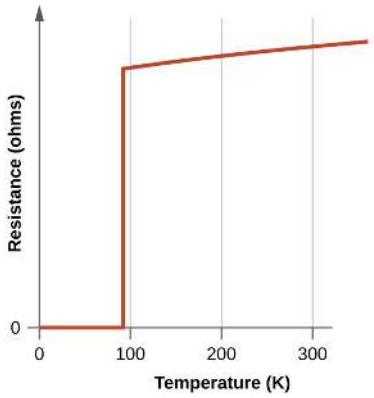


Figure **5.0.10**: The resistance of the high-temperature superconductor $YBa_2Cu_3O_7$ varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.

Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss of power due to resistance in the wires. This could allow generating stations to be located in areas remote from population centers and near the natural resources necessary for power production. The first project demonstrating the viability of high-temperature superconductor power transmission was established in New York in 2008.



(a) (b)

Figure 5.0.11: (a) This magnetic levitation train (or maglev) uses superconductor technology to move along its tracks. (b) A magnet can be levitated using a dish like this as a superconductor. (credit a: modification of work by Alex Needham; credit b: modification of work by Kevin Jarrett)

Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors (Figure 5.0.11).



Video* 5.0.1: Watch how a high-temperature superconductor levitates around a magnetic racetrack in the video.*

Contributors

Summary

The transition metals are elements with partially filled *d* orbitals, located in the *d*-block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals. The type of chemistry used in the isolation of the elements from their ores depends upon the concentration of the element in its ore and the difficulty of reducing ions of the elements to the metals. Metals that are more active are more difficult to reduce.

Transition metals exhibit chemical behavior typical of metals. For example, they oxidize in air upon heating and react with elemental halogens to form halides. Those elements that lie above hydrogen in the activity series react with acids, producing salts and hydrogen gas. Oxides, hydroxides, and carbonates of transition metal compounds in low oxidation states are basic. Halides and other salts are generally stable in water, although oxygen must be excluded in some cases. Most transition metals form a variety of stable oxidation states, allowing them to demonstrate a wide range of chemical reactivity.

Glossary

actinide series

(also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

coordination compound

stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

_d_-block element

one of the elements in groups 3–11 with valence electrons in *d* orbitals

_f_-block element

(also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

first transition series

transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

fourth transition series

transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

hydrometallurgy

process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

lanthanide series

(also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

platinum metals

group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

rare earth element

collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

second transition series

transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

smelting

process of extracting a pure metal from a molten ore

steel

material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

superconductor

material that conducts electricity with no resistance

third transition series

transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

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5.1: Metal Complexes

Learning Objectives

- To introduce complex ions and the basic principles of metal-ligand bonding

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.

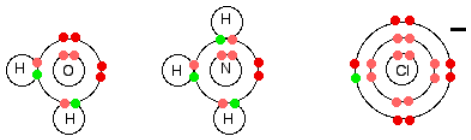


Figure 5.1.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as Lewis bases.

Bonding in Simple Complex Ions

We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $Al(H_2O)_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

Example 5.1.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

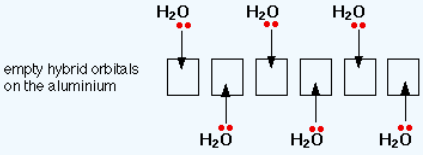
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

When it forms an Al^{3+} ion it loses the 3-level electrons to leave

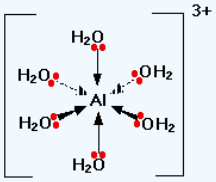
$$1s^2 2s^2 2p^6$$

That means that all the 3-level orbitals are now empty. The aluminium uses all six of these empty 3-level orbitals to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that will fit around an aluminum ion (and most other metal ions) due to steric constraints. By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

Example 5.1.2: $Fe(H_2O)_6^{3+}$

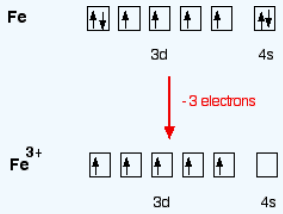
Iron has the electronic structure

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$$

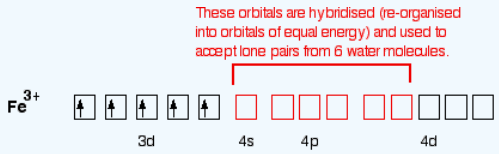
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$$

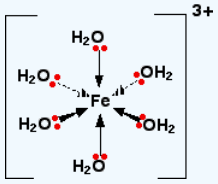
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminium ion.



Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

Example 5.1.3: $CuCl_4^{2-}$

This is a simple example of the formation of a complex ion with a negative charge.

Copper has the electronic structure

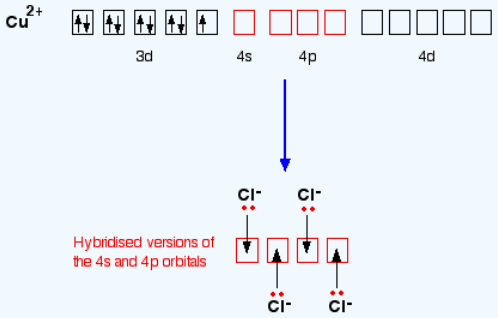
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$$

When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

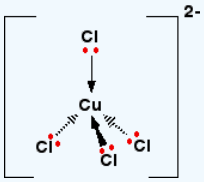
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridized form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the

central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Contributors

- Jim Clark (Chemguide.co.uk)

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5.2: Ligands with more than one Donor Atom

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.



Figure 5.2.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites

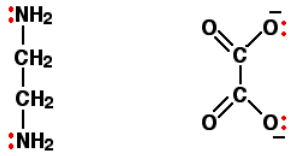
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "chelate effect." This term comes from the Greek chelos, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something.for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

Complex metal ions containing more complicated ligands

In the examples previously disccussedt, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

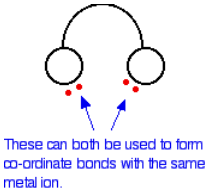
Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).



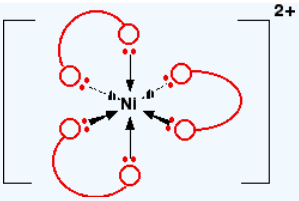
1,2-diaminoethane ethanedioate ion

In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



Example 5.2.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$. The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the NH2 groups - and the "bit that goes over your head " is the $-CH_2CH_2-$ group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

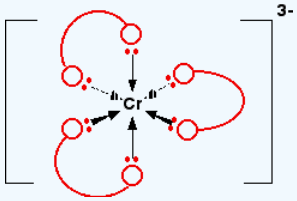
Example 5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3) + (3 \times -2) = -3 \tag{5.2.1}$$

.

The structure of the ion looks like this:

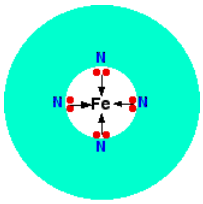


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below

the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

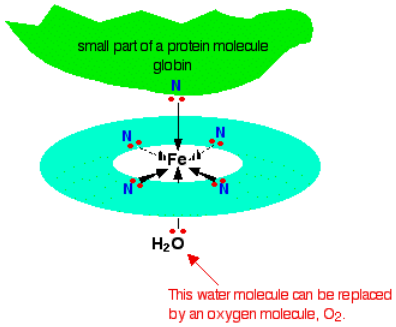


Figure 5.2.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

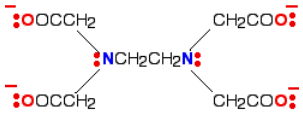
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

Carbon Monoxide Poisoning

You probably know that carbon monoxide is poisonous because it reacts with hemeoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that hemeoglobin molecule useless for any further oxygen transfer.

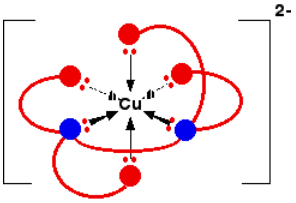
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. EDTA is used as a negative ion - EDTA4-. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the $EDTA^{4-}$ ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the $[Cu(EDTA)]^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

Contributors

- Jim Clark (Chemguide.co.uk)

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5.3: Nomenclature of Coordination Chemistry

Learning Objectives

- To learn the basis for complex ion and compound nomenclature

Coordination complexes have their own classes of isomers, different magnetic properties and colors, and various applications (photography, cancer treatment, etc), so it makes sense that they would have a naming system as well. Consisting of a metal and ligands, their formulas follow the pattern [Metal Anions Neutrals]$^{\pm Charge}$, while names are written Prefix Ligands Metal(Oxidation State).

Introduction

According to the Lewis base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. Coordination complexes consist of a ligand and a metal center cation. The overall charge can be positive, negative, or neutral. Coordination compounds are complex or contain complex ions, for example:

- Complex Cation: $[CO(NH_3)_6]^{3+}$
- Complex Anion: $[CoCl_4(NH_3)_2]^-$
- Neutral Complex: $[CoCl_3(NH_3)_3]$
- Coordination Compound: $K_4[Fe(CN)_6]$

A ligand can be an anion or a neutral molecule that *donates an electron pair* to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is monodentate, bidentate, or polydentate. For more information, see Ligands and Chelation. To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, noted by a Roman numeral in parentheses (II, IV).

Rule 1: Anionic Ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table **5.3.1**: Anionic Monodentate Ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Rule 2: Neutral Ligands

Most neutral molecules that are ligands carry their normal name. The few exceptions are the first four on the chart: ammine, aqua, carbonyl, and nitrosyl.

Table **5.3.2**: Select Neutral Monodentate Ligands. Note: Ammine is spelled with two m's when referring to a ligand. Amines are a class of organic nitrogen-containing compounds.

Molecular Formula of Ligand	Ligand Name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table **5.3.3**: Select Polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: Ligand Multiplicity

The number of ligands present in the complex is indicated with the prefixes di, tri, etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use *bis*, *tris*, and *tetrakis*.

Table **5.3.4**: Prefixes for indicating number of ligands in a complex.

Number of Ligands	Monodentate Ligands	Polydentate Ligands
1	mono	-
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	-
6	hexa	-

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triammine*chloro*dicarbonyliron(III) ion. Remember that ligands are always named first, before the metal is.

Example 5.3.1

What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Solution

Let's start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are 4 aqua's and 2 chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium(III) ion. See the next section for an explanation of the (III).

? Exercise 5.3.1

What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

Solution

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that *en* is a polydentate ligand with a prefix in its name (ethylene**di**amine), so "bis" is used instead of "bi", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt(III) ion.

Rule 4: The Metals

When naming the metal center, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside parenthesis. For example, in the problems above, chromium and cobalt have the oxidation state of +3, so that is why they have (III) after them. Copper, with an oxidation state of +2, is denoted as copper(II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal center. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate(II). The following change to their Latin names when part of an anion complex:

Table 5.3.5: Latin terms for Select Metal Ion

Transition Metal	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

The rest of the metals simply have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. This is not necessary if it is neutral or part of a coordination compound (Example 5.3.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

✓ Example 5.3.2

What is the name of $[Cr(OH)_4]^-$?

Solution

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four of them, so we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 (x+(-1)4=-1). Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate(III) ion.

? Exercise 5.3.2

What is the name of $[CuCl_4]^{2-}$?

Solution

tetrachlorocuprate(II) ion

A last little side note: when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Think of NaCl. Na, the positive cation, comes first and Cl, the negative anion, follows.

Example 5.3.3

What is the name of $[Pt(NH_3)_4)][Pt(Cl)_4]$?

Solution

NH_3 is neutral, making the first complex positively charged overall. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum(II) tetrachloroplatinate(II).

Distinguishing between linkage isomers.

Example 5.3.4

What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

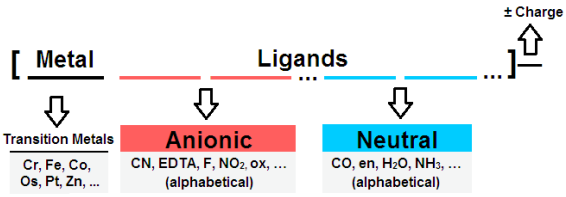
Solution

This coordination complex is called tetraamminechloronitrito-N-cobalt(III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt(III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraamminechloronitrocobalt(III) and tetraamminechloronitritocobalt(III).

Writing Formulas of Coordination Complexes

The formula of a coordination complex is written in a different order than its name. The chemical symbol of the metal center is written first. The ligands are written next, with anion ligands coming before neutral ligands. If there is more than one anion or neutral ligand, they are written in alphabetical order according to the first letter in their chemical formula.



In a coordination compound's name, when one of the ions is just an element, the number of atoms is not indicated with a prefix. Since it still has to be written in the formula, it is determined by balancing the overall charge of the compound. (For example, tetrafluorochromium(VI) *chloride* becomes $[CrF_4]Cl_2$.

