General College Chemistry

Volume 2

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Foreword

Rebecca Sansom

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The chapters are organized by the day of class that they correspond to; a standard semester at BYU has 42 class days, so there are 41 chapters, reserving one day for a holiday or review. At the end of each chapter, there are additional resources housed on google drive that contain pdf files of lecture slides for use by the instructor, participation worksheets for use by students working in groups during class, and problem sets of practice problems and exercises for students to complete after class or after reading the textbook chapter.

The author, Dr. Rebecca Sansom, is an Associate Professor of Chemistry and Biochemistry at BYU. She has taught at BYU since 2014. Dr. Sansom was the recipient of the Oustanding Teaching Award from the BYU College of Physical and Mathematical Sciences in 2022. This award provided funding to develop the ancillaries and support several undergraduate students, including Mikaela Anderson, Andrea Augustus, Amanda Carlson, and Elia Hafen, who assisted in that process. Many of the practice problems were derived from earlier versions created by other faculty

members at BYU. The online General College Chemistry book was built and constructed by Abby Boekweg, a graduate student in the Instructional Psychology and Technology department at BYU as part of her Master's project. We gratefully acknowledge her effort, care, and diligence in preparing this text for use by students.

Instructors who wish to adopt and use this text in their classrooms may contact the author, Dr. Rebecca Sansom, at rsansom@chem.byu.edu to get access to instructor PowerPoint files, word document versions of participation and problem sets, and answer keys for the problem sets. Be sure to use your institutional email and include a link to the institution's website showing that you are an instructor there. If there are errors that you would like to report, please contact Dr. Sansom at the email given above with sufficient detail to explain where the error is located in the book, and what content you find problematic.

Thank you for your interest in using *General College Chemistry*. We hope that it will help you on your chemistry learning journey.

Rebecca Sansom

Brigham Young University

Dr. Rebecca Sansom is an associate professor of chemistry at Brigham Young University. Prior to her work at BYU, she served as an Albert Einstein Distinguished Educator Fellow at the National Science Foundation in the Division of Undergraduate Education, after teaching high school chemistry and biology for several years. Dr. Sansom earned her PhD in Educational Inquiry, Measurement, and Evaluation at Brigham Young University. She also completed an MEd in Educational Leadership at Southern Utah University after her AM in Chemistry and Chemical Biology from Harvard University and BA in Chemistry from Boston University.

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Unit 1

Solutions and Colligative Properties

Introduction and Review of Thermodynamics
Solutions
Osmotic Pressure
Vapor Pressure
Melting/Boiling

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1

Introduction and Review of Thermodynamics

Matter Energy Enthalpy Entropy

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the "disorder" of the system. For a given substance, entropy depends on phase with S_{solid} S_{liquid} S_{gas}. For different substances in the same physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium.

How to Study Chem 1.0.1 More Effectively

Watch on YouTube

1.1 Spontaneity

Learning Objectives

By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

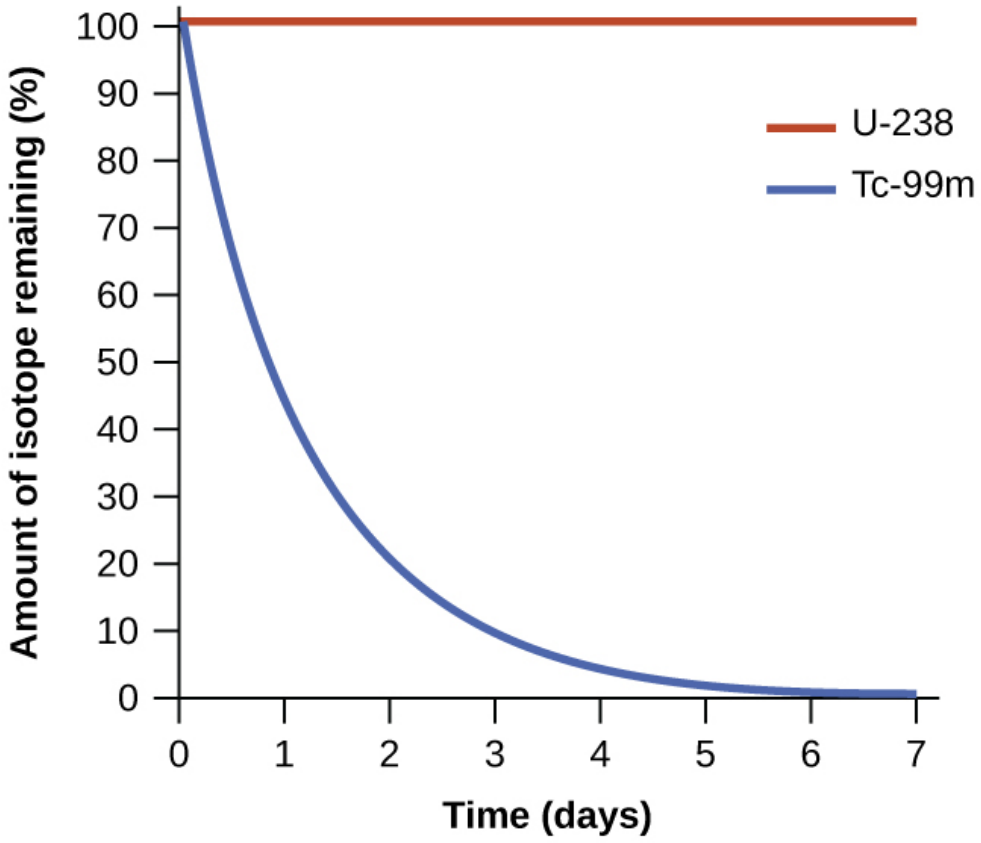
Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode but rust is not converted to iron without intentional chemical treatment. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this

concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium and its decay occurs much more slowly exhibiting a half-life of more than four billion years (Figure 1.1).

Figure 1.1

Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.



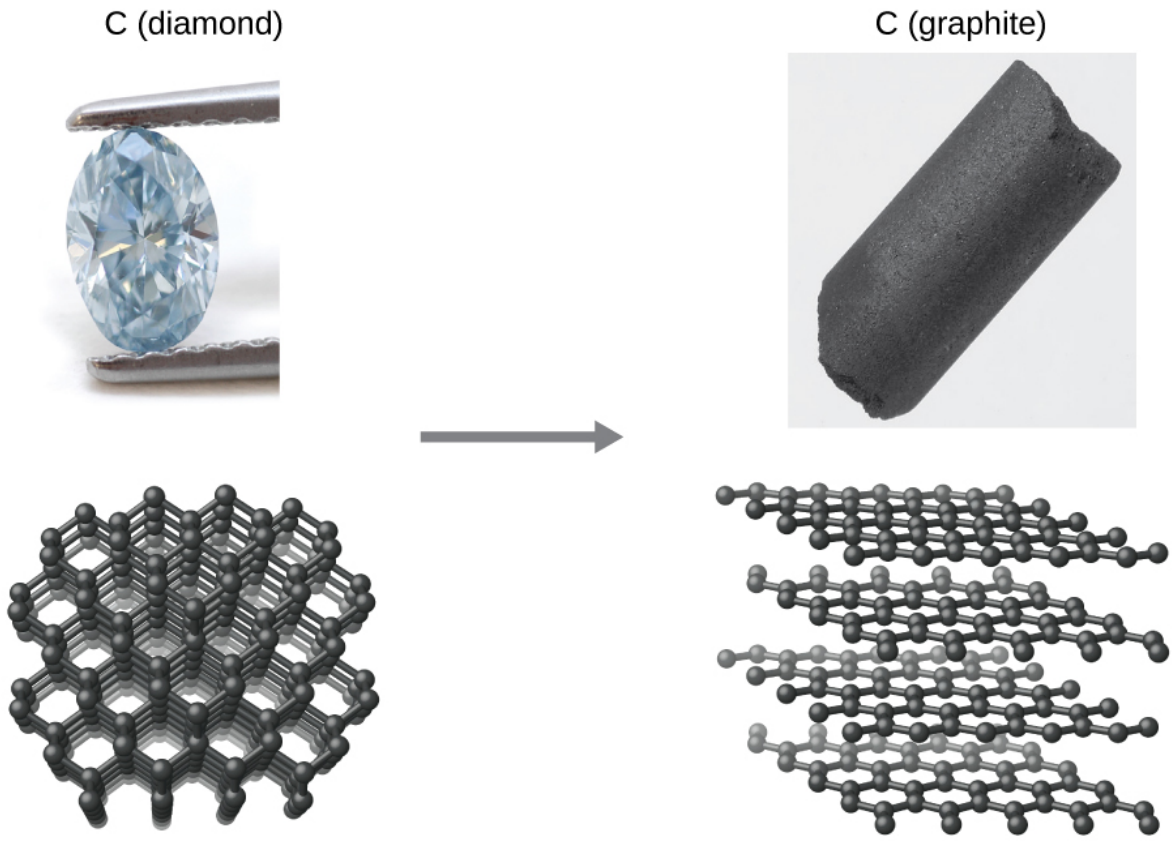
As another example, consider the conversion of diamond into graphite (Figure 1.2).

$$\mathrm{C}(s,\ \text{diamond}) \longrightarrow \mathrm{C}(s,\ \text{graphite})$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure while diamond is the stable allotrope at very high pressures such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

Figure 1.2

The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)



1.1.1 Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$). (Figure 1.3). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V = 0 \qquad (P = 0 \text{ in a vacuum})$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

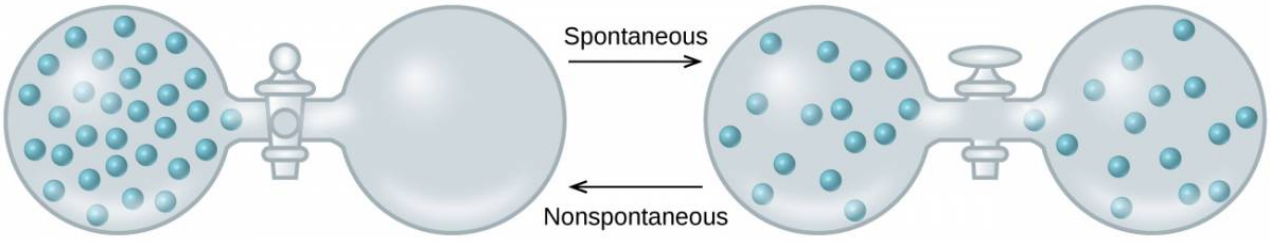
$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask

containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

Figure 1.3

An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.



Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \qquad \text{and} \qquad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.

Figure 1.4

When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

EXAMPLE 1.1.2

Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

(a) A solid sublimes.