Examples 5.3.5

a. Amminetetraaquachromium(II)
b. Amminesulfatochromium(II)
c. Amminetetraaquachromium(II) sulfate
d. Potassium hexacyanoferrate(III)

Solution

a. Amminetetraaquachromium(II) ion would be written as $[Cr(H_2O)_4(NH_3)]^{+2}$. Both ligands are neutral, so they are ordered alphabetically with H_2O before NH_3. Their order in the formula is the opposite of that in the complex's name since one uses their chemical symbols and the other uses the names of the ligands.

b. Amminesulfatochromium(II) is written as $[Cr(SO_4)(NH_3)]$. SO_4 is an anion, so it comes before NH_3.
c. Amminetetraaquachromium(II) sulfate -> Try this on your own. Did you get $[Cr(H_2O)_4(NH_3)]SO_4$? If you did, you are correct.
d. Potassium hexacyanoferrate(III) -> Try this on your own. Did you get $K_3[Fe(CN)_6]$? Remember to balance the K!

References

1. Petrucci, Ralph H. General Chemistry Principles and Modern Applications. 9th ed. Upper Saddle River: Pearson Prentice Hall, 2002.

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5.4: Isomerization

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

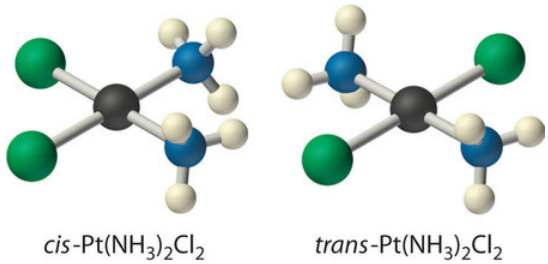


Figure 5.4.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced,

and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

? Exercise 5.4.1

Draw the cis and trans isomers of the following compounds:

a. $(NH_3)_2IrCl(CO)$
b. $(H_3P)_2PtHBr$
c. $(AsH_3)_2PtH(CO)$

? Exercise 5.4.2

Only one isomer of (tmeda)$PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum]. Draw this isomer and explain why the other isomer is not possible.

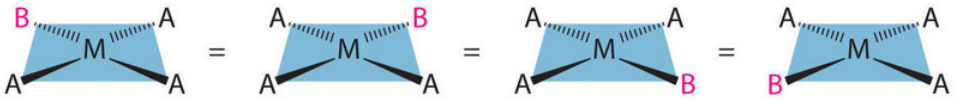
Geometric Isomers

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

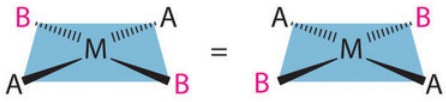


MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:



MA_2B_2 square planar complex, *cis* isomer

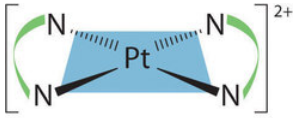


MA_2B_2 square planar complex, *trans* isomer

Figure **5.4.1**).

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

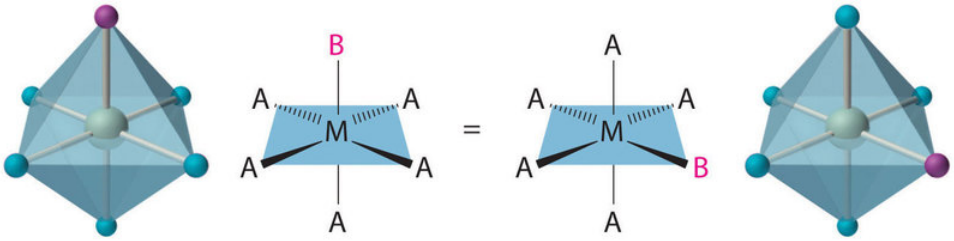
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

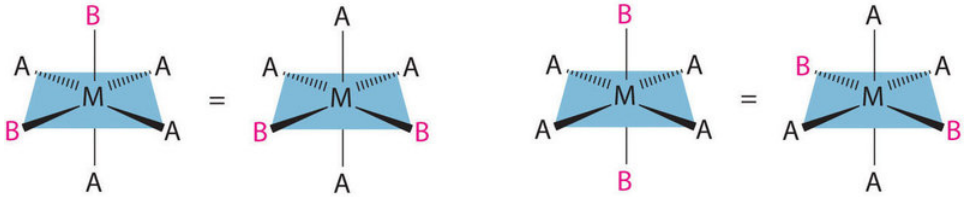
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



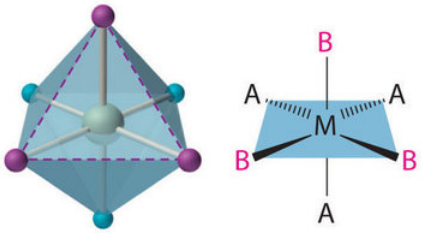
MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:

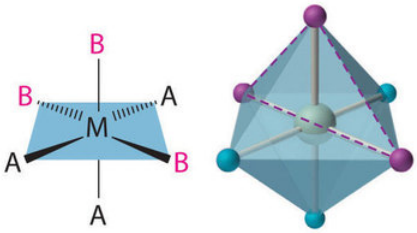


MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer



MA_3B_3 octahedral complex, *mer* isomer

Example 5.4.1

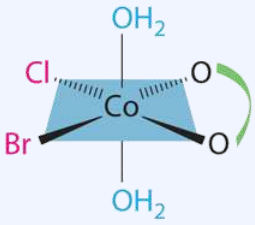
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

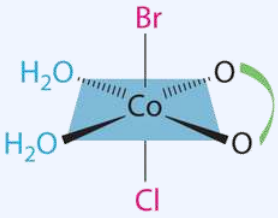
Asked for: structures of geometrical isomers

Solution

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:

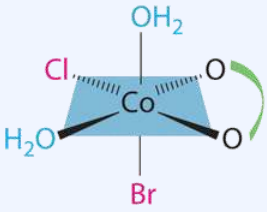


H_2O's *trans*

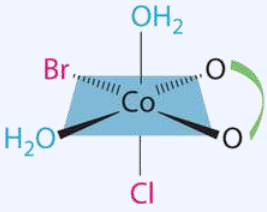


Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

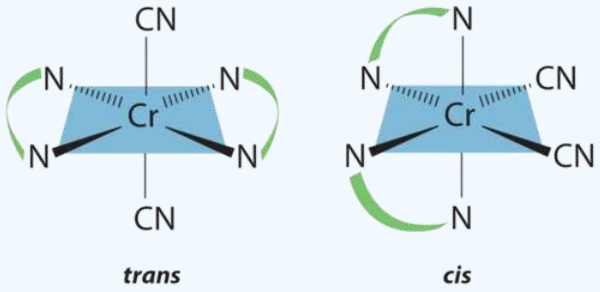
This complex can therefore exist as four different geometrical isomers.

Exercise 5.4.1

Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer

Two geometrical isomers are possible: trans and cis.



Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

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5.5: Color and Magnetism

Learning Objectives

- To get a simple overview of the origin of color and magnetism in complex ions.

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 5.5.1).

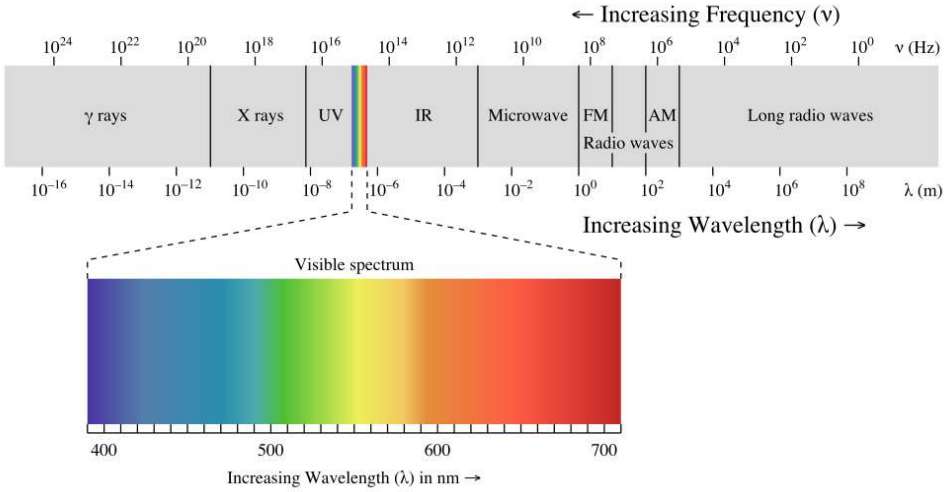


Figure 5.5.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

1. Electromagnetic radiation can travel through empty space, while most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through to be heard.
2. The speed of light (c) is always a constant (2.99792458 x 10^8 m s^{-1}).
3. Wavelengths (λ) are measured between the distances of either crests or troughs.

The energy of a photon is expressed by Planck's law in terms of the frequency (u) of the photon

$$E = hu \tag{5.5.1}$$

since $\lambda u = c$ for all light Plancks law can be also expressed in terms of the wavelength of the photon

$$E = hu = \frac{hc}{\lambda} \tag{5.5.2}$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 5.5.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer = 10^{-9} meters).

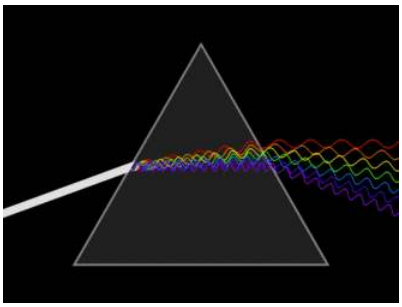
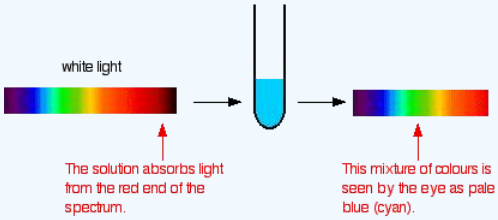


Figure 5.5.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

Example 5.5.1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.



Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You would not have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

Origin of Colors

The process of absorption involves the excitation of the valence electrons in the molecule typically from the low lying level called the Highest Occupied Molecular Orbital (HOMO) into a higher lying state called the the Lowest Unoccupied Molecular Orbital (**LUMO**). When this HOMO and LUMO transition (Figure 5.5.3) involves the absorption of visible light, the sample is colored.

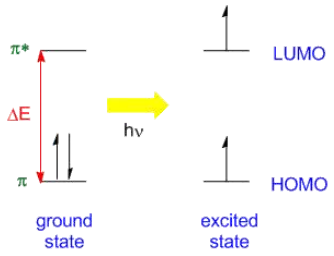


Figure 5.5.4: The general electron excitation process from a HOMO to a LUMO.

The HOMO-LUMO energy difference

$$\Delta E = E_{HOMO} - E_{LUMO} \tag{5.5.3}$$

depends on the nature of the molecule and can be connected to the wavelength of the light absorbed

$$\Delta E = hu = \frac{hc}{\lambda} \tag{5.5.4}$$

> *Equation 5.5.4 is the most important equation in the field of light-matter interactions (spectroscopy).*

As Example 5.5.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 5.5.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

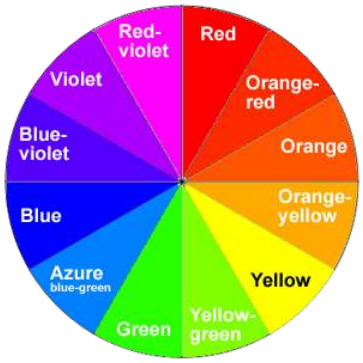


Figure 5.5.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 5.5.1).

Table 5.5.1: The Visible Spectrum

Color	Wavelength (nm)	ΔE HOMO - LUMO gap (eV)
UV	100 - 400	12.4 - 3.10
Violet	400 - 425	3.10 - 2.92
Blue	425 - 492	2.92 - 2.52
Green	492 - 575	2.52 - 2.15
Yellow	575 - 585	2.15 - 2.12
Orange	585 - 647	2.12 - 1.92
Red	647 - 700	1.92 - 1.77
Near IR	700 - 10,000	1.77 - 0.12

If the compound absorbs in one region of the spectra, it appears with the opposite (complementary) color, since all of the absorbed color has been removed. For example:

- the material absorbs violet light ⇒ color is yellow
- the material absorbs blue light ⇒ color is orange
- the material absorbs yellow-green light ⇒ color is red-violet

The Origin of Color in Complex Ions

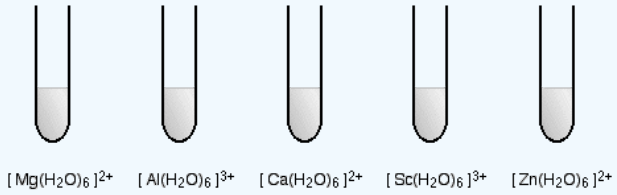
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar]

$3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^14s^2$) does not really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.

Example 5.5.3: Hexaaqua Metal Ions

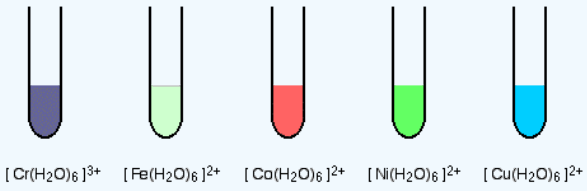
The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[\ M(H_2O)_6\ ]^{n+}$. The charge on these ions is typically 2+ or 3+.

- Non-transition metal ions



These ions are all colorless.

- Transition metal ions



The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion? This is discussed in the next sections.

Magnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only the first two are introduced below.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



A chemical demonstration of the paramagnetism of oxygen, as shown by the attraction of liquid oxygen to a magnet. Carleton University, Ottawa, Canada.

As shown in the video, molecular oxygen (O_2 is paramagnetic and is attracted to the magnet. Incontrast, Molecular nitrogen, N_2, however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure **5.5.6**.

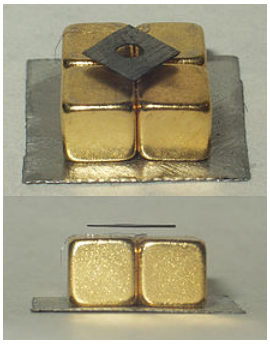


Figure **5.5.6**: Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

How to Tell if a Substance is Paramagnetic or Diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration

2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic (one or more unpaired electrons) or diamagnetic (all electrons paired)

Example 5.5.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

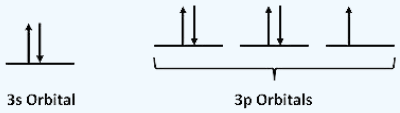
Solution

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

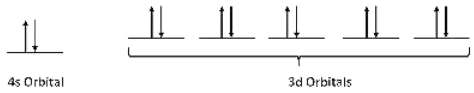
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

Example 2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

References

1. Pettrucci, Ralph H. General Chemistry: Principles and Modern Applications. 9th. Upper Saddle River: Pearson Prentice Hall, 2007
2. Sherman, Alan, Sharon J. Sherman, and Leonard Russikoff. Basic Concepts of Chemistry Fifth Edition. Boston, MA: Houghton Mifflin Company, 1992. Print.

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5.6: Crystal Field Theory

Learning Objectives

- To understand how crystal field theory explains the electronic structures and colors of metal complexes.

One of the most striking characteristics of transition-metal complexes is the wide range of colors they exhibit. In this section, we describe crystal field theory (CFT), a bonding model that explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. The central assumption of CFT is that metal–ligand interactions are purely electrostatic in nature. Even though this assumption is clearly not valid for many complexes, such as those that contain neutral ligands like CO, CFT enables chemists to explain many of the properties of transition-metal complexes with a reasonable degree of accuracy. The Learning Objective of this Module is to understand how crystal field theory explains the electronic structures and colors of metal complexes.

d-Orbital Splittings

CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion. We will focus on the application of CFT to octahedral complexes, which are by far the most common and the easiest to visualize. Other common structures, such as square planar complexes, can be treated as a distortion of the octahedral model. According to CFT, an octahedral metal complex forms because of the electrostatic interaction of a positively charged metal ion with six negatively charged ligands or with the negative ends of dipoles associated with the six ligands. In addition, the ligands interact with one other electrostatically. As you learned in our discussion of the valence-shell electron-pair repulsion (VSEPR) model, the lowest-energy arrangement of six identical negative charges is an octahedron, which minimizes repulsive interactions between the ligands.

We begin by considering how the energies of the d orbitals of a transition-metal ion are affected by an octahedral arrangement of six negative charges. Recall that the five d orbitals are initially degenerate (have the same energy). If we distribute six negative charges uniformly over the surface of a sphere, the d orbitals remain degenerate, but their energy will be higher due to repulsive electrostatic interactions between the spherical shell of negative charge and electrons in the d orbitals (Figure **5.6.1*a***). Placing the six negative charges at the vertices of an octahedron does not change the average energy of the d orbitals, but it does remove their degeneracy: the five d orbitals split into two groups whose energies depend on their orientations. As shown in Figure **5.6.1*b***, the d_{z^2} and $d_{x^2-y^2}$ orbitals point directly at the six negative charges located on the x, y, and z axes. Consequently, the energy of an electron in these two orbitals (collectively labeled the e_g orbitals) will be greater than it will be for a spherical distribution of negative charge because of increased electrostatic repulsions. In contrast, the other three d orbitals (d_{xy}, d_{xz}, and d_{yz}, collectively called the t_{2g} orbitals) are all oriented at a 45° angle to the coordinate axes, so they point between the six negative charges. The energy of an electron in any of these three orbitals is lower than the energy for a spherical distribution of negative charge.

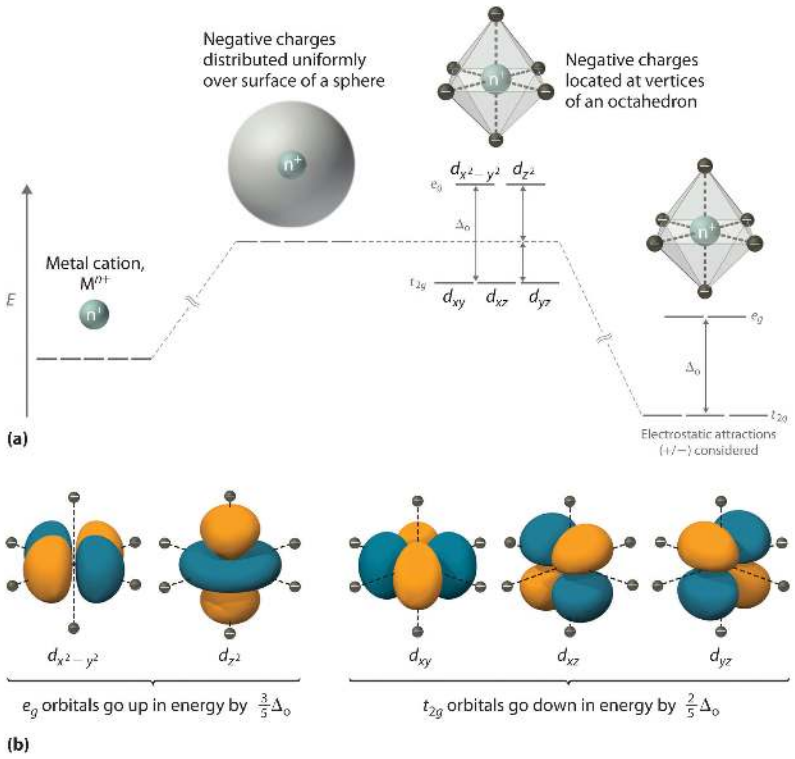


Figure **5.6.1**: An Octahedral Arrangement of Six Negative Charges around a Metal Ion Causes the Five d Orbitals to Split into Two Sets with Different Energies. (a) Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ *and* d_{z^2} *orbitals increase in energy, while the,* d_{xy}, d_{xz}, *and* d_{yz} *orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. (b) The two* e_g *orbitals (left) point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three* t_{2g} *orbitals (right) point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.*

The difference in energy between the two sets of d orbitals is called the crystal field splitting energy (Δ_o), where the subscript o stands for octahedral. As we shall see, the magnitude of the splitting depends on the charge on the metal ion, the position of the metal in the periodic table, and the nature of the ligands. (Crystal field splitting energy also applies to tetrahedral complexes: Δ_t.) It is important to note that the splitting of the d orbitals in a crystal field does not change the total energy of the five d orbitals: the two e_g orbitals increase in energy by $0.6\Delta_o$, whereas the three t_{2g} orbitals decrease in energy by $0.4\Delta_o$. Thus the total change in energy is

$$2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0. \tag{5.6.1}$$

> *Crystal field splitting does not change the total energy of the d orbitals.*

Thus far, we have considered only the effect of repulsive electrostatic interactions between electrons in the d orbitals and the six negatively charged ligands, which increases the total energy of the system and splits the d orbitals. Interactions between the positively charged metal ion and the ligands results in a net stabilization of the system, which decreases the energy of all five d orbitals without affecting their splitting (as shown at the far right in Figure **5.6.1***a*).

Electronic Structures of Metal Complexes

We can use the d-orbital energy-level diagram in Figure **5.6.1** to predict electronic structures and some of the properties of transition-metal complexes. We start with the Ti^{3+} ion, which contains a single d electron, and proceed across the first row of the transition metals by adding a single electron at a time. We place additional electrons in the lowest-energy orbital available, while keeping their spins parallel as required by Hund's rule. As shown in Figure 24.6.2, for d^1–d^3 systems—such as $[Ti(H_2O)_6]^{3+}$,

$[V(H_2O)_6]^{3+}$, and $[Cr(H_2O)_6]^{3+}$, respectively—the electrons successively occupy the three degenerate t_{2g} orbitals with their spins parallel, giving one, two, and three unpaired electrons, respectively. We can summarize this for the complex $[Cr(H_2O)_6]^{3+}$, for example, by saying that the chromium ion has a d^3 electron configuration or, more succinctly, Cr^{3+} is a d^3 ion.

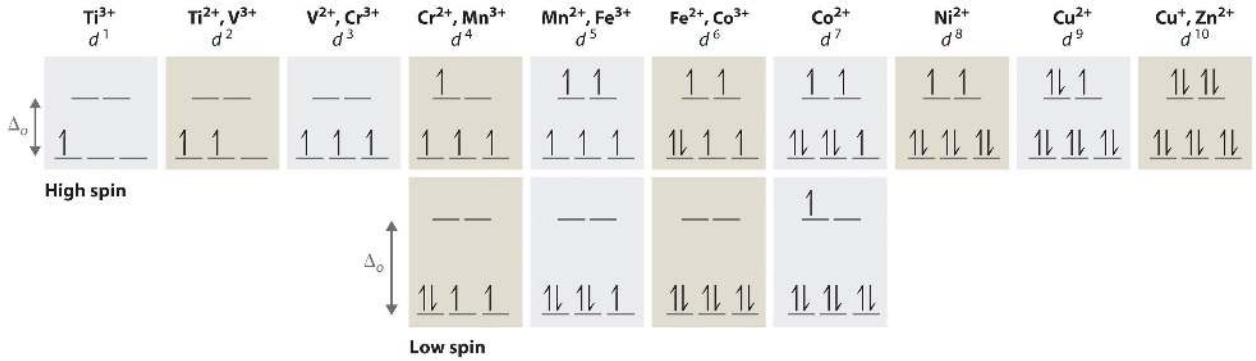


Figure **5.6.2**: The Possible Electron Configurations for Octahedral d^n Transition-Metal Complexes (n = 1–10). Two different configurations are possible for octahedral complexes of metals with d^4, d^5, d^6, and d^7 configurations; the magnitude of Δ_o determines which configuration is observed.

When we reach the d^4 configuration, there are two possible choices for the fourth electron: it can occupy either one of the empty e_g orbitals or one of the singly occupied t_{2g} orbitals. Recall that placing an electron in an already occupied orbital results in electrostatic repulsions that increase the energy of the system; this increase in energy is called the spin-pairing energy (P). If Δ_o is less than P, then the lowest-energy arrangement has the fourth electron in one of the empty e_g orbitals. Because this arrangement results in four unpaired electrons, it is called a high-spin configuration, and a complex with this electron configuration, such as the $[Cr(H_2O)_6]^{2+}$ ion, is called a high-spin complex. Conversely, if Δ_o is greater than P, then the lowest-energy arrangement has the fourth electron in one of the occupied t_{2g} orbitals. Because this arrangement results in only two unpaired electrons, it is called a low-spin configuration, and a complex with this electron configuration, such as the $[Mn(CN)_6]^{3-}$ ion, is called a low-spin complex. Similarly, metal ions with the d^5, d^6, or d^7 electron configurations can be either high spin or low spin, depending on the magnitude of Δ_o.

In contrast, only one arrangement of d electrons is possible for metal ions with d^8–d^{10} electron configurations. For example, the $[Ni(H_2O)_6]^{2+}$ ion is d^8 with two unpaired electrons, the $[Cu(H_2O)_6]^{2+}$ ion is d^9 with one unpaired electron, and the $[Zn(H_2O)_6]^{2+}$ ion is d^{10} with no unpaired electrons.