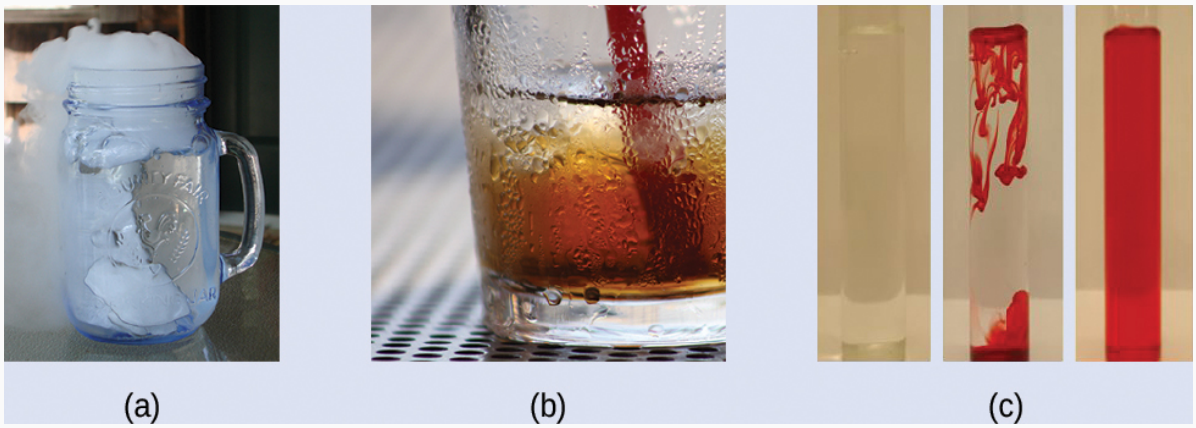
(b) A gas condenses.

(c) A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

Figure 1.5

(credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Paul A. Flowers)



(a) Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) The process in question is diffusion. This process yields a more uniform dispersal of matter since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Check Your Learning

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

1.2 Entropy

Learning Objectives

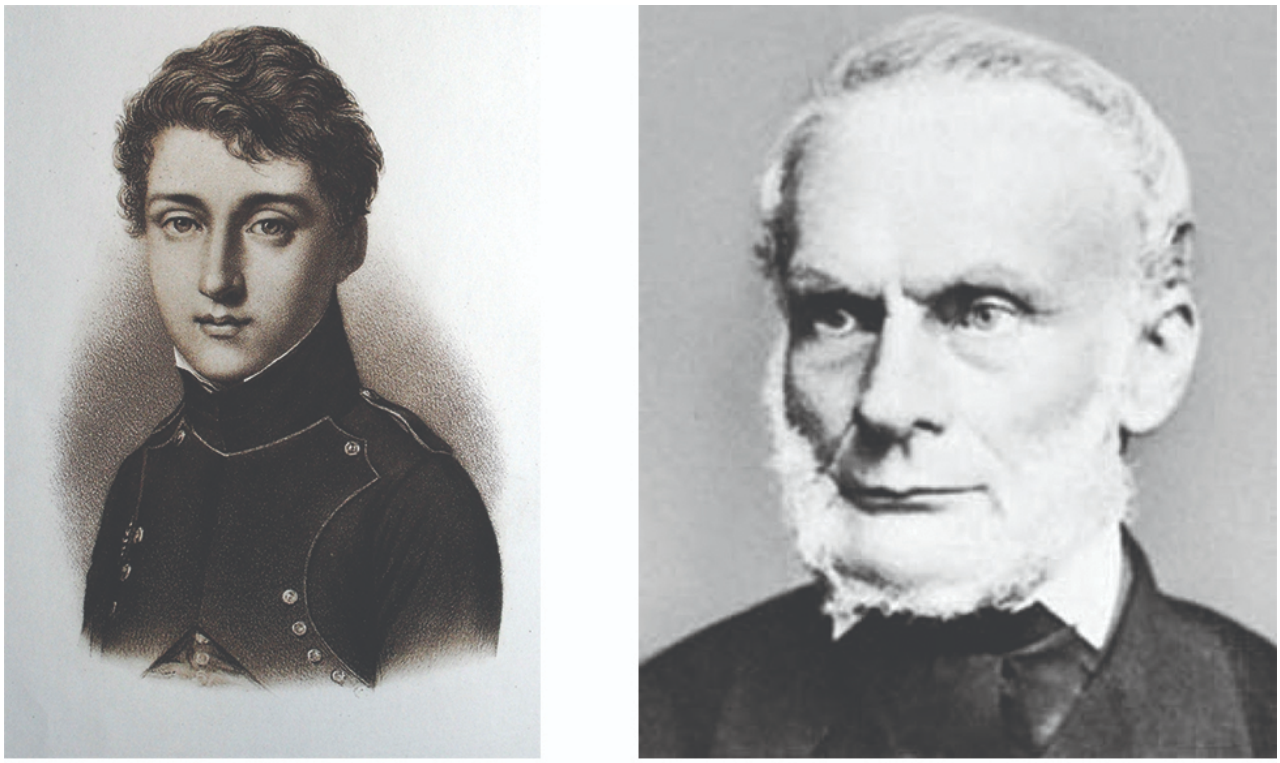
By the end of this section, you will be able to:

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 1.6) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a reversible process is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible rather they are classified as *irreversible*.

Figure 1.6

(a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.



(a) (b)

Similar to other thermodynamic properties, this new quantity is a state function so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (*S*) and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

1.2.1 Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (*W*) possible for the system. A microstate is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

where *k* is the Boltzmann constant, 1.38

×

10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

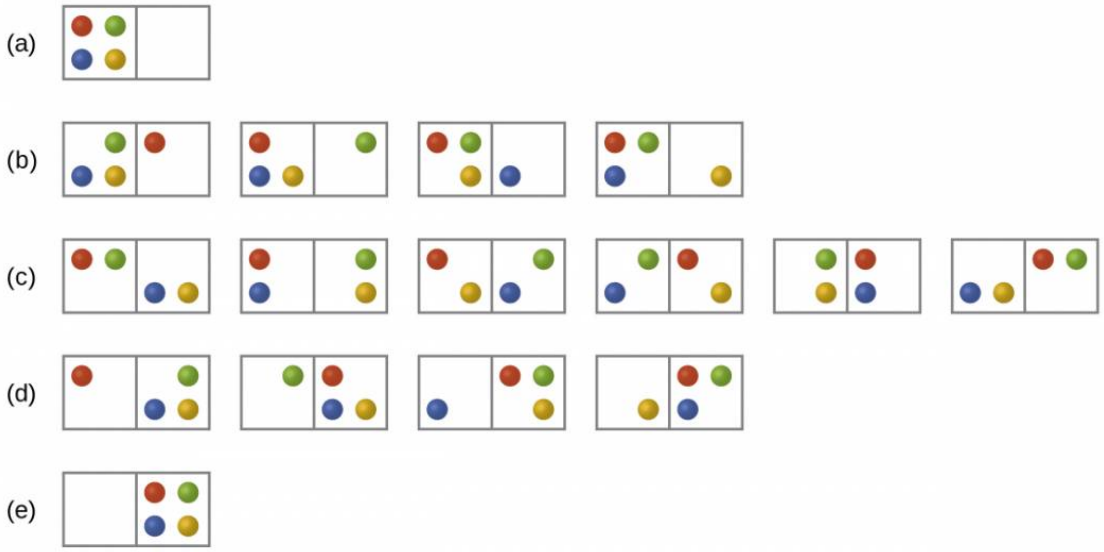
$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure 1.7. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

Figure 1.7

The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.



For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$\frac{6}{16}$

or

$\frac{3}{8}$.

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}.$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16}$$

or

$$\frac{1}{8}.$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 1.3) is a macroscopic example of this particle-in-a-box model. For this system the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as "*") in Figure 1.8. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is

$$\frac{3}{10}.$$

More likely is the flow of heat to yield one of the other two distribution, the combined probability being

$$\frac{7}{10}.$$

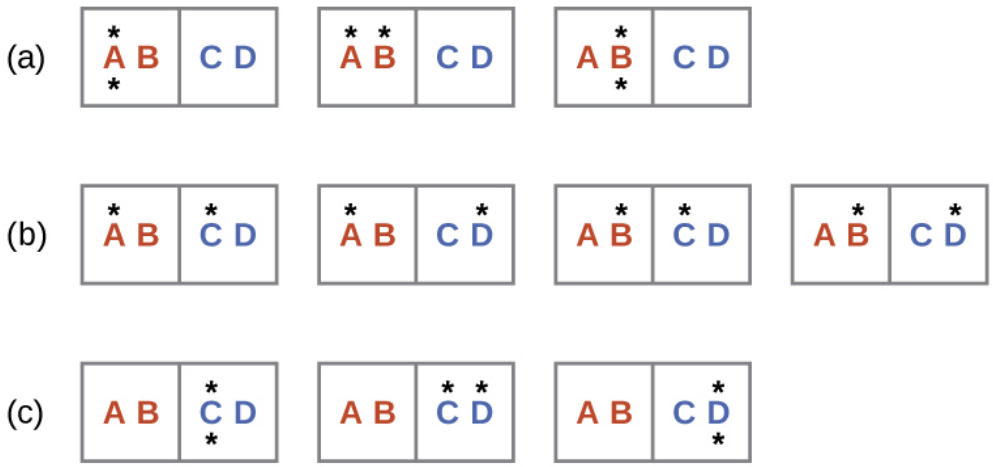
The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being

$\frac{4}{10}$.

This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

Figure 1.8

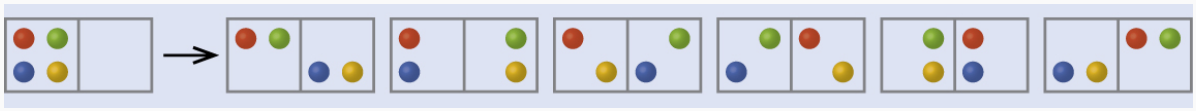
*This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.*



EXAMPLE 1.2.2

Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23}\ \text{J/K}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Check Your Learning

Consider the system shown in Figure 1.8. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

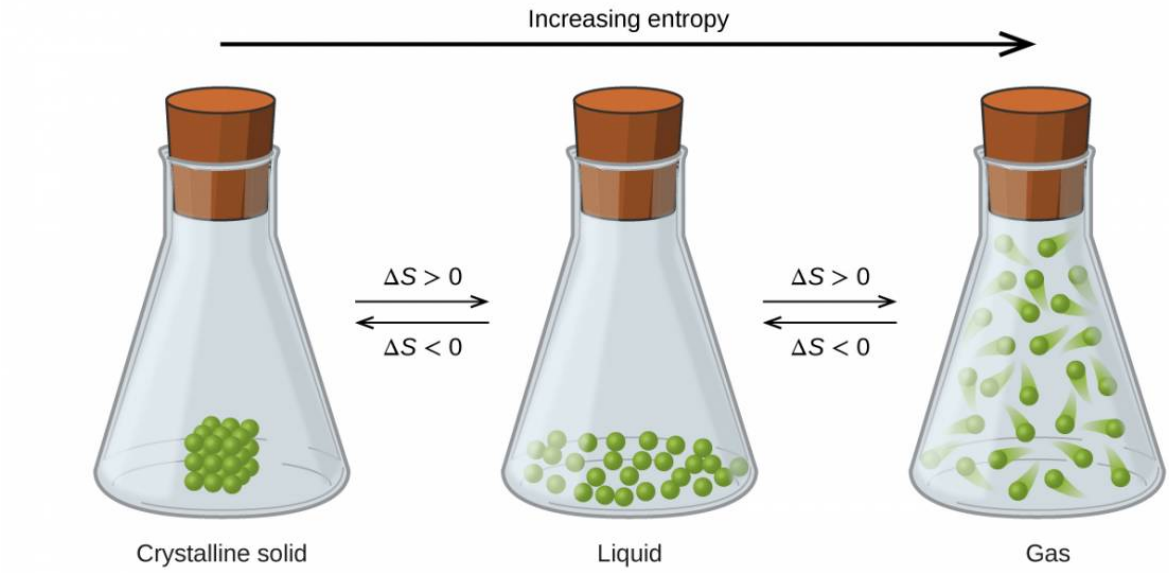
0 J/K

1.2.3 Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 1.9. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