> *If Δ_o is less than the spin-pairing energy, a high-spin configuration results. Conversely, if Δ_o is greater, a low-spin configuration forms.*

Factors That Affect the Magnitude of Δ_o

The magnitude of Δ_o dictates whether a complex with four, five, six, or seven d electrons is high spin or low spin, which affects its magnetic properties, structure, and reactivity. Large values of Δ_o (i.e., $\Delta_o > P$) yield a low-spin complex, whereas small values of Δ_o (i.e., $\Delta_o < P$) produce a high-spin complex. As we noted, the magnitude of Δ_o depends on three factors: the charge on the metal ion, the principal quantum number of the metal (and thus its location in the periodic table), and the nature of the ligand. Values of Δ_o for some representative transition-metal complexes are given in Table **5.6.1**.

Table **5.6.1***: Crystal Field Splitting Energies for Some Octahedral (Δ_o)* and Tetrahedral (Δ_t) Transition-Metal Complexes*

Octahedral Complexes	Δ_o (cm^{-1})	Octahedral Complexes	Δ_o (cm^{-1})	Tetrahedral Complexes	Δ_t (cm^{-1})
$[Ti(H_2O)_6]^{3+}$	20,300	$[Fe(CN)_6]^{4-}$	32,800	VCl_4	9010
$[V(H_2O)_6]^{2+}$	12,600	$[Fe(CN)_6]^{3-}$	35,000	$[CoCl_4]^{2-}$	3300
$[V(H_2O)_6]^{3+}$	18,900	$[CoF_6]^{3-}$	13,000	$[CoBr_4]^{2-}$	2900
$[CrCl_6]^{3-}$	13,000	$[Co(H_2O)_6]^{2+}$	9300	$[CoI_4]^{2-}$	2700
$[Cr(H_2O)_6]^{2+}$	13,900	$[Co(H_2O)_6]^{3+}$	27,000		
$[Cr(H_2O)_6]^{3+}$	17,400	$[Co(NH_3)_6]^{3+}$	22,900		
$[Cr(NH_3)_6]^{3+}$	21,500	$[Co(CN)_6]^{3-}$	34,800		
$[Cr(CN)_6]^{3-}$	26,600	$[Ni(H_2O)_6]^{2+}$	8500		
$Cr(CO)_6$	34,150	$[Ni(NH_3)_6]^{2+}$	10,800		
$[MnCl_6]^{4-}$	7500	$[RhCl_6]^{3-}$	20,400		
$[Mn(H_2O)_6]^{2+}$	8500	$[Rh(H_2O)_6]^{3+}$	27,000		
$[MnCl_6]^{3-}$	20,000	$[Rh(NH_3)_6]^{3+}$	34,000		
$[Mn(H_2O)_6]^{3+}$	21,000	$[Rh(CN)_6]^{3-}$	45,500		
$[Fe(H_2O)_6]^{2+}$	10,400	$[IrCl_6]^{3-}$	25,000		
$[Fe(H_2O)_6]^{3+}$	14,300	$[Ir(NH_3)_6]^{3+}$	41,000		

*Energies obtained by spectroscopic measurements are often given in units of wave numbers (cm^{-1}); the wave number is the reciprocal of the wavelength of the corresponding electromagnetic radiation expressed in centimeters: 1 cm^{-1} = 11.96 J/mol.

Source of data: Duward F. Shriver, Peter W. Atkins, and Cooper H. Langford, Inorganic Chemistry, 2nd ed. (New York: W. H. Freeman and Company, 1994).

Charge on the Metal Ion

Increasing the charge on a metal ion has two effects: the radius of the metal ion decreases, and negatively charged ligands are more strongly attracted to it. Both factors decrease the metal–ligand distance, which in turn causes the negatively charged ligands to interact more strongly with the d orbitals. Consequently, the magnitude of Δ_o increases as the charge on the metal ion increases. Typically, Δ_o for a tripositive ion is about 50% greater than for the dipositive ion of the same metal; for example, for $[V(H_2O)_6]^{2+}$, Δ_o = 11,800 cm^{-1}; for $[V(H_2O)_6]^{3+}$, Δ_o = 17,850 cm^{-1}.

Principal Quantum Number of the Metal

For a series of complexes of metals from the same group in the periodic table with the same charge and the same ligands, the magnitude of Δ_o increases with increasing principal quantum number: Δ_o (3d) < Δ_o (4d) < Δ_o (5d). The data for hexaammine complexes of the trivalent group 9 metals illustrate this point:

$$[Co(NH_3)_6]^{3+}: \Delta_o = 22{,}900\ cm^{-1}$$

$$[Rh(NH_3)_6]^{3+}: \Delta_o = 34{,}100\ cm^{-1}$$

$$[Ir(NH_3)_6]^{3+}: \Delta_o = 40{,}000\ cm^{-1}$$

The increase in Δ_o with increasing principal quantum number is due to the larger radius of valence orbitals down a column. In addition, repulsive ligand–ligand interactions are most important for smaller metal ions. Relatively speaking, this results in shorter M–L distances and stronger d orbital–ligand interactions.

The Nature of the Ligands

Experimentally, it is found that the Δ_o observed for a series of complexes of the same metal ion depends strongly on the nature of the ligands. For a series of chemically similar ligands, the magnitude of Δ_o decreases as the size of the donor atom increases. For example, Δ_o values for halide complexes generally decrease in the order $F^- > Cl^- > Br^- > I-$ because smaller, more localized charges, such as we see for F^-, interact more strongly with the d orbitals of the metal ion. In addition, a small neutral ligand with a highly localized lone pair, such as NH_3, results in significantly larger Δ_o values than might be expected. Because the lone pair points directly at the metal ion, the electron density along the M–L axis is greater than for a spherical anion such as F^-. The experimentally observed order of the crystal field splitting energies produced by different ligands is called the spectrochemical series, shown here in order of decreasing Δ_o:

$$\underset{\text{strong-field ligands}}{CO \approx CN^- > NO_2^-} > en > NH_3 > \underset{\text{intermediate-field ligands}}{SCN^- > H_2O > oxalate^{2-} > OH^- > F} > acetate^- > \underset{\text{weak-field ligands}}{Cl^- > Br^- > I^-}$$

The values of Δ_o listed in Table **5.6.1** illustrate the effects of the charge on the metal ion, the principal quantum number of the metal, and the nature of the ligand.

> *The largest Δ_o splittings are found in complexes of metal ions from the third row of the transition metals with charges of at least +3 and ligands with localized lone pairs of electrons.*

Colors of Transition-Metal Complexes

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a d–d transition (Figure 24.6.3). For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o.

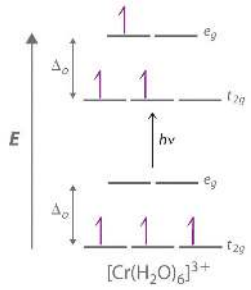


Figure **5.6.3**: A d–d Transition. In a d–d transition, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

Recall that the color we observe when we look at an object or a compound is due to light that is transmitted or reflected, not light that is absorbed, and that reflected or transmitted light is complementary in color to the light that is absorbed. Thus a green compound absorbs light in the red portion of the visible spectrum and vice versa, as indicated by the color wheel. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex. For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color. A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

We can now understand why emeralds and rubies have such different colors, even though both contain Cr^{3+} in an octahedral environment provided by six oxide ions. Although the chemical identity of the six ligands is the same in both cases, the Cr–O distances are different because the compositions of the host lattices are different (Al_2O_3 in rubies and $Be_3Al_2Si_6O_{18}$ in emeralds). In ruby, the Cr–O distances are relatively short because of the constraints of the host lattice, which increases the d orbital–ligand interactions and makes Δ_o relatively large. Consequently, rubies absorb green light and the transmitted or reflected light is red, which gives the gem its characteristic color. In emerald, the Cr–O distances are longer due to relatively large $[Si_6O_{18}]^{12-}$ silicate rings; this results in decreased d orbital–ligand interactions and a smaller Δ_o. Consequently, emeralds absorb light of a longer

wavelength (red), which gives the gem its characteristic green color. It is clear that the environment of the transition-metal ion, which is determined by the host lattice, dramatically affects the spectroscopic properties of a metal ion.



Gem-quality crystals of ruby and emerald. The colors of both minerals are due to the presence of small amounts of Cr^{3+} impurities in octahedral sites in an otherwise colorless metal oxide lattice.

Crystal Field Stabilization Energies

Recall that stable molecules contain more electrons in the lower-energy (bonding) molecular orbitals in a molecular orbital diagram than in the higher-energy (antibonding) molecular orbitals. If the lower-energy set of d orbitals (the t_{2g} orbitals) is selectively populated by electrons, then the stability of the complex increases. For example, the single d electron in a d^1 complex such as $[Ti(H_2O)_6]^{3+}$ is located in one of the t_{2g} orbitals. Consequently, this complex will be more stable than expected on purely electrostatic grounds by $0.4\Delta_o$. The additional stabilization of a metal complex by selective population of the lower-energy d orbitals is called its crystal field stabilization energy (CFSE). The CFSE of a complex can be calculated by multiplying the number of electrons in t_{2g} orbitals by the energy of those orbitals ($-0.4\Delta_o$), multiplying the number of electrons in e_g orbitals by the energy of those orbitals ($+0.6\Delta_o$), and summing the two. Table **5.6.2** gives CFSE values for octahedral complexes with different d electron configurations. The CFSE is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. The other low-spin configurations also have high CFSEs, as does the d^3 configuration.

Table **5.6.2**: CFSEs for Octahedral Complexes with Different Electron Configurations (in Units of Δo)

	High Spin		CFSE (Δ_o)	Low Spin		CFSE (Δ_o)
d^0			0			
d^1	↑		0.4			
d^2	↑ ↑		0.8			
d^3	↑ ↑ ↑		1.2			
d^4	↑ ↑ ↑	↑	0.6	↑↓ ↑ ↑		1.6
d^5	↑ ↑ ↑	↑ ↑	0.0	↑↓ ↑↓ ↑		2.0
d^6	↑↓ ↑ ↑	↑ ↑	0.4	↑↓ ↑↓ ↑↓		2.4
d^7	↑↓ ↑↓ ↑	↑ ↑	0.8	↑↓ ↑↓ ↑↓	↑	1.8
d^8	↑↓ ↑↓ ↑↓	↑ ↑	1.2			
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	0.6			
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0.0			

CFSEs are important for two reasons. First, the existence of CFSE nicely accounts for the difference between experimentally measured values for bond energies in metal complexes and values calculated based solely on electrostatic interactions. Second, CFSEs represent relatively large amounts of energy (up to several hundred kilojoules per mole), which has important chemical consequences.

> *Octahedral d^3 and d^8 complexes and low-spin d^6, d^5, d^7, and d^4 complexes exhibit large CFSEs.*

Example 5.6.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[CoF_6]^{3-}$
b. $[Rh(CO)_2Cl_2]^-$

Given: complexes

Asked for: structure, high spin versus low spin, and the number of unpaired electrons

Strategy:

a. From the number of ligands, determine the coordination number of the compound.
b. Classify the ligands as either strong field or weak field and determine the electron configuration of the metal ion.
c. Predict the relative magnitude of Δ_o and decide whether the compound is high spin or low spin.
d. Place the appropriate number of electrons in the d orbitals and determine the number of unpaired electrons.

Solution

a. A With six ligands, we expect this complex to be octahedral.

B The fluoride ion is a small anion with a concentrated negative charge, but compared with ligands with localized lone pairs of electrons, it is weak field. The charge on the metal ion is +3, giving a d^6 electron configuration.

C Because of the weak-field ligands, we expect a relatively small Δ_o, making the compound high spin.

D In a high-spin octahedral d^6 complex, the first five electrons are placed individually in each of the d orbitals with their spins parallel, and the sixth electron is paired in one of the t_{2g} orbitals, giving four unpaired electrons.

b. A This complex has four ligands, so it is either square planar or tetrahedral.

B C Because rhodium is a second-row transition metal ion with a d^8 electron configuration and CO is a strong-field ligand, the complex is likely to be square planar with a large Δ_o, making it low spin. Because the strongest d-orbital interactions are along the x and y axes, the orbital energies increase in the order $d_{z^2}d_{yz}$, and d_{xz} (these are degenerate); d_{xy}; and $d_{x^2-y^2}$.

D The eight electrons occupy the first four of these orbitals, leaving the $d_{x^2-y^2}$. orbital empty. Thus there are no unpaired electrons.

Exercise 5.6.1

For each complex, predict its structure, whether it is high spin or low spin, and the number of unpaired electrons present.

a. $[Mn(H_2O)_6]^{2+}$
b. $[PtCl_4]^{2-}$

Answers

a. octahedral; high spin; five
b. square planar; low spin; no unpaired electrons

Summary

Crystal field theory, which assumes that metal–ligand interactions are only electrostatic in nature, explains many important properties of transition-metal complexes, including their colors, magnetism, structures, stability, and reactivity. Crystal field theory (CFT) is a bonding model that explains many properties of transition metals that cannot be explained using valence bond theory. In CFT, complex formation is assumed to be due to electrostatic interactions between a central metal ion and a set of negatively charged ligands or ligand dipoles arranged around the metal ion. Depending on the arrangement of the ligands, the d orbitals split into sets of orbitals with different energies. The difference between the energy levels in an octahedral complex is called the crystal field splitting energy (Δ_o), whose magnitude depends on the charge on the metal ion, the position of the metal in the periodic table,

and the nature of the ligands. The spin-pairing energy (P) is the increase in energy that occurs when an electron is added to an already occupied orbital. A high-spin configuration occurs when the Δ_o is less than P, which produces complexes with the maximum number of unpaired electrons possible. Conversely, a low-spin configuration occurs when the Δ_o is greater than P, which produces complexes with the minimum number of unpaired electrons possible. Strong-field ligands interact strongly with the d orbitals of the metal ions and give a large Δ_o, whereas weak-field ligands interact more weakly and give a smaller Δ_o. The colors of transition-metal complexes depend on the environment of the metal ion and can be explained by CFT.

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5.E: Chemistry of Coordination Chemistry (Exercises)

Questions migrated to ADAPT

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CHAPTER OVERVIEW

6: Organic and Biological Chemistry

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

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Carbon is unique among the elements in its ability to *catenate*, to form a wide variety of compounds that contain long chains and/or rings of carbon atoms. Some of the most complex chemical structures known are those of the organic molecules found in living organisms. In spite of their size and complexity, these biological molecules obey the same chemical principles as simpler organic molecules. Thus we can use Lewis electron structures to understand the preferred mode of reactivity of a variety of organic compounds, relative electronegativities and bond polarities to predict how certain groups of atoms will react, and molecular orbital theory to explain why certain organic species that contain multiple bonds are especially stable or undergo particular reactions when they interact with light.

In this chapter, we continue our description of organic compounds by focusing on their molecular structures and reactivity; we will also introduce some of the fundamental types of reactions and reaction mechanisms you will encounter in organic and biological chemistry. We discuss why butter is a solid and oils are liquids despite the apparent similarities in their structures, why the widely used anti-inflammatory drug ibuprofen takes longer than half an hour to relieve pain, and the identity of the major carcinogen in grilled meats and cigarette smoke. The chapter concludes with a brief introduction to the molecules of life, which will explain how the consumption of lactose can result in mental retardation and cirrhosis of the liver in some individuals, how hibernating animals survive during the winter, and how certain groups of antibiotics kill bacteria that are harmful to humans.

6.0: General Characteristics of Organic Molecules
6.1: Introduction to Hydrocarbons
6.2: Alkanes
6.3: Unsaturated Hydrocarbons
6.4: Functional Groups
6.5: Compounds with a Carbonyl Group
6.6: Chirality in Organic Chemistry
6.7: Introduction to Biochemistry
6.8: Proteins
6.9: Carbohydrates
6.10: Nucleic Acids
6.E: Organic and Biological Chemistry (Exercises)
6.S: Organic and Biological Chemistry (Summary)

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6.0: General Characteristics of Organic Molecules

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Organic substances have been used throughout this text to illustrate the differences between ionic and covalent bonding and to demonstrate the intimate connection between the structures of compounds and their chemical reactivity. You learned, for example, that even though NaOH and alcohols (ROH) both have OH in their formula, NaOH is an ionic compound that dissociates completely in water to produce a basic solution containing Na^+ and OH^- ions, whereas alcohols are covalent compounds that do not dissociate in water and instead form neutral aqueous solutions. You also learned that an amine (RNH_2), with its lone pairs of electrons, is a base, whereas a carboxylic acid (RCO_2H), with its dissociable proton, is an acid.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{6.0.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and **inorganic chemistry** is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table **6.0.1**.

Table **6.0.1**: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table **6.0.1** also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table **6.0.1**.

Key Takeaway

- Organic chemistry is the study of carbon compounds, nearly all of which also contain hydrogen atoms.

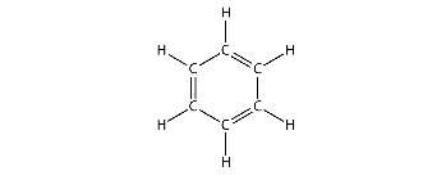
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6.1: Introduction to Hydrocarbons

Learning Objectives

- Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

  The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

1. 

   The inherent ability of hydrocarbons to bond to themselves is known as catenation, and allows hydrocarbon to form more complex molecules, such as cyclohexane, and in rarer cases, arenes such as benzene. This ability comes from the fact that the bond character between carbon atoms is entirely non-polar, in that the distribution of electrons between the two elements is somewhat even due to the same electronegativity values of the elements (~0.30).

Contributors

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6.2: Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure **6.2.1**.

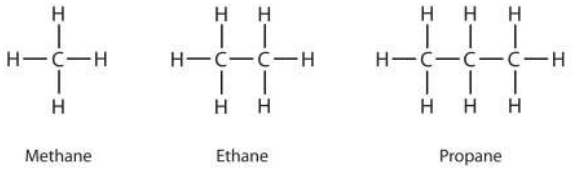


Figure **6.2.1**: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure **6.2.2**).

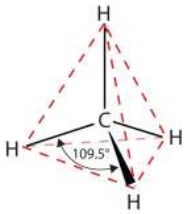


Figure **6.2.2**: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table **6.2.1**.

Table **6.2.1**: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure **6.2.3**. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

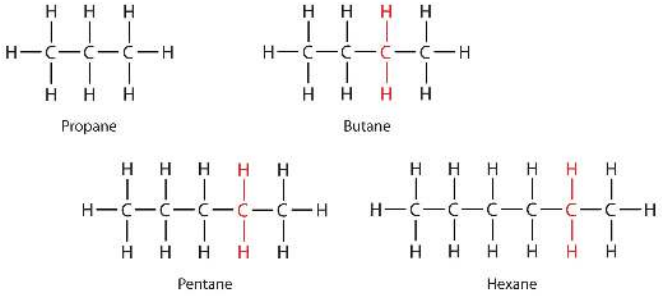


Figure **6.2.3**: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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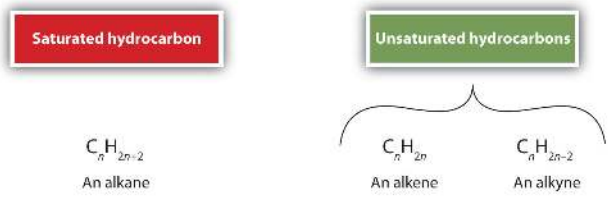
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6.3: Unsaturated Hydrocarbons

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

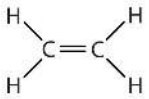


Some representative alkenes—their names, structures, and physical properties—are given in Table **6.3.1**.

Table **6.3.1**: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table **6.3.1**. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table **6.3.1**, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure **6.3.1**). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

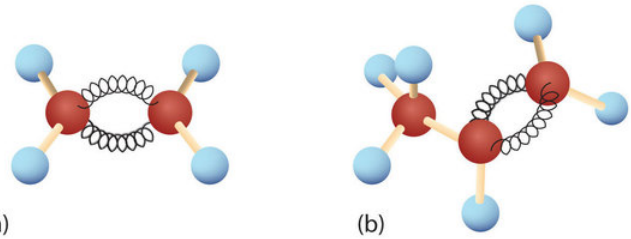
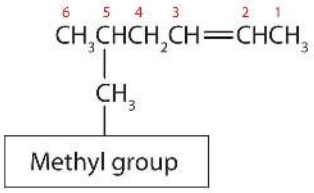


Figure **6.3.1**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

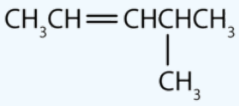
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

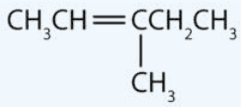
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 6.3.1

Name each compound.

a. 

b. 

Solution

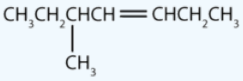
a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 6.3.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

Example 6.3.2

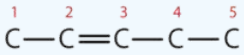
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

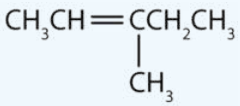
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

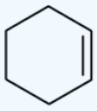


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 6.3.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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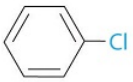
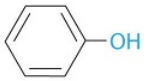
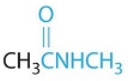
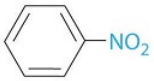
- **13.1: Alkenes- Structures and Names** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.

6.4: Functional Groups

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure **6.4.1** summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	RR′C=O		acetone (2-propanone)	-one
Carboxylic acids	RCO_2H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′		*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

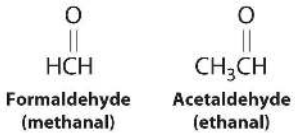
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[a] R indicates an alkyl group [b] Ar indicates an aryl group

Figure 6.4.1: Major Classes of Organic Compounds

The first family listed in Figure **6.4.1** is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure **6.4.2**). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para- compounds, the name is meta-xylene or m-xylene.

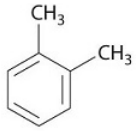
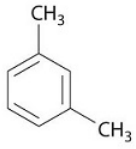
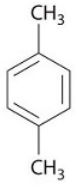
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure **6.4.2**: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

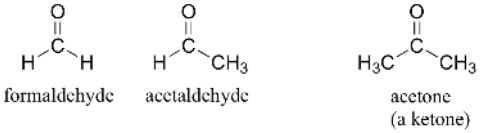
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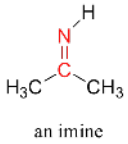
6.5: Compounds with a Carbonyl Group

Aldehydes and Ketones

There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.

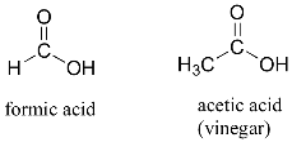


Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.

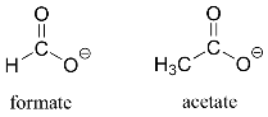


Carboxylic acids and acid derivatives

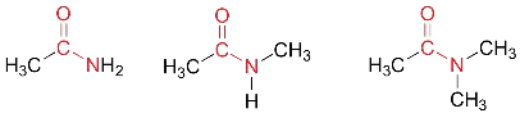
If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives'**, a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.



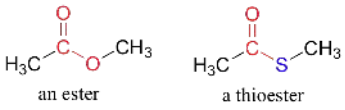
As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).



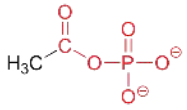
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.



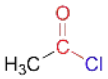
In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.



In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.

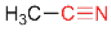


an acyl phosphate



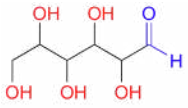
an acid chloride

Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.

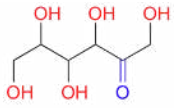


a nitrile

A single compound often contains several functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

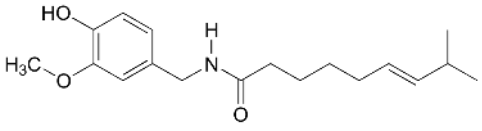


glucose



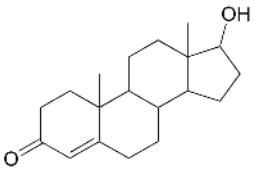
fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.

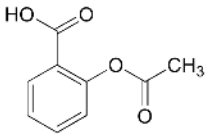


capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.



testosterone



acetylsalicylic acid
(aspirin)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table on the inside back cover provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

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6.6: Chirality in Organic Chemistry

Organic compounds, molecules created around a chain of carbon atom (more commonly known as carbon backbone), play an essential role in the chemistry of life. These molecules derive their importance from the energy they carry, mainly in a form of potential energy between atomic molecules. Since such potential force can be widely affected due to changes in atomic placement, it is important to understand the concept of an isomer, a molecule sharing same atomic make up as another but differing in structural arrangement.

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of their most interesting type of isomer is the mirror-image stereoisomers, a non-superimposable set of two molecules that are mirror image of one another. The existence of these molecules are determined by concept known as chirality.

Stereoisomers

Molecules with the same connectivity but different arrangements of the atoms in space are called stereoisomers. There are two types of stereoisomers: geometric and optical. Geometric isomers differ in the relative position(s) of substituents in a rigid molecule. Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement. Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either cis or trans, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, cis and trans isomers are actually two distinct chemical compounds.