Figure 1.9

The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

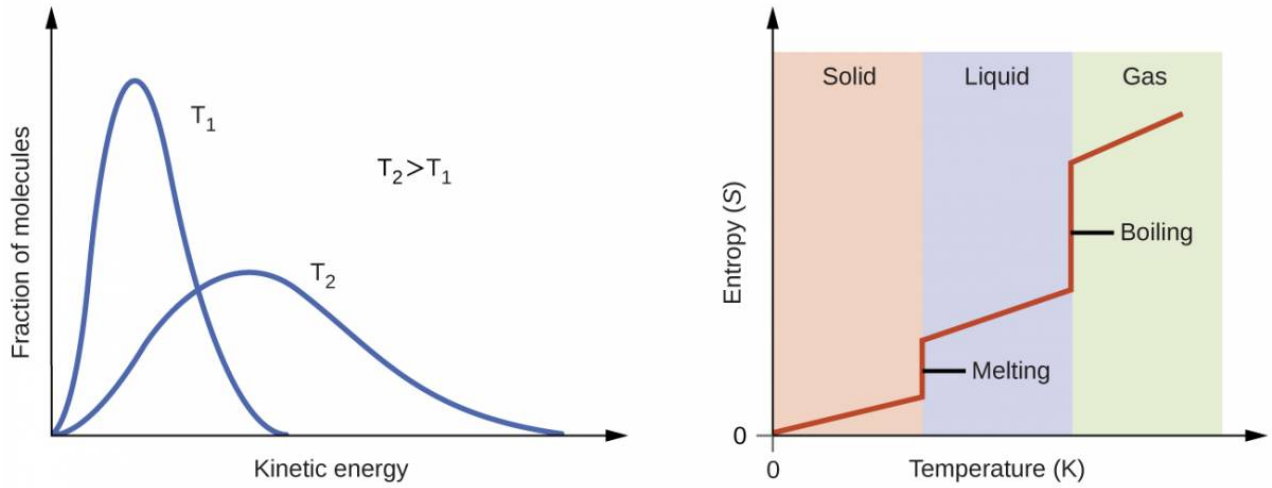


Now consider the gaseous phase in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 1.10).

Figure 1.10

Entropy increases as the temperature of a substance is raised which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition its entropy changes significantly.



LINK TO LEARNING

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example 1.3.

Example 1.2.4

Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.
(a) One mole liquid water at room temperature

$\longrightarrow$

one mole liquid water at 50 °C

(b)

$$\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$$

(c)

$$\mathrm{C_6H_6}(l) + \tfrac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\mathrm{CO_2}(g) + 3\mathrm{H_2O}(l)$$

(d)

$$\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$$

Solution

(a) positive, temperature increases
(b) negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

(c) negative, net decrease in the amount of gaseous species

(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

Check Your Learning

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.
(a)

$$\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$$

(b) the freezing of liquid water

(c)

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$$

(d)

$$\mathrm{CaCO_3}\,(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}\,(g)$$

Answer

(a) Positive; The solid dissolves to give an increase of mobile ions in solution. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There is a net increase in the amount of gaseous species.

1.3 The Second and Third Laws of Thermodynamics

Learning Objectives

By the end of this section, you will be able to:

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

1.3.1 The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

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

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \qquad \text{and} \qquad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

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

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \qquad \text{and} \qquad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

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

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 1.1.

Table 1.11

The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen

molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 1.4.

EXAMPLE 1.3.2

Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.
At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} = -0.7\ \text{J/K}\end{aligned}$$

S_{univ} < 0, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{283.15\ \text{K}} = +0.9\ \text{J/K}\end{aligned}$$

S_{univ} > 0, so melting *is* spontaneous at 10.00 °C.

Check Your Learning

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, so $\Delta S_{\text{freezing}} = -\Delta S_{\text{melting}}$ = −22.1 J/K and q_{surr} = +6.00 kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

1.3.3 The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as

its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies ($S°$) are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The standard entropy change ($\Delta S°$) for a reaction may be computed using standard entropies as shown below:

$$\Delta S° = \sum \nu S°(\text{products}) - \sum \nu S°(\text{reactants})$$

where v represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D},$$

is computed as:

$$= [xS°(\text{C}) + yS°(\text{D})] - [mS°(\text{A}) + nS°(\text{B})]$$

A partial listing of standard entropies is provided in Table 1.2, and additional values are provided in Appendix G. The example exercises that follow demonstrate the use of $S°$ values in calculating standard entropy changes for physical and chemical processes.

Table 1.12

Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	$S°$ **(J mol^{-1} K^{-1})**
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
CO_2(*g*)	213.8
CH_4(*g*)	186.3
C_2H_4(*g*)	219.5
C_2H_6(*g*)	229.5
CH_3OH(*l*)	126.8

Substance	$S°$ (J mol^{-1} K^{-1})
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
$H(g)$	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
$HCl(g)$	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

EXAMPLE 1.3.4

Determination of $\Delta S°$

Calculate the standard entropy change for the following process:

$$\mathrm{H_2O(g) \longrightarrow H_2O(}l\mathrm{)}$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S° = (1\ \mathrm{mol})(70.0\ \mathrm{J\ mol^{-1}\ K^{-1}}) - (1\ \mathrm{mol})(188.8\ \mathrm{J\ mol^{-1}\ K^{-1}}) = -118.8\ \mathrm{J/K}$$

The value for $\Delta S°$ is negative, as expected for this phase transition (condensation), which the previous section discussed.

Check Your Learning

Calculate the standard entropy change for the following process:

$$\mathrm{H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)}$$

Answer

−120.6 J K^{-1} mol^{-1}

Example 1.3.5

Determination of $\Delta S°$

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3\,OH(l) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 4H_2\,O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S° = \sum \nu S°(\text{products}) - \sum \nu S°(\text{reactants})$$

$$[2\text{ mol} \times S°(CO_2\,(g)) + 4\text{ mol} \times S°(H_2\,O(l))] - [2\text{ mol} \times S°(CH_3\,OH(l)) + 3\text{ mol} \times S°(O_2$$
$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1\text{ J/K}$$

Check Your Learning

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2\,(s) \longrightarrow CaO(s) + H_2\,O(l)$$

Answer

24.7 J/K

1.4 Free Energy

Learning Objectives

By the end of this section, you will be able to:

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An

alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the free energy change (ΔG) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 1.3 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 1.13

Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	at equilibrium

1.4.1 What's "Free" about ΔG?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (*w*) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S$$

may be interpreted as representing the difference between the energy produced by the process, Δ*H*, and the energy lost to the surroundings, *T*Δ*S*. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, Δ*G*. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{\text{max}}$$

where

w_{max}

refers to all types of work except expansion (pressure-volume) work.

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., batteries) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done on the system to carry out the process.

1.4.2 Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes, Δ*G*°, according to the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Example 1.4.3

Using Standard Enthalpy and Entropy Changes to Calculate $\Delta G°$

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G° = \Delta H° - T\Delta S°$$

From Appendix G:

Substance	ΔH_f° (kJ/mol)	$S°$ (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\Delta H° = \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l))$$
$$= [-241.82\ \mathrm{kJ/mol} - (-286.83)]\ \mathrm{kJ/mol} = 45.01\ \mathrm{kJ}$$

$$\Delta S° = 1\ \mathrm{mol} \times S°(\mathrm{H_2O}(g)) - 1\ \mathrm{mol} \times S°(\mathrm{H_2O}(l))$$
$$= (1\ \mathrm{mol})188.8\ \mathrm{J/mol\cdot K} - (1\ \mathrm{mol})70.0\ \mathrm{J/mol\ K} = 118.8\ \mathrm{J/mol\cdot K}$$

$$\Delta G° = \Delta H° - T\Delta S°$$

Substitution into the standard free energy equation yields:

$$\Delta G° = \Delta H° - T\Delta S°$$
$$= 45.01\ \mathrm{kJ} - (298\ \mathrm{K} \times 118.8\ \mathrm{J/K}) \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}$$

$$45.01\ \mathrm{kJ} - 35.4\ \mathrm{kJ} = 9.6\ \mathrm{kJ}$$

At 298 K (25 °C)

$$\Delta G° > 0,$$

so boiling is nonspontaneous (*not* spontaneous).

Check Your Learning

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

$$C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)$$

Answer

$$\Delta G° = 102.0 \text{ kJ/mol};$$

the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

The standard free energy change for a reaction may also be calculated from standard free energy of formation $\Delta G°_f$ values of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation,

$$\Delta G_f^\circ$$

is by definition zero for elemental substances in their standard states. The approach used to calculate

$$\Delta G^\circ$$

for a reaction from

$$\Delta G_f^\circ$$

values is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$mA + nB \longrightarrow xC + yD,$$

the standard free energy change at room temperature may be calculated as

$$\begin{aligned}\Delta G° &= \sum \nu \, \Delta G°(\text{products}) - \sum \nu \, \Delta G°(\text{reactants}) \\ &= [x\Delta G_f^\circ(C) + y\Delta G_f^\circ(D)] - [m\Delta G_f^\circ(A) + n\Delta G_f^\circ(B)].\end{aligned}$$

Example 1.4.4

Using Standard Free Energies of Formation to Calculate $\Delta G°$

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\ \text{yellow}) \longrightarrow \mathrm{Hg}(l) + \frac{1}{2}\mathrm{O_2}\,(g)$$

Calculate the standard free energy change at room temperature,

$\Delta G°$,

using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix G and are shown here.