> *Stereoisomers have the same connectivity, but different arrangements of atoms in space.*

Optical isomers are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have identical physical properties, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be chiral (pronounced “ky-ral,” from the Greek cheir, meaning “hand”). Examples of some familiar chiral objects are your hands, feet, and ears. As shown in Figure **6.6.1*a***, your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An achiral object is one that can be superimposed on its mirror image, as shown by the superimposed flasks in Figure **6.6.1*b***.

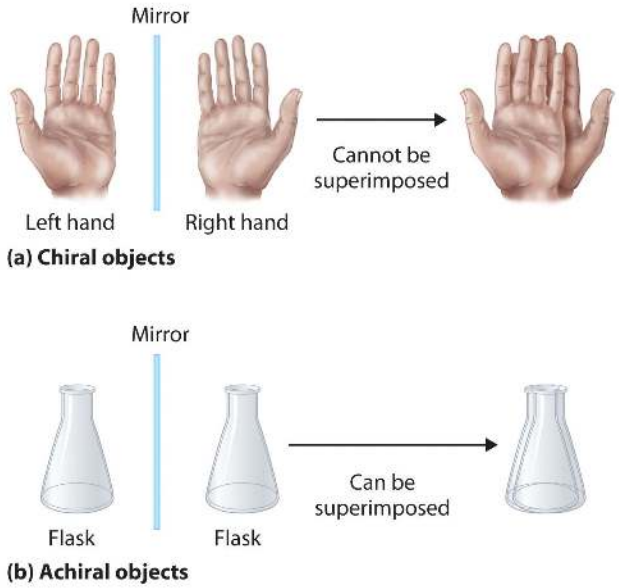


Figure **6.6.1**: Chiral and Achiral Objects. (a) Objects that are nonsuperimposable mirror images of each other are chiral, such as the left and the right hand. (b) The unmarked flask is achiral because it can be superimposed on its mirror image.

Most chiral organic molecules have at least one carbon atom that is bonded to four different groups, as occurs in the bromochlorofluoromethane molecule shown in part (a) in Figure **6.6.2**. This carbon, often designated by an asterisk in structural drawings, is called a chiral center or asymmetric carbon atom. If the bromine atom is replaced by another chlorine (Figure **6.6.2*b***), the molecule and its mirror image can now be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Asymmetric carbon atoms are found in many naturally occurring molecules, such as lactic acid, which is present in milk and muscles, and nicotine, a component of tobacco. A molecule and its nonsuperimposable mirror image are called enantiomers (from the Greek enantiou, meaning "opposite").

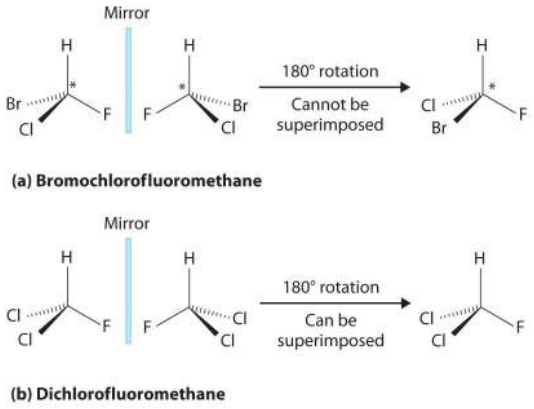
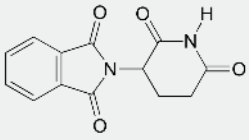


Figure **6.6.2**: Comparison of Chiral and Achiral Molecules. (a) Bromochlorofluoromethane is a chiral molecule whose stereocenter is designated with an asterisk. Rotation of its mirror image does not generate the original structure. To superimpose the mirror images, bonds must be broken and reformed. (b) In contrast, dichlorofluoromethane and its mirror image can be rotated so they are superimposable.

Thalidomide

In the 1960's, a drug called thalidomide was widely prescribed in the Western Europe to alleviate morning sickness in pregnant women.



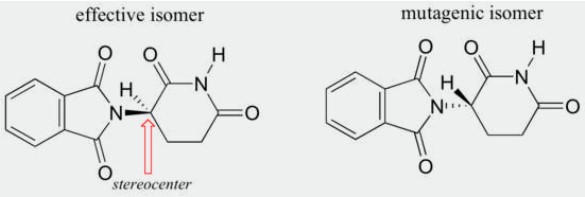
thalidomide

Thalidomide had previously been used in other countries as an antidepressant, and was believed to be safe and effective for both purposes. The drug was not approved for use in the U.S.A. It was not long, however, before doctors realized that something had gone horribly wrong: many babies born to women who had taken thalidomide during pregnancy suffered from severe birth defects.



Baby born to a mother who had taken thalidomide while pregnant.

Researchers later realized the that problem lay in the fact that thalidomide was being provided as a mixture of two different isomeric forms.



One of the isomers is an effective medication, the other caused the side effects. Both isomeric forms have the same molecular formula and the same atom-to-atom connectivity, so they are not constitutional isomers. Where they differ is in the arrangement in three-dimensional space about one tetrahedral, sp^3-hybridized carbon. These two forms of thalidomide are **stereoisomers**.

Looking for planes of symmetry in a molecule is useful, but often difficult in practice. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions, the general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral. Carbon stereocenters are also referred to quite frequently as **chiral carbons**.

When evaluating a molecule for chirality, it is important to recognize that the question of whether or not the dashed/solid wedge drawing convention is used is irrelevant. Chiral molecules are sometimes drawn without using wedges (although obviously this means that stereochemical information is being omitted). Conversely, wedges may be used on carbons that are not stereocenters – look, for example, at the drawings of glycine and citrate in the figure above. Just because you see dashed and solid wedges in a structure, do not automatically assume that you are looking at a stereocenter.

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6.7: Introduction to Biochemistry

Biochemistry is the study of chemical processes in living organisms, including, but not limited to, living matter. Biochemistry governs all living organisms and living processes. By controlling information flow through biochemical signaling and the flow of chemical energy through metabolism, biochemical processes give rise to the incredible complexity of life.

Over the last decades of the 20th century, biochemistry become so successful at explaining living processes that now almost all areas of the life sciences from botany to medicine to genetics are engaged in biochemical research. Today, the main focus of pure biochemistry is in understanding how biological molecules give rise to the processes that occur within living cells, which in turn relates greatly to the study and understanding of whole organisms.

Biochemistry is closely related to molecular biology, the study of the molecular mechanisms by which genetic information encoded in DNA is able to result in the processes of life. Depending on the exact definition of the terms used, molecular biology can be thought of as a branch of biochemistry, or biochemistry as a tool with which to investigate and study molecular biology.

Much of biochemistry deals with the structures, functions and interactions of biological macromolecules, such as proteins, nucleic acids, carbohydrates and lipids, which provide the structure of cells and perform many of the functions associated with life. The chemistry of the cell also depends on the reactions of smaller molecules and ions. These can be inorganic, for example water and metal ions, or organic, for example the amino acids which are used to synthesize proteins. The mechanisms by which cells harness energy from their environment via chemical reactions are known as metabolism. The findings of biochemistry are applied primarily in medicine, nutrition, and agriculture. In medicine, biochemists investigate the causes and cures of disease. In nutrition, they study how to maintain health and study the effects of nutritional deficiencies. In agriculture, biochemists investigate soil and fertilizers, and try to discover ways to improve crop cultivation, crop storage and pest control. Much of biochemistry deals with the structures and functions of cellular components such as proteins, carbohydrates, lipids, nucleic acids and other biomolecules—although increasingly processes rather than individual molecules are the main focus.

Contributors

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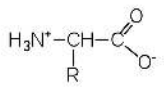
6.8: Proteins

Learning Objectives

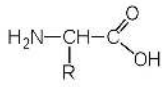
- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion

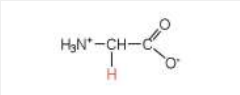
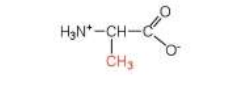
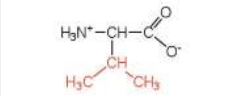
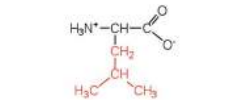
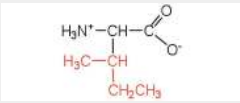
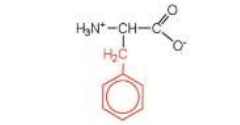
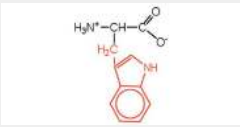
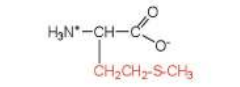
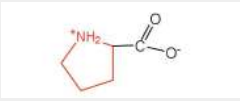
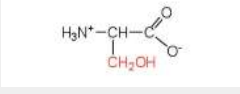
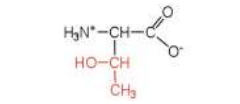
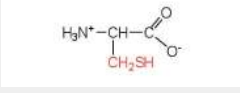


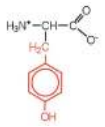
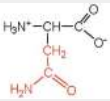
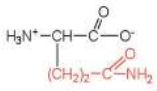
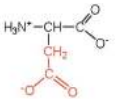
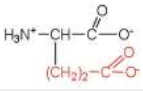
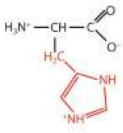
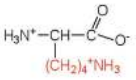
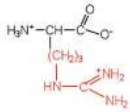
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

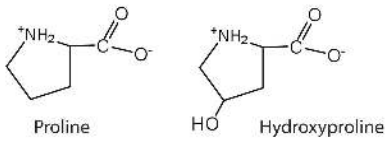
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table **6.8.1**.

Table **6.8.1**: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

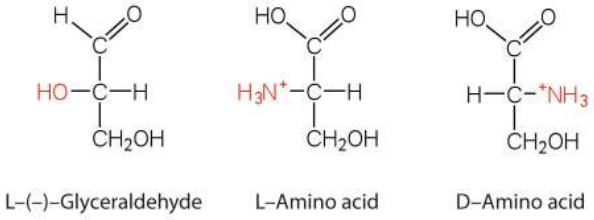
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Configuration

Notice in Table 6.8.1 that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

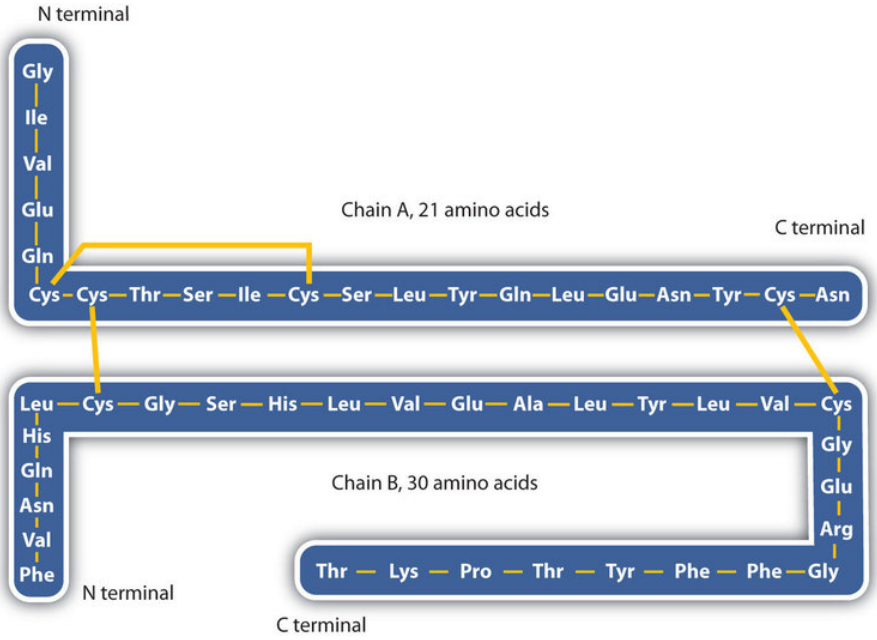


Figure **6.8.1**: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the primary structure, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure **6.8.1**.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure **6.8.2**). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

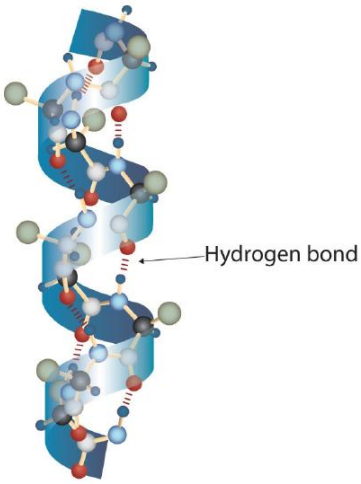


Figure **6.8.2** A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure **6.8.3**). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

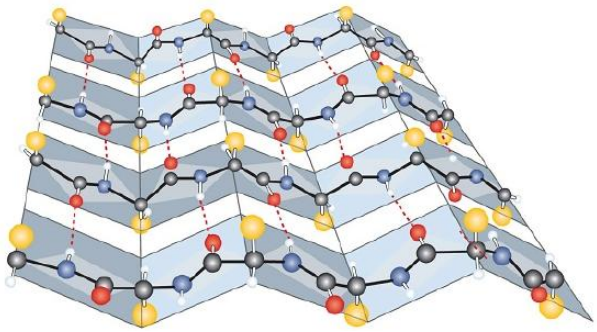


Figure **6.8.3**: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure **6.8.4** shows a depiction of the three-dimensional structure of insulin.