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	$S°$ (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
O_2(*g*)	0	0	205.2

(a) Using free energies of formation:

$$\Delta G° = \sum \nu G_f^\circ\,(\text{products}) - \sum \nu \Delta G_f^\circ\,(\text{reactants})$$

$$= [1\Delta G_f^\circ\,\mathrm{Hg}(l) + \frac{1}{2}\Delta G_f^\circ\,\mathrm{O_2}\,(g)] - 1\Delta G_f^\circ\,\mathrm{HgO}(s,\ \text{yellow})$$

$$= [1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\ \text{mol}(0\ \text{kJ/mol})] - 1\ \text{mol}(-58.43\ \text{kJ/mol}) = 58.43\ \text{kJ/mol}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H° = \sum \nu \Delta H_f^\circ\,(\text{products}) - \sum \nu \Delta H_f^\circ\,(\text{reactants})$$

$$= [1\Delta H_f^\circ\,\mathrm{Hg}(l) + \frac{1}{2}\Delta H_f^\circ\,\mathrm{O_2}\,(g)] - 1\Delta H_f^\circ\,\mathrm{HgO}(s,\ \text{yellow})$$

$$= [1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\ \text{mol}(0\ \text{kJ/mol})] - 1\ \text{mol}(-90.46\ \text{kJ/mol}) = 90.46\ \text{kJ/mol}$$

$$\Delta S^\circ = \sum \nu \Delta S^\circ(\text{products}) - \sum \nu \Delta S^\circ(\text{reactants})$$

$$= [1\Delta S^\circ \text{Hg}(l) + \frac{1}{2}\Delta S^\circ \text{O}_2(g)] - 1\Delta S^\circ \text{HgO}(s, \text{ yellow})$$

$$= [1 \text{ mol}\,(75.9 \text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2 \text{ J/mol K})] - 1 \text{ mol}(71.13 \text{ J/mol K}) = 107.4 \text{ J/mol K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 90.46 \text{ kJ} - 298.15 \text{ K} \times 107.4 \text{ J/K·mol} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta G^\circ = (90.46 - 32.01) \text{ kJ/mol} = 58.45 \text{ kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

Check Your Learning

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix G). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer

(a) 140.8 kJ/mol, nonspontaneous
(b) 141.5 kJ/mol, nonspontaneous

1.4.5 Free Energy Changes for Coupled Reactions

The use of free energies of formation to compute free energy changes for reactions as described above is possible because ΔG is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:

$$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$\begin{array}{ll} \mathrm{H_2\,(g) + \tfrac{1}{2}O_2\,(g) \;\rightarrow\; H_2\,O(g)} & \Delta G^\circ_{\mathrm{f,gas}} \\ \mathrm{H_2\,O(\mathit{l}) \;\rightarrow H_2\,(g) + \tfrac{1}{2}O_2\,(g)} & -\Delta G^\circ_{\mathrm{f,liquid}} \\ \hline \mathrm{H_2\,O(\mathit{l}) \;\rightarrow H_2\,O(g)} & \Delta G = \Delta G^\circ_{\mathrm{f,gas}} - \Delta G^\circ_{\mathrm{f,liquid}} \end{array}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG°:

$$\mathrm{ZnS}(\mathit{s}) \rightarrow \mathrm{Zn}(\mathit{s}) + \mathrm{S}(\mathit{s}) \qquad \Delta G^\circ_1 = 201.3\ \mathrm{kJ}$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$\mathrm{S}(\mathit{s}) + \mathrm{O_2\,(g)} \rightarrow \mathrm{SO_2\,(g)} \qquad \Delta G^\circ_2 = -300.1\ \mathrm{kJ}$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$\mathrm{ZnS}(\mathit{s}) + \mathrm{O_2\,(g)} \rightarrow \mathrm{Zn}(\mathit{s}) + \mathrm{SO(g)} \qquad \Delta G^\circ = 201.3\ \mathrm{kJ} + -300.1\ \mathrm{kJ} = -98.8\ \mathrm{kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate. The gist of the calculation, however, holds true.

Example 1.4.6

Calculating Free Energy Change for a Coupled Reaction

Is a reaction coupling the decomposition of ZnS to the formation of H_2S expected to be spontaneous under standard conditions?

Solution

Following the approach outlined above and using free energy values from Appendix G:

Decomposition of zinc sulfide:	$\mathrm{Zn}(s) \rightarrow \mathrm{Zn}(s) + \mathrm{S}(s)$	$\Delta G_1^\circ = 201$
Formation of hydrogen sulfide:	$\mathrm{S}(s) + \mathrm{H_2}\,(g) \rightarrow \mathrm{H_2\,S}(g)$	$\Delta G_2^\circ = -33$
Coupled reaction:	$\mathrm{ZnS}(s) + \mathrm{H_2}\,(g) \rightarrow \mathrm{Zn}(s) + \mathrm{H_2\,S}(g)$	$\Delta G° = 201.3\ \mathrm{kJ} + -33$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Check Your Learning

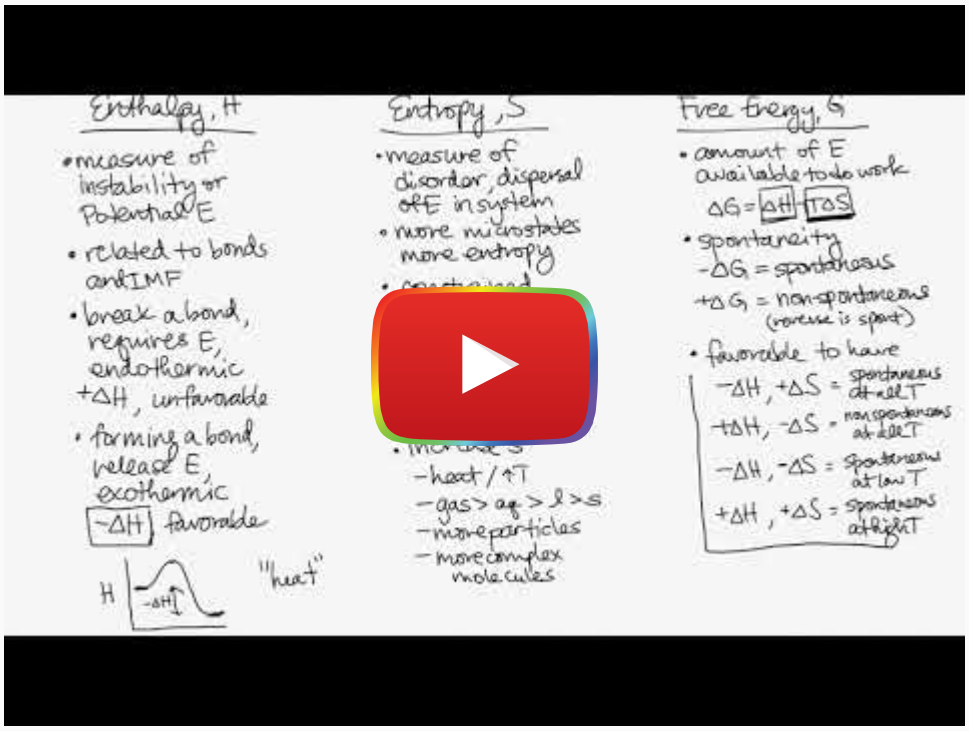
What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$$\mathrm{FeS}(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{Fe}(s) + \mathrm{SO_2}\,(g)$$

Answer

−199.7 kJ; spontaneous

Summary of Enthalpy, Entropy, and Free Energy



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1.5 Equilibrium

Learning Objectives

By the end of this section, you will be able to:

- Explain how temperature affects the spontaneity of some processes

Temperature Dependence of Spontaneity

As was previously demonstrated in the section on entropy in an earlier chapter, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH. If the $T\Delta S$ term is less than ΔH, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*
2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH. If the $T\Delta S$ term's magnitude is greater than ΔH, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*
3. **ΔH is positive and ΔS is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*
4. **ΔH is negative and ΔS is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in Figure 1.11.

Figure 1.14

There are four possibilities regarding the signs of enthalpy and entropy changes.

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

EXAMPLE 1.5.1

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\mathrm{C}(s) + \mathrm{O}_2\,(g) \longrightarrow 2\mathrm{CO}(g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\mathrm{Fe}(s) + 3\mathrm{O}_2\,(g) \longrightarrow 2\mathrm{Fe}_2\,\mathrm{O}_3\,(s)$$

How does the spontaneity of this process depend upon temperature?

Answer

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

$$\Delta G = \Delta H - T\Delta S$$

$$y = b + mx$$

Such a plot is shown in Figure 1.12. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero:

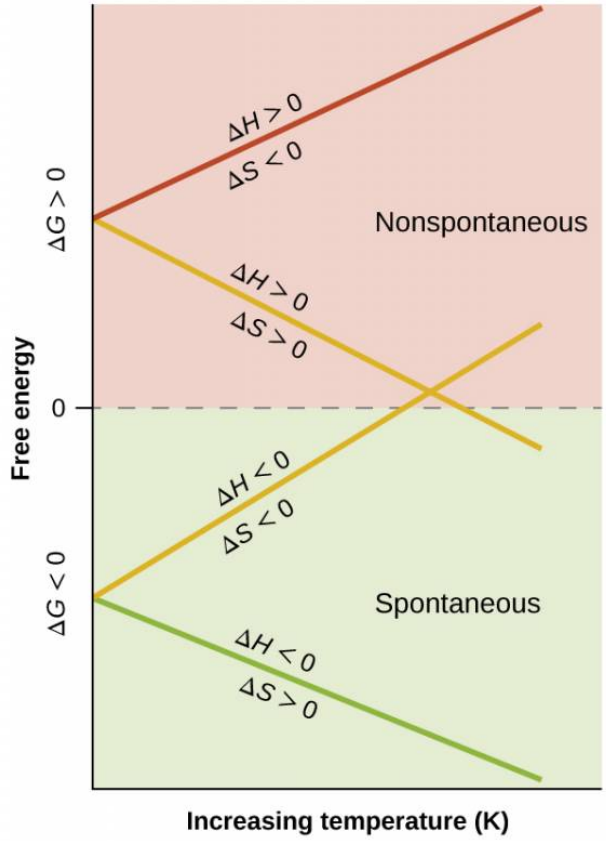
$$\Delta G = 0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, the condition of ΔG = 0 describes a system at equilibrium.

Figure 1.15

These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS.



Supplemental Activities

Supplemental activities will be added here...

Files

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Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (12.1-12.4, 13.4)

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2

Solutions

Laws Moles Pressure

Solutions are homogeneous mixtures. Many solutions contain one component called the solvent in which other components called solutes are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution. Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

Learning Objectives

By the end of this section, you will be able to:

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

Preceding sections of this chapter focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see Figure 2.1). This section will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

Figure 2.1

Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

2.1 Solutions

Solutions have previously been defined as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. A more thorough treatment of solution properties is provided in the chapter on solutions and colloids, but provided here is an introduction to some of the basic properties of solutions.

The relative amount of a given solution component is known as its concentration. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the solvent and may be viewed as the medium in which the other components are dispersed, or dissolved. Solutions in which water is the solvent are, of course very common on our planet. A solution in which water is the solvent is called an aqueous solution.

A solute is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as dilute (of relatively low concentration) and concentrated (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. Molarity (*M*) is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

EXAMPLE 2.1.1

Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} = 0.375\ M$$

Check Your Learning

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer

0.05 M

EXAMPLE 2.1.2

Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 2.1?

Solution

Rearrange the definition of molarity to isolate the quantity sought, moles of sugar, then substitute the value for molarity derived in Example 2.1, 0.375 *M*:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 0.375 \frac{\text{mol sugar}}{\text{L}} \times \left(10 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}\right) = 0.004 \text{ mol sugar}$$

Check Your Learning

What volume (mL) of the sweetened tea described in Example 2.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

EXAMPLE 2.1.3

Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 2.2) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?

Figure 2.2

Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. Since the mass of solute is provided instead of its molar amount, use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\ \text{g}\ CH_3CO_2H \times \frac{1\ \text{mol}\ CH_3CO_2H}{60.052\ \text{g}\ CH_3CO_2H}}{0.500\ \text{L solution}} = 0.839\ M$$

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M$$

$$M = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}}$$

Check Your Learning

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 *M*

EXAMPLE 2.1.4

Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 2.2:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

$$\text{mol solute} = M \times \text{L solution}$$

$$\text{mol solute} = 5.30 \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\ \text{mol NaCl} \times \frac{58.44\ \text{g NaCl}}{\text{mol NaCl}} = 77.4\ \text{g NaCl}$$

Check Your Learning

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-*M* solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in Example 2.4, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 2.4, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If the guard digit had not been retained, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, rounding errors may also be avoided by performing computations in a single step (see Example 2.5). This eliminates intermediate steps so that only the final result is rounded.

EXAMPLE 2.1.5

Determining the Volume of Solution Containing a Given Mass of Solute

In Example 2.3, the concentration of acetic acid in white vinegar was determined to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution}$$

$$75.6\ \text{g}\ \text{CH}_3\text{CO}_2\text{H}\left(\frac{\text{mol}\ \text{CH}_3\text{CO}_2\text{H}}{60.05\ \text{g}}\right)\left(\frac{\text{L solution}}{0.839\ \text{mol}\ \text{CH}_3\text{CO}_2\text{H}}\right) = 1.50\ \text{L solution}$$

Check Your Learning

What volume of a 1.50-*M* KBr solution contains 66.0 g KBr?

Answer

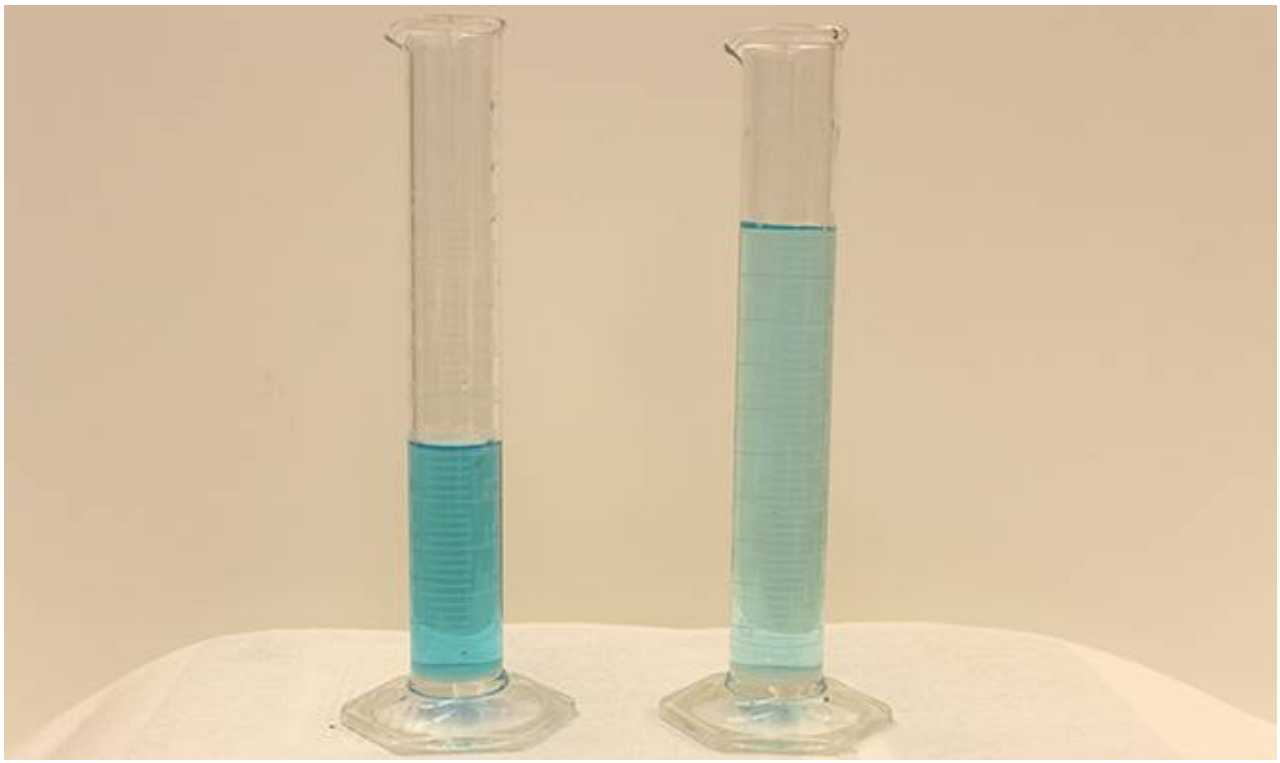
0.370 L

2.2 Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 2.3).

Figure 2.3

Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)



Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, a solution of lesser concentration may be prepared. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents.

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the number of moles of solute in a solution (n) is equal to the product of the solution's molarity (M) and its volume in liters (L):

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1$$

$$n_2 = M_2 L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution,* $n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1 L_1 = M_2 L_2$$

This relation is commonly referred to as the dilution equation. Although this equation uses molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used as long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1 V_1 = C_2 V_2$$

where C and V are concentration and volume, respectively.

LINK TO LEARNING

Use the simulation to explore the relations between solute amount, solution volume, and concentration and to confirm the dilution equation.

EXAMPLE 2.2.1

Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

The stock concentration, C_1, and volume, V_1, are provided as well as the volume of the diluted solution, V_2. Rearrange the dilution equation to isolate the unknown property, the concentration of the diluted solution, C_2:

$$C_1 V_1 = C_2 V_2$$

$$C_2 = \frac{C_1 V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), the diluted solution's concentration is expected to be less than one-half 5 *M*. This ballpark estimate will be compared to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850\ \text{L} \times 5.00\ \frac{\text{mol}}{\text{L}}}{1.80\ \text{L}} = 2.36\ M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 *M*).

Check Your Learning

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-*M* solution of CH_3OH to 500.0 mL?

Answer

0.102 *M* CH_3OH

EXAMPLE 2.2.2

Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

Provided are the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. Find the volume of the diluted solution, V_2 by rearranging the dilution equation to isolate V_2:

$$C_1 V_1 = C_2 V_2$$

$$V_2 = \frac{C_1 V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), the volume of the diluted solution is expected to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\ M)(0.011\ \text{L})}{(0.12\ M)}$$

$$V_2 = 0.041\ \text{L}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with the rough estimate.

Check Your Learning

A laboratory experiment calls for 0.125 *M* HNO_3. What volume of 0.125 *M* HNO_3 can be prepared from 0.250 L of 1.88 *M* HNO_3?

Answer

3.76 L

EXAMPLE 2.2.3

Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

Given are the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. Find the volume of the stock solution, V_1 by rearranging the dilution equation to isolate V_1:

$$C_1 V_1 = C_2 V_2$$
$$V_1 = \frac{C_2 V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), the volume of the stock solution is expected to be about one-sixteenth that of the diluted solution or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M}$$
$$V_1 = 0.314\ \text{L}$$

Thus, 0.314 L of the 1.59-*M* solution is needed to prepare the desired solution. This result is consistent with the rough estimate.

Check Your Learning

What volume of a 0.575-*M* solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

Answer

0.261 L

Learning Objectives

By the end of this section, you will be able to:

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units

The previous section introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. This section will describe some other units of concentration

that are commonly used in various applications, either for convenience or by convention.

2.3 Mass Percentage

Earlier in this chapter, percent composition was introduced as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\%$$

Mass percentage is also referred to by similar names such as *percent mass, percent weight, weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 2.4) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.

Figure 2.4

Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

EXAMPLE 2.3.1

Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

$$\%\ \text{glucose} = \frac{3.75\ \text{mg glucose} \times \frac{1\ \text{g}}{1000\ \text{mg}}}{5.0\ \text{g spinal fluid}} = 0.075\%$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, the solute mass unit in the numerator was converted from mg to g to match the units in the denominator. Alternatively, the spinal fluid mass unit in the denominator could have been converted from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

Check Your Learning

A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?

Answer

14.8%

EXAMPLE 2.3.2

Calculations using Mass Percentage

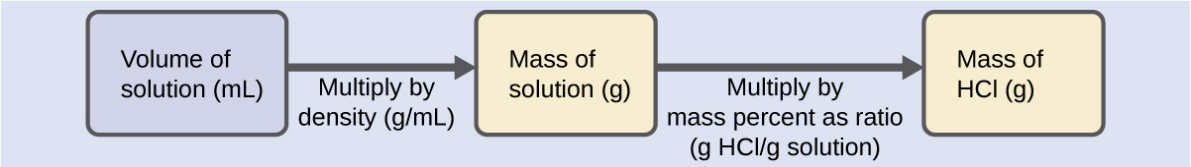
"Concentrated" hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or 5

×

40 = 200 g. In order to derive the mass of solute in a solution from its mass percentage, the mass of the solution must be known. Using the solution density given, convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

$$500 \text{ mL solution} \left(\frac{1.19 \text{ g solution}}{\text{mL solution}}\right)\left(\frac{37.2 \text{ g HCl}}{100 \text{ g solution}}\right) = 221 \text{ g HCl}$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

Check Your Learning

What volume of concentrated HCl solution contains 125 g of HCl?

Answer

282 mL

2.4 Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a volume percentage, %vol or (v/v)%:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

EXAMPLE 2.4.1

Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$(355 \text{ mL solution}) \left(\frac{70 \text{ mL isopropyl alcohol}}{100 \text{ mL solution}}\right) \left(\frac{0.785 \text{ g isopropyl alcohol}}{1 \text{ mL isopropyl alcohol}}\right) = 195 \text{ g isopropyl alchol}$$

Check Your Learning

Wine is approximately 12% ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

Answer

1.5 mol ethanol

2.5 Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A mass-volume percent is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 2.5).

Figure 2.5

“Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly)

(a)

(b)

2.6 Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as parts per million (ppm) or parts per billion (ppb). Like percentage ("part per hundred") units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

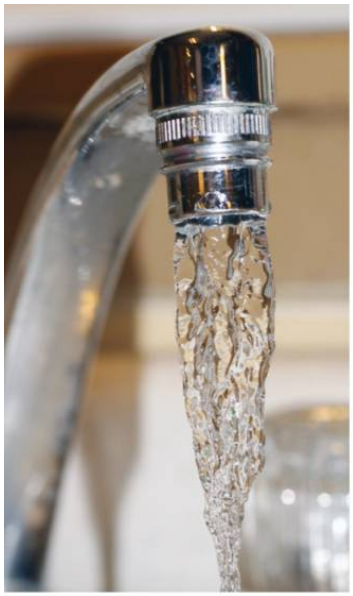
The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm}$$
$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 2.6).