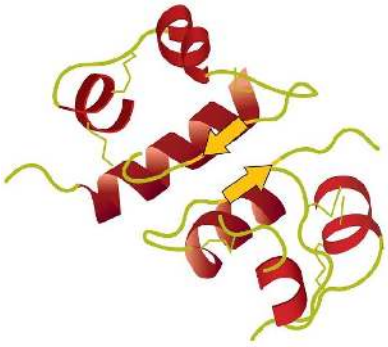
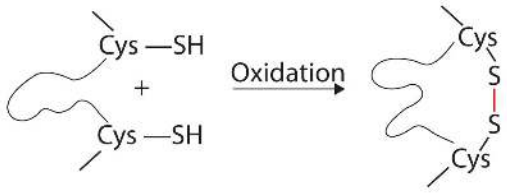


Figure **6.8.4**: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure **6.8.5**).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure **6.8.5**).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure **6.8.5**). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure **6.8.1**) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure **6.8.5**). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

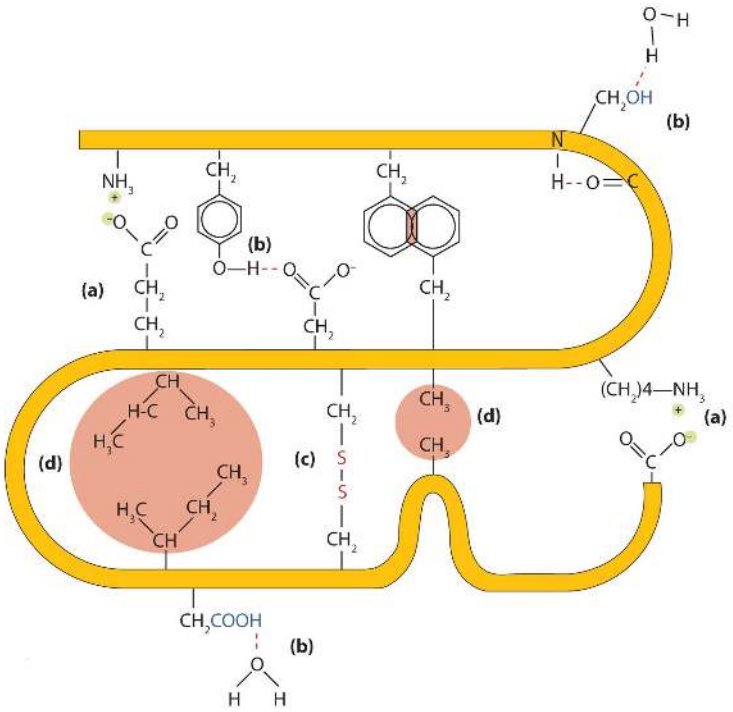


Figure 6.8.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 6.8.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 6.8.7.

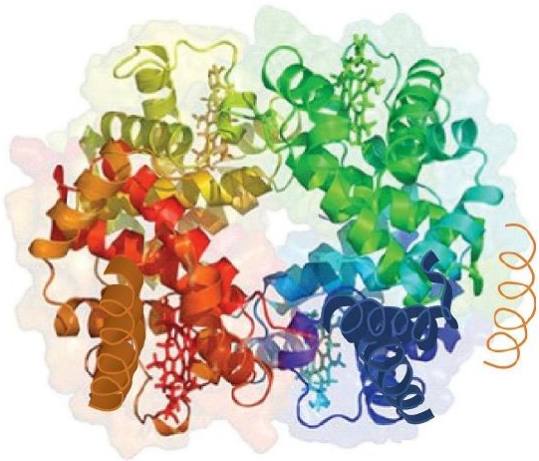


Figure 6.8.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

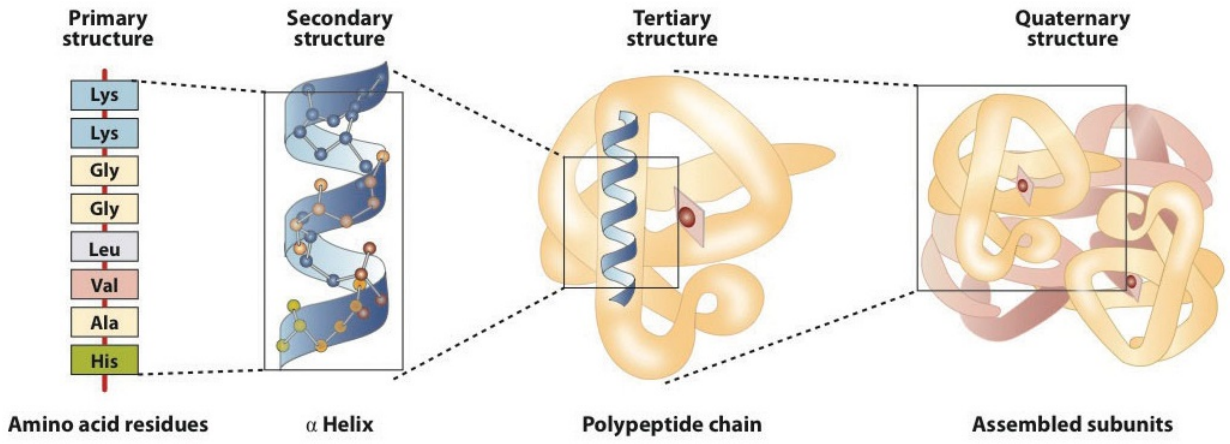


Figure **6.8.7**: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure **6.8.1**).

Figure **6.8.1**: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure **6.8.8**). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

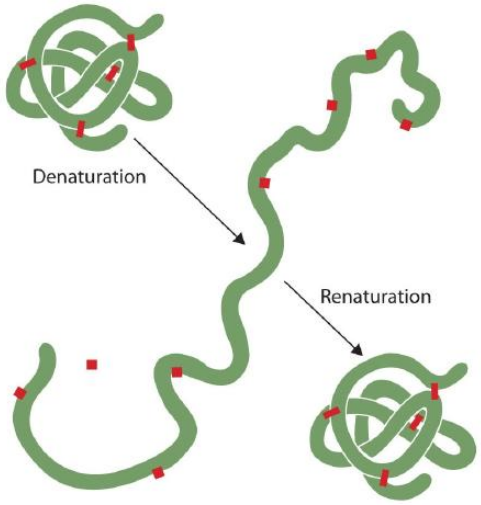


Figure **6.8.8**: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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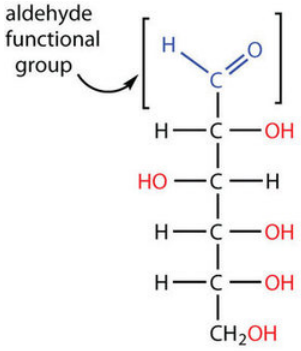
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6.9: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

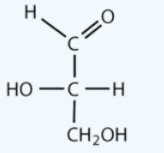
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_6{\cdot}6H_2O$.

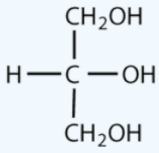


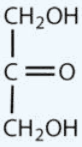
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

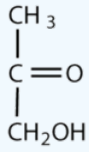
Example 6.9.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.

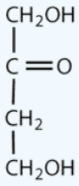
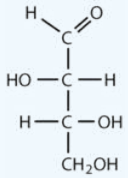
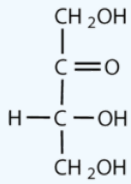
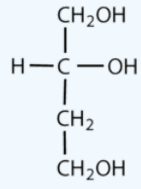
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

? Exercise 6.9.1

Which compounds would be classified as carbohydrates?

1. 
2. 
3. 
4. 

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{6.9.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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6.10: Nucleic Acids

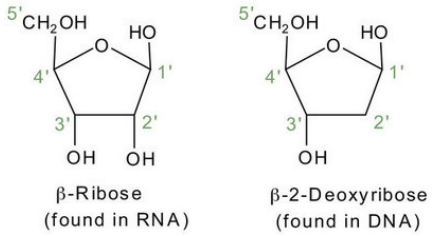
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure **6.10.1**).

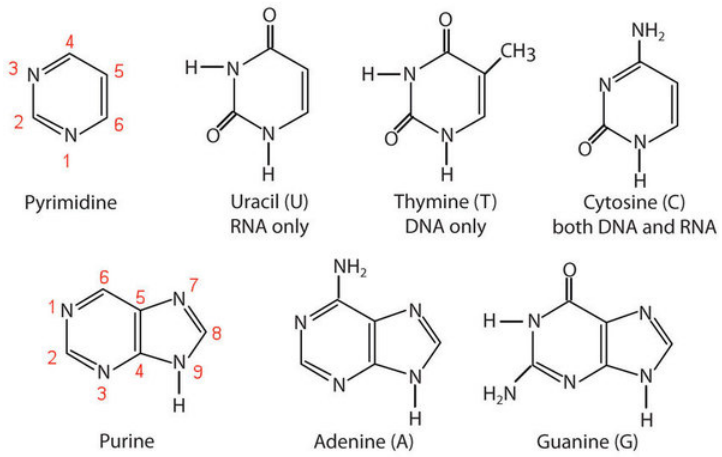


Figure **6.10.1**: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table **6.10.1** summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table **6.10.1**: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure **6.10.2**.

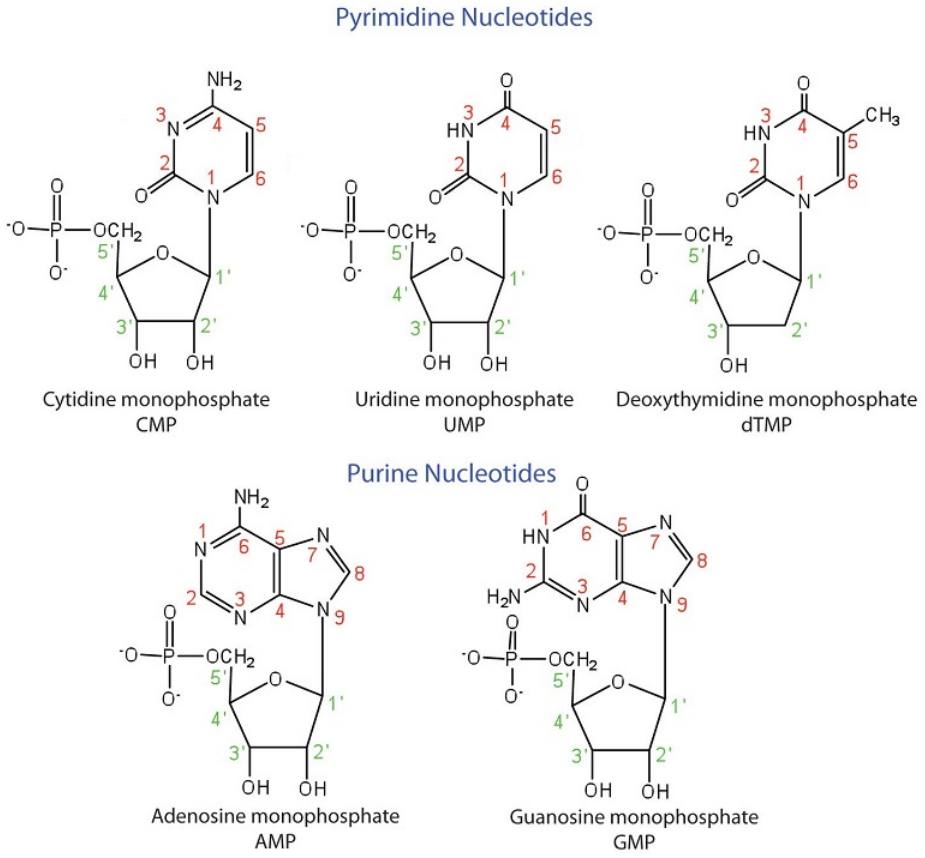


Figure **6.10.2**: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure **6.10.3**, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