Figure 2.6

(a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons)



(a)

(b)

EXAMPLE 2.6.1

Calculation of Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15 \text{ ppb} \times \frac{1 \text{ ppm}}{10^3 \text{ ppb}} = 0.015 \text{ ppm}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. Since the volume of solution (300 mL) is given, its density must be used to derive the corresponding mass. Assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \frac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g}$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \text{ μg}}{10^{-6} \text{ g}} = 4.5 \text{ μg}$$

Check Your Learning

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Answer

9.6 ppm, 9600 ppb

2.7 Electrolytes

Learning Objectives

By the end of this section, you will be able to:

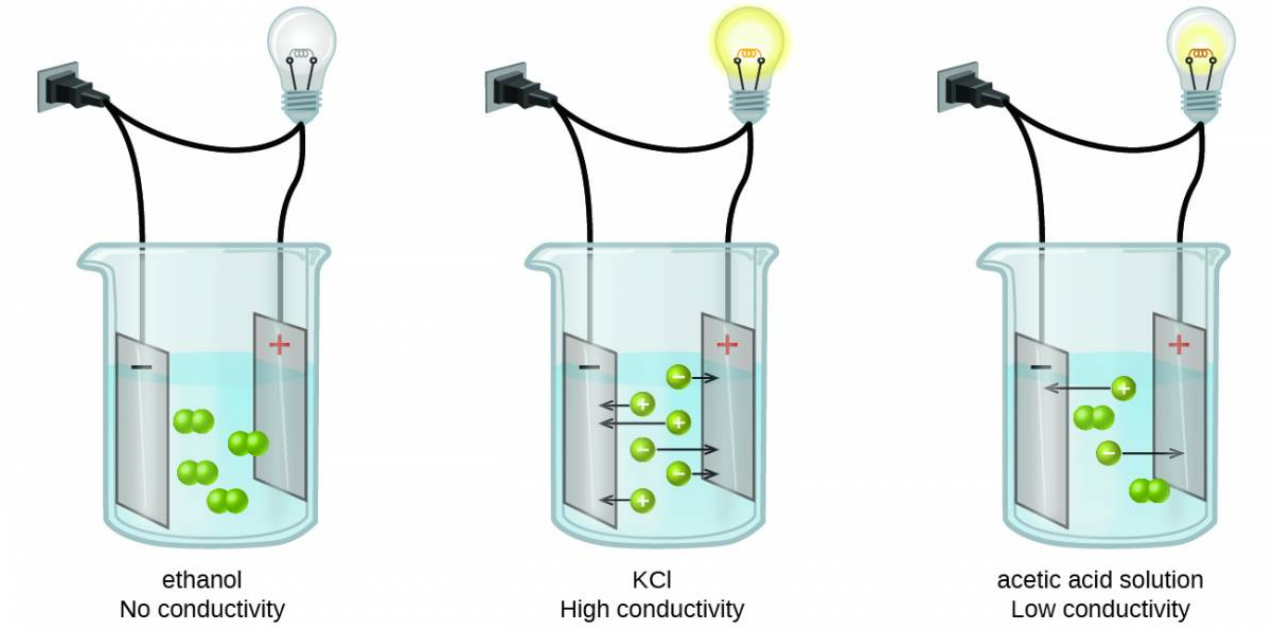
- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called nonelectrolytes. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 2.7).

Figure 2.7

Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

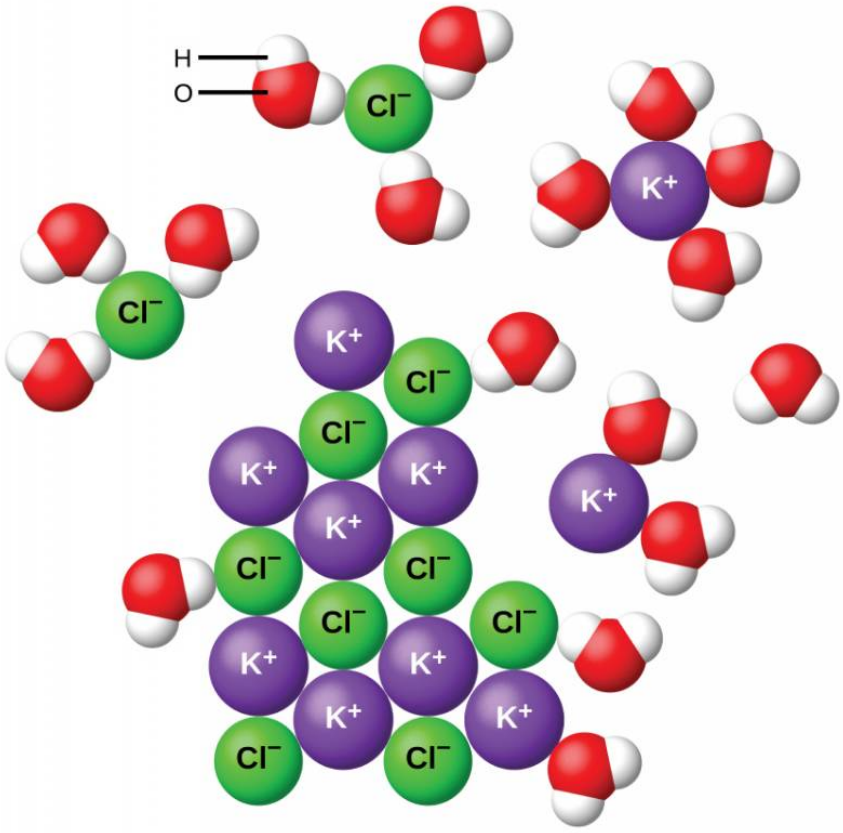


2.8 Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 2.8. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

Figure 2.8

As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.



When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes. Even sparingly, soluble ionic compounds are strong electrolytes, since the small amount that does dissolve will dissociate completely.

Consider what happens at the microscopic level when solid KCl is added to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules surround individual K^+ and Cl^- ions, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure 2.8 shows. Overcoming the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution as the ions transition from fixed positions in the undissolved compound to widely dispersed, solvated ions in solution.

2.9 Covalent Electrolytes

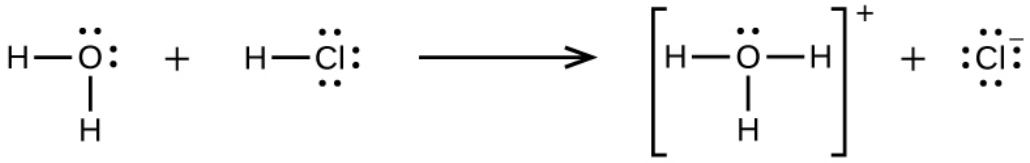
Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton (H^+ ion) to another molecule of water, yielding hydronium and hydroxide ions.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

In some cases, solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl

molecules. This gas contains no ions. However, an aqueous solution of HCl is a very good conductor, indicating that an appreciable concentration of ions exists within the solution.

Because HCl is an *acid*, its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

Files

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Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (6.3-6.4, 11.2)

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3

Osmotic Pressure

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as a substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law. Properties of a solution that depend only on the concentration of solute particles are called colligative properties. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

3.1 Solubility

Learning Objectives

By the end of this section, you will be able to:

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

3.1.1 Solutions of Gases in Liquids

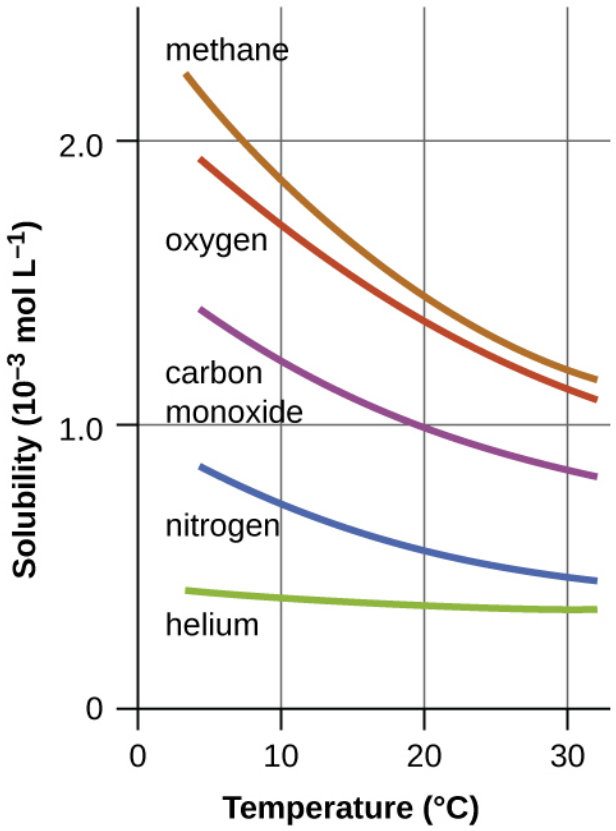
As for any solution, the solubility of a gas in a liquid is affected by the intermolecular attractive forces between solute and solvent species. Unlike solid and liquid solutes, however, there is no solute-solute intermolecular attraction to overcome when a gaseous solute dissolves in a liquid solvent (see Figure 11.4) since the atoms or molecules comprising a gas are far separated and experience negligible interactions. Consequently, solute-solvent interactions are

the sole energetic factor affecting solubility. For example, the water solubility of oxygen is approximately three times greater than that of helium (there are greater dispersion forces between water and the larger oxygen molecules) but 100 times less than the solubility of chloromethane, $CHCl_3$ (polar chloromethane molecules experience dipole–dipole attraction to polar water molecules). Likewise note the solubility of oxygen in hexane, C_6H_{14}, is approximately 20 times greater than it is in water because greater dispersion forces exist between oxygen and the larger hexane molecules.

Temperature is another factor affecting solubility, with gas solubility typically decreasing as temperature increases (Figure 3.1). This inverse relation between temperature and dissolved gas concentration is responsible for one of the major impacts of thermal pollution in natural waters.

Figure 3.1

The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.



When the temperature of a river, lake, or stream is raised, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure 3.2).

Figure 3.2

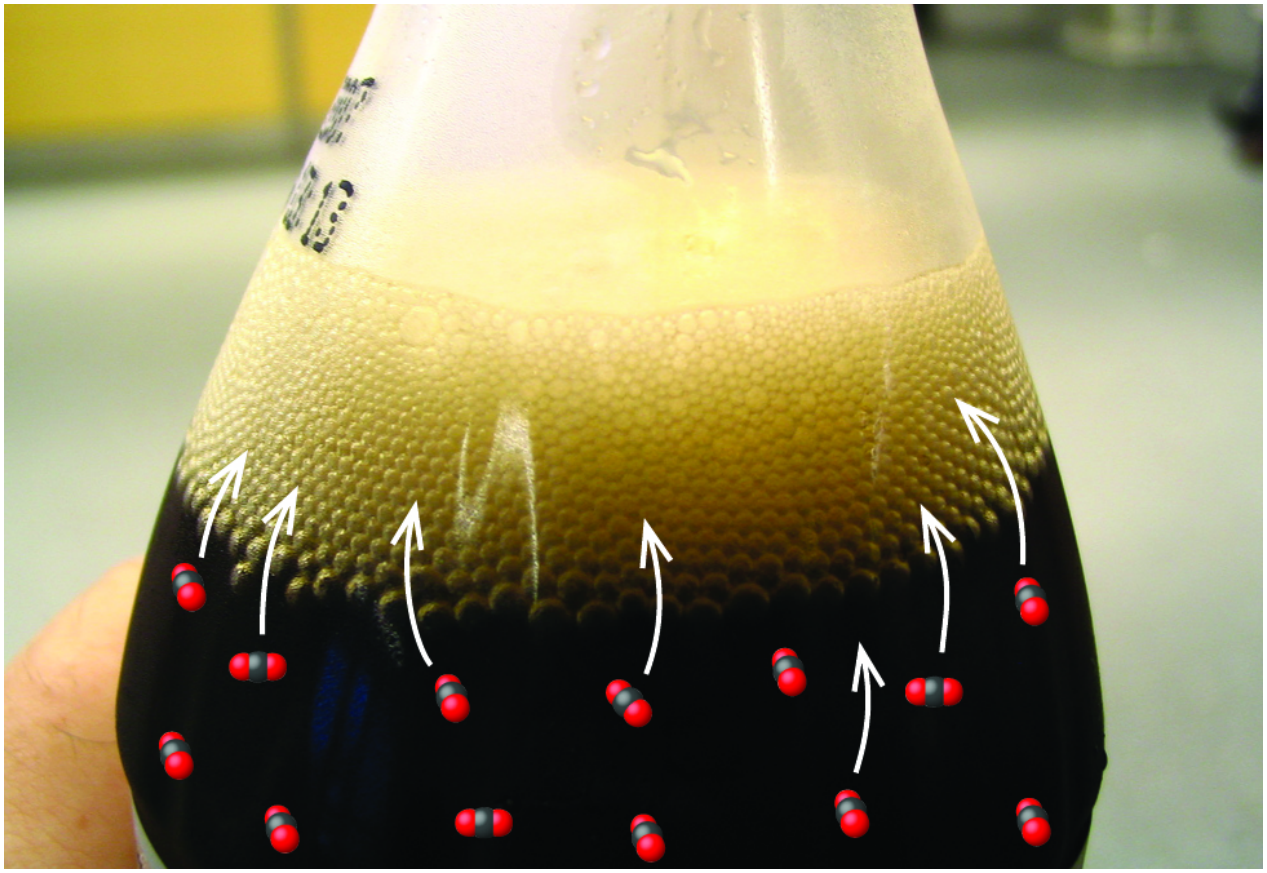
(a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

(a) (b)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 3.3). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”

Figure 3.3

Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)



For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identity of the gaseous solute, the identity of the solvent, and the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

EXAMPLE 3.1.2

Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa, the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa in this case). Because both C_g and P_g are known, this relation can be rearranged and used to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \end{aligned}$$

Now, use k to find the solubility at the lower pressure.

$$\begin{aligned} C_g &= kP_g \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Check Your Learning

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 152 torr resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 760 torr.

Answer

7.25

\(\times \)

10^{-3} in 100.0 mL or 0.0725 g/L

EXAMPLE 3.1.3

Thermal Pollution and Oxygen Solubility

A certain species of freshwater trout requires a dissolved oxygen concentration of 7.5 mg/L. Could these fish thrive in a thermally polluted mountain stream (water temperature is 30.0 °C, partial pressure of atmospheric oxygen is 0.17 atm)? Use the data in Figure 3.1 to estimate a value for the Henry's law constant at this temperature.

Solution

First, estimate the Henry's law constant for oxygen in water at the specified temperature of 30.0 °C (Figure 3.1 indicates the solubility at this temperature is approximately ~1.2 mol/L).

$$k = \frac{C_g}{P_g} = 1.2 \times 10^{-3} \text{ mol/L}/1.00 \text{ atm} = 1.2 \times 10^{-3} \text{ mol/L atm}$$

Then, use this *k* value to compute the oxygen solubility at the specified oxygen partial pressure, 0.17 atm.

$$C_g = kP_g = (1.2 \times 10^{-3} \text{ mol/L atm})(0.17 \text{ atm}) = 2.0 \times 10^{-4} \text{ mol/L}$$

Finally, convert this dissolved oxygen concentration from mol/L to mg/L.

$$(2.0 \times 10^{-4} \text{ mol/L})(32.0 \text{ g/1 mol})(1000 \text{ mg/g}) = 6.4 \text{ mg/L}.$$

This concentration is lesser than the required minimum value of 7.5 mg/L, and so these trout would likely not thrive in the polluted stream.

Check Your Learning

What dissolved oxygen concentration is expected for the stream above when it returns to a normal summer time temperature of 15 °C?

Answer

8.2 mg/L

3.1.4 CHEMISTRY IN EVERYDAY LIFE

Decompression Sickness or “The Bends”

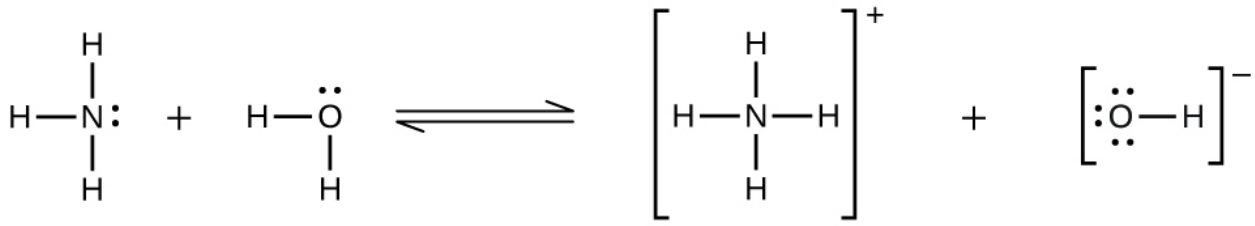
Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver’s blood are proportionally higher per Henry’s law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver’s blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 3.4). Researchers are also investigating related body reactions and defenses in order to develop better testing and treatment for decompression sicknetss. For example, Ingrid Eftedal, a barophysiologist specializing in bodily reactions to diving, has shown that white blood cells undergo chemical and genetic changes as a result of the condition; these can potentially be used to create biomarker tests and other methods to manage decompression sickness.

Figure 3.4

(a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Deviations from Henry’s law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water increases more rapidly with increasing pressure than predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas almost certainly carbon dioxide bubbled from Lake Nyos (Figure 3.5) a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released and the colorless gas which is denser than air flowed down the valley below the lake and suffocated humans and animals living in the valley.

Figure 3.5

(a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

(a) (b)

3.1.5 Solutions of Liquids in Liquids

Some liquids may be mixed in any proportions to yield solutions; in other words, they have infinite mutual solubility and are said to be miscible. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure 3.6) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline, mixtures of which are used as lubricating fuels for various types of outdoor power equipment (chainsaws, leaf blowers, and so on).

Figure 3.6

Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: "dno1967"/Wikimedia commons)

Miscible liquids are typically those with very similar polarities. Consider for example, liquids that are polar or capable of hydrogen bonding. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is again an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called immiscible. Separate layers are formed when immiscible liquids are poured into the same container. Gasoline, oil (Figure 3.7), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. Relatively weak attractive forces between the polar water molecules and the nonpolar liquid molecules are not adequate to overcome much stronger hydrogen bonding between water molecules. The distinction between immiscibility and miscibility is really one of extent, so that miscible liquids are of infinite mutual solubility while liquids said to be immiscible are of very low (though not zero) mutual solubility.

Figure 3.7

Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Two liquids such as bromine and water that are of *moderate* mutual solubility are said to be partially miscible. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (Figure 3.8).

Figure 3.8

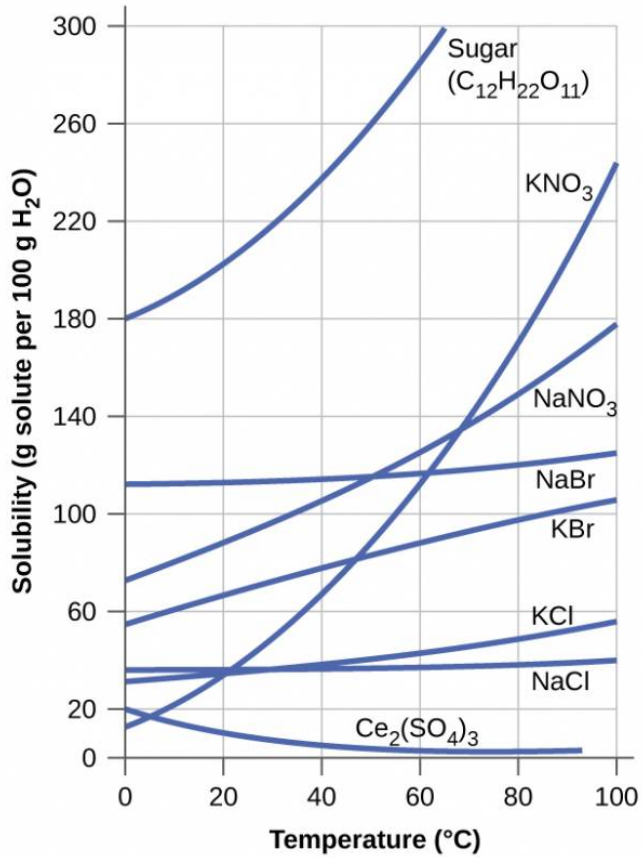
Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

3.1.6 Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of solids in water is shown by the solubility curves in Figure 3.9. Reviewing these data indicates a general trend of increasing solubility with temperature, although there are exceptions as illustrated by the ionic compound cerium sulfate.

Figure 3.9

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



The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers such as the one pictured in Figure 3.10 take advantage of this behavior.

Figure 3.10

This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is "clicked." (credit: modification of work by "Velela"/Wikimedia Commons)

LINK TO LEARNING

This video shows the crystallization process occurring in a hand warmer.

3.2 Colligative Properties

Learning Objectives

By the end of this section, you will be able to:

- Express concentrations of solution components using mole fraction and molality.
- Describe the effect of solute concentration on various solution properties.
- Explain the process of osmosis and describe how it is applied industrially and in nature.

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties however, that depend *only* upon the total concentration of solute species regardless of their identities. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications as will be described in this module.

3.2.1 Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (*M*) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, *X*, of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$X_{\text{A}} = \frac{\text{mol A}}{\text{total mol of all components}}$$

By this definition, the sum of mole fractions for all solution components (the solvent and all solutes) is equal to one.

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and thus, are better suited for applications requiring temperature-independent concentrations including several colligative properties, as will be described in this chapter module.