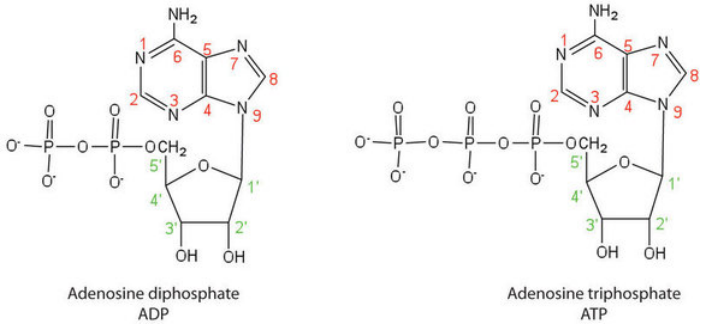


Figure **6.10.3**: Structures of Two Important Adenine-Containing Nucleotides

Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

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6.E: Organic and Biological Chemistry (Exercises)

25.1: General Characteristics of Organic Molecules

Concept Review Exercises

1. Classify each compound as organic or inorganic.

   a. C_3H_8O
   b. $CaCl_2$
   c. $Cr(NH_3)_3Cl_3$
   d. $C_{30}H_{48}O_3N$

2. Which compound is likely organic and which is likely inorganic?

   a. a flammable compound that boils at 80°C and is insoluble in water
   b. a compound that does not burn, melts at 630°C, and is soluble in water

Answers

1. a. organic
   b. inorganic
   c. inorganic
   d. organic

2. a. organic
   b. inorganic

Exercises

1. Classify each compound as organic or inorganic.

   a. C_6H_{10}
   b. $CoCl_2$
   c. $C_{12}H_{22}O_{11}$

2. Classify each compound as organic or inorganic.

   a. CH_3NH_2
   b. $NaNH_2$
   c. $Cu(NH_3)_6Cl_2$

3. Which member of each pair has a higher melting point?

   a. CH_3OH and NaOH
   b. CH_3Cl and KCl

4. Which member of each pair has a higher melting point?

   a. C_2H_6 and $CoCl_2$
   b. CH_4 and LiH

Answers

1. a. organic
   b. inorganic
   c. organic

3. a. NaOH
   b. KCl

25.2: Introduction to Hydrocarbons

25.3: Alkanes

25.4: Unsaturated Hydrocarbons

25.5: Functional Groups

Concept Review Exercises

1. What is the functional group of an alkene? An alkyne?
2. Does $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ have a functional group? Explain.

Answers

1. carbon-to-carbon double bond; carbon-to-carbon triple bond
2. No; it has nothing but carbon and hydrogen atoms and all single bonds.

Exercises

1. What is the functional group of 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. What is the functional group of butyl bromide, $CH_3CH_2CH_2CH_2Br$?

Answer

1. OH

25.6: Compounds with a Caronyl Group

25.7: Chirality in Organic Chemistry

25.8: Introduction to Biochemistry

25.9: Proteins

25.10: Carbohydrates

25.11: Nucleic Acids

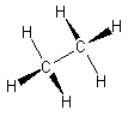
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6.S: Organic and Biological Chemistry (Summary)

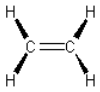
- **organic chemistry** – the study of carbon compounds
- **biochemistry** – the stuyd of the chemistry of living species

25.2: Introduction to Hydrocarbons

- made of only hydrogen and carbon
- 4 types: alkanes, alkenes, alkynes, and aromatic hydrocarbons
- **alkanes** – only single bonds
- also called saturated hydrocarbons



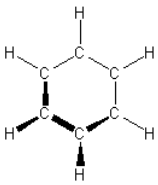
- have the largest amount of hydrogen atoms bonded to a single carbon atom
-



- **alkenes** (olefins) – have double carbon bonds
- - **alkynes** – triple carbon bonds



- - **aromatic hydrocarbons** – carbon atoms connected in a planar ring structure, joined by s and p bonds between carbon atoms

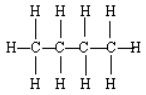


- - **alkenes, alkynes and aromatic hydrocarbons** – unsaturated hydrocarbons
  - less volatile with increasing molar mass
  - very low molecular weight = gas at room temperature
  - moderate molecular weight = liquid
  - high molecular weight = solid

25.3: Alkanes

- methane major part of natural gas
- used in home heating, gas stoves, hot-water heaters
- propane major part of bottled gas
- used for home heating, cooking
- butane – used in disposable lighters, fuel canisters
- alkanes with 5-12 carbon atoms are found in gasoline
- formla for alkanes is called *condensed structural formulas*

Molecular Formula	Condensed Structural Formula	Name	Boiling point (°C)
CH_4	CH_4	Methane	-161
C_2H_6	$CH_3\ CH_3$	Ethane	-89
C_3H_8	$CH_3\ CH_2\ CH_3$	Propane	-44
C_4H_{10}	$CH_3\ CH_2\ CH_2\ CH_3$	Butane	-0.5
C_5H_{12}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_3$	Pentane	36
C_6H_{14}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Hexane	68
C_7H_{16}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Heptane	98
C_8H_{18}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Octane	125
C_9H_{20}	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Nonane	151
$C_{10}H_{22}$	$CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_2\ CH_3$	Decane	174



Lewis Structure

1. **Structures of Alkanes**

- tetrahedral geometry
- carbon-carbon single bond rotates easily at room temperature
- long chains tend to change shape

1. **Structural Isomers**

- straight-chained hydrocarbons – carbons atoms that are joined in a continuous chain
- branched-chain hydrocarbons – hydrocarbons with branched chains, 4 or more carbon atoms
- **structural isomers** – compounds with the same molecular formula but different bonding arrangements

1. **Nomenclature of Alkanes**

- **1)** Find the longest continuous chain of carbon atoms, and use the name of this chain as the base name of the compound.
- **2)** Number the carbon atoms in the longest chain, beginning with the end of the chain that is nearest to a substituent
- **3)** Name and give the location of each substituent group
- **4)** When two or more substituents are present list them in alphabetical order

1. **Cycloalkanes**

- alkanes that form rings or cycles
- carbon rings with fewer than five carbon atoms are strained
- more reactive

1. **Reactions of Alkanes**

- at room temperature alkanes do not react with acids, bases, or strong oxidizing agents
- important for it’s combustion in air; bases for fuels

25.4: Unsaturated Hydrocarbons

- **Alkenes**
- - double carbon bonds
  - ethene or ethylene simplest alkene\
  - nomenclature of alkenes come from the name of the corresponding alkane
  - the –ane ending is changed to –ene
  - **geometrical isomers** – compounds that have the same molecular formula and the same groups bonded to one another but differ in the spatial arrangement of these groups
  - geometrical isomers have distinct physical properties and differ in chemical behavior
  - the double carbon bond is resistant to twisting
  - rotation about a double bond is a key process in the chemistry of vision

1. **Alkynes**

- - one or more triple bonds
  - simplest alkyne is acetylene
  - highly reactive
  - named by changing the alkane ending (-ane) to –yne

1. **Addition Reactions of Alkenes and Alkynes**

- - **addition reactions** – a reactant is added to the two atoms that form the multiple bond
  - **hyrogenation** – reaction between al alkene and H_2

1. **Aromatic Hydrocarbons**

- - simplest is benzene
  - stability comes from the stabilization of the p electrons through delocalization in the p orbitals
  - represented by a hexagon with an inscribed circle
  - **substitution reactions** – one atom of a molecule is removed and replaced by another atom or group of atoms

25.5: Functional Groups

functional group – site of reactivity in an organic molecule; controls how the molecule behaves or functions

- chemistry of an organic molecule is determined by the functional groups it contains

1. **Alcohols (R-OH)**

- **alcohols** – hydrocarbon derivatives in which one ore more hydrogens of a parent hydrocarbon have been replaced by a hydroxyle or alcohol functional group

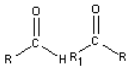
1. **Ethers (R-O-R')**

- - **ethers** – two hyrocarbon groups are bonded to one oxygen
  - formed from two molecules of alcohol by splitting out a molecule of water
  - **condensation reaction** – reaction where water is split out from two substances
  - used in solvents

25.6: Compounds with a Carbonyl Group

- - carbon oxygen double bonds

1. **Aldehydes and Ketones**

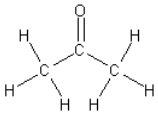


- - carbonyl group in aldehydes has at least one attached hydrogen atom



formaldehyde

- carbonyl group in ketones occurs at the interior of a carbon chain



Acetone

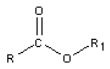
- prepared by oxidizing alcohols

1. **Carboxylic Acids**



- carboxylic acids contain carboxyl functional group (COOH)
- important for manufacturing of polymers
- produced by oxidation in which the OH group is attached to the CH_2

1. **Esters**



- carboxylic acids that undergo condensation with alcohols
- have pleasant odors
- saponification – hydrolysis of an ester in a base

1. **Amines and Amides**

- **amines** – organic bases; general formula R_3N
- **amides** – anines containing a hydrogen bonded to nitrogen that undergoes condensation

25.8: Introduction to Biochemistry

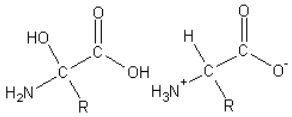
- **biosphere** – part of the earth where living organisms are formed and living
- includes influences on life of the atmosphere, natural waters, solid earth
- living organisms require a large amount of energy
- **biopolymers** – three categories: proteins, polysaccharides (carbohydrates), and nucleic acids

25.9: Proteins

- macromolecular substances
- 50% body's dry weight is proteins
- composed of amino acids

1. **Amino Acids**

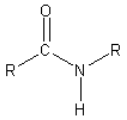
- differ in the R group
- building block of all proteins - a -amino acid
- general form:



- - **chiral -** any molecule containing a carbon with four different attached groups
  - **enantiomers** – mirror-image of chiral
  - enantiomers and chiral have the same physical properties
  - differ in chemical reactivity toward other chiral molecules

1. **Polypeptides and Proteins**

- **peptide bond** – condesation reaction between the carboxyl group of one amino acid and the amino group of another amino acid



- **polypeptides** – large number of amino acids that are linked together by peptide bonds
- proteins are polypeptide molecules
- weighs from 6000 to over 50 million amu

1. **Protein Structure**

- - **primary structure** – arrangement of amino acids along a protein chain
  - makes the protein unique
  - **secondary structure** – the way segments of the protein chain are oriented in a regular pattern
  - **a -helix** – most important and common secondary structure arrangement
  - first propoesed by Linus Pauling and R. B. Corey
  - **tertiary structure** – overal shape of a protein
  - **globular protein** – a protein that folds into a compact spherical shape
  - soluble in water, mobile within cells
  - **enzymes** – large protein molecules that serve as catalysts

25.10: Carbohydrates

- - written as $C_x(H_2O)_y$
  - glucose the most abundant carbohydrate $C_6H_{12}O_6$
  - not really hydrates of carbon but polyhydroxly aldehydes and ketones

1. **Disaccharides**

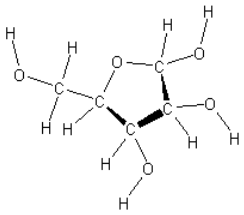
- - **monosaccharides** – simple sugars that can't be broken into smaller molecules by hydrolysis with aqueous acids
  - **disaccharide** – two linked monosaccharides
  - two common disaccharides: sucrose, lactose

1. **Polysaccharides**

- - made of several monosaccharide units
  - **starch** – group of polysaccharides
  - food storage in plant seeds and tuers
  - **glycogen** – starchlike substance synthesized in the body
  - 5000 to more than 5 million amu
  - energy bank in the body; muscles and liver
  - cellulose – major strructural unit of plants
  - straight chains of glucose units
  - more than 500,000 amu

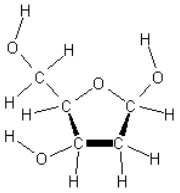
25.11: Nucleic Acids

- **nucleic acids** – biopolymers that are chemical carriers of an organisn't genetic information
- **deoxyribonucleic acids (DNA)** – huge molecules with molar weights of 6-16million amu
- **ribonucleic acids (RNA)** – smaller molecules with molecular weights of 20,000 to 40,000 amu
- DNA found inside the nucleus of a cell, RNA found outside nucleus in the cytoplasm
- DNA stores the genetic information of the cell and controls the production of proteins
- RNA carries information from the DNA out of the nucleus
- Monomers of nucleic acids (nucleotides) have three parts:
  - A phosphoric acid molecule, H_3PO_4
  - A five-carbon sugar



ribose

- A nitrogen-containing organic base



deoxyribose

- - deoxyribose has one less oxygen atom at carbon 2 than ribose
  - nucleic acids are polynucleotides
  - DNA molecules made of two DNA chains that form a double helix

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