EXAMPLE 3.2.2

Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from 2.22

\(\times \)

10^3 g of ethylene glycol and 2.00

\(\times \)

10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the definition of mole fraction.

$$\text{mol } C_2H_4(OH)_2 = 2.22 \times 10^3 \text{ g} \times \frac{1 \text{ mol } C_2H_4(OH)_2}{62.07 \text{ g } C_2H_4(OH)_2} = 35.8 \text{ mol } C_2H_4(OH)_2$$

$$\text{mol } H_2O = 2.00 \times 10^3 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 111 \text{ mol } H_2O$$

$$X_{\text{ethylene glycol}} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{(35.8 + 111) \text{ mol total}} = 0.244$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) Derive moles of solute and mass of solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2.22 \times 10^3 \text{ g } C_2H_4(OH)_2 \left(\frac{\text{mol } C_2H_2(OH)_2}{62.07 \text{ g}}\right) = 35.8 \text{ mol } C_2H_4(OH)_2$$

Then, convert the mass of the water from grams to kilograms:

$$2.00 \times 10^3 \text{ g } H_2O \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 2.00 \text{ kg } H_2O$$

Finally, calculate molality per its definition:

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

$$\text{molality} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{2 \text{ kg } H_2O}$$

$$\text{molality} = 17.9 \, m$$

Check Your Learning

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Answer

7.14

\(\times \)

10^{-3}; 0.399 *m*

EXAMPLE 3.2.3

Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0\ \text{mol NaCl}}{1\ \text{kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0\ \text{kg H}_2\text{O}\left(\frac{1000\ \text{g}}{1\ \text{kg}}\right)\left(\frac{\text{mol H}_2\text{O}}{18.02\ \text{g}}\right) = 55\ \text{mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

$$\begin{aligned} X_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\ X_{\text{H}_2\text{O}} &= \frac{55\ \text{mol H}_2\text{O}}{3.0\ \text{mol NaCl} + 55\ \text{mol H}_2\text{O}} \\ X_{\text{H}_2\text{O}} &= 0.95 \\ X_{\text{NaCl}} &= \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\ X_{\text{NaCl}} &= \frac{3.0\ \text{mol NaCl}}{3.0\ \text{mol NaCl} + 55\ \text{mol H}_2\text{O}} \\ X_{\text{NaCl}} &= 0.052 \end{aligned}$$

Check Your Learning

The mole fraction of iodine, I_2, dissolved in dichloromethane, CH_2Cl_2, is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Answer

1.50 *m*

EXAMPLE 3.2.4

Molality and Molarity Conversions

Intravenous infusion of a 0.556 *M* aqueous solution of glucose (density of 1.04 g/mL) is part of some post-operative recovery therapies. What is the molal concentration of glucose in this solution?

Solution

The provided molal concentration may be explicitly written as:

$$M = 0.556 \text{ mol glucose/1 L solution}$$

Consider the definition of molality:

$$m = \text{mol solute/kg solvent}$$

The amount of glucose in 1-L of this solution is 0.556 mol, so the mass of water in this volume of solution is needed.

First, compute the mass of 1.00 L of the solution:

$$(1.0 \text{ L soln})\,(1.04 \text{ g/mL})\,(1000 \text{ mL/1L})\,(1 \text{ kg/1000 g}) = 1.04 \text{ kg soln}$$

This is the mass of both the water and its solute, glucose, and so the mass of glucose must be subtracted. Compute the mass of glucose from its molar amount:

$$(0.556 \text{ mol glucose})\,(180.2 \text{ g/1 mol}) = 100.2 \text{ g or } 0.1002 \text{ kg}$$

Subtracting the mass of glucose yields the mass of water in the solution:

$$1.04 \text{ kg solution} - 0.1002 \text{ kg glucose} = 0.94 \text{ kg water}$$

Finally, the molality of glucose in this solution is computed as:

$$m = 0.556 \text{ mol glucose/0.94 kg water} = 0.59 \text{ m}$$

Check Your Learning

Nitric acid, $HNO_3(aq)$, is commercially available as a 33.7 m aqueous solution (density = 1.35 g/mL). What is the molarity of this solution?

Answer

14.6 M

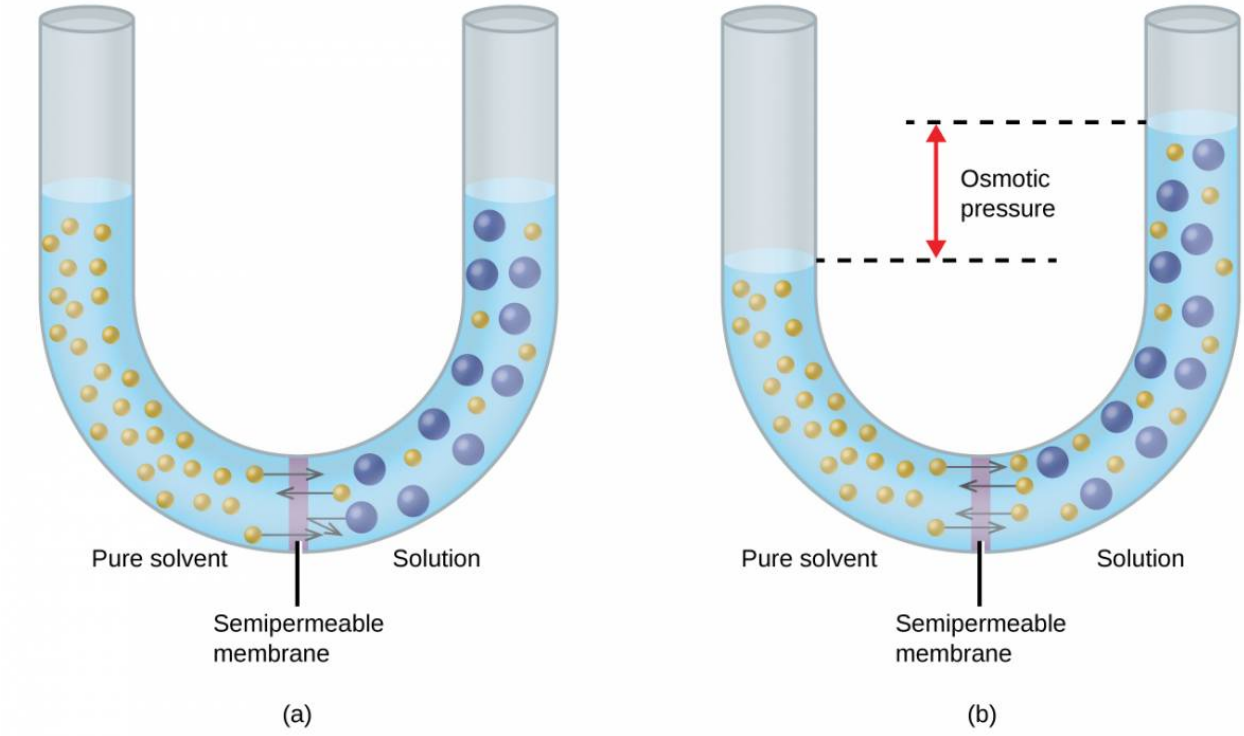
3.2.5 Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as semipermeable membranes.

Consider the apparatus illustrated in Figure 3.11, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis.

Figure 3.11

(a) A solution and pure solvent are initially separated by an osmotic membrane. (b) Net transfer of solvent molecules to the solution occurs until its osmotic pressure yields equal rates of transfer in both directions.



When osmosis is carried out in an apparatus like that shown in Figure 3.11, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic

pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the osmotic pressure (Π) of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M, and absolute temperature, T, according to the equation

$$\Pi = MRT$$

where R is the universal gas constant.

EXAMPLE 3.2.6

Calculation of Osmotic Pressure

Assuming ideal solution behavior, what is the osmotic pressure (atm) of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

Find the osmotic pressure, Π, using the formula $\Pi = MRT$, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

$$\begin{aligned} \Pi &= MRT \\ &= 0.30\ \text{mol/L} \times 0.08206\ \text{L atm/mol K} \times 310\ \text{K} \\ &= 7.6\ \text{atm} \end{aligned}$$

Check Your Learning

Assuming ideal solution behavior, what is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH, in water at 37 °C?

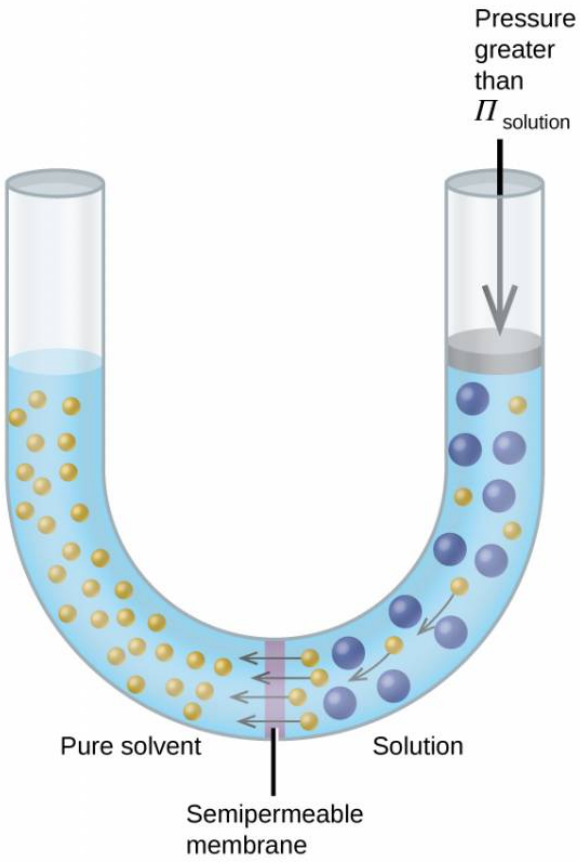
Answer

5.3 atm

If a solution is placed in an apparatus like the one shown in Figure 3.12, applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.

Figure 3.12

Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.


Pressure greater than $\Pi_{solution}$
Pure solvent
Solution
Semipermeable membrane

3.2.7 CHEMISTRY IN EVERYDAY LIFE

Reverse Osmosis Water Purification

In the process of osmosis, diffusion serves to move water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. Osmotic pressure is the amount of pressure that must be applied to the more concentrated solution to cause osmosis to stop. If greater pressure is applied, the water will go from the more concentrated solution to a less concentrated (more pure) solution. This is called reverse osmosis. Reverse osmosis (RO) is used to purify water in many applications, from desalination plants in coastal cities, to water-purifying machines in grocery stores (Figure 3.13), and smaller reverse-osmosis household units. With a hand-operated pump, small RO units can be used in third-world countries, disaster areas, and in lifeboats. Our military forces have a variety of generator-operated RO units that can be transported in vehicles to remote locations.

Figure 3.13

Reverse osmosis systems for purifying drinking water are shown here on (a) small and (b) large scales. (credit a: modification of work by Jerry Kirkhart; credit b: modification of work by Willard J. Lathrop)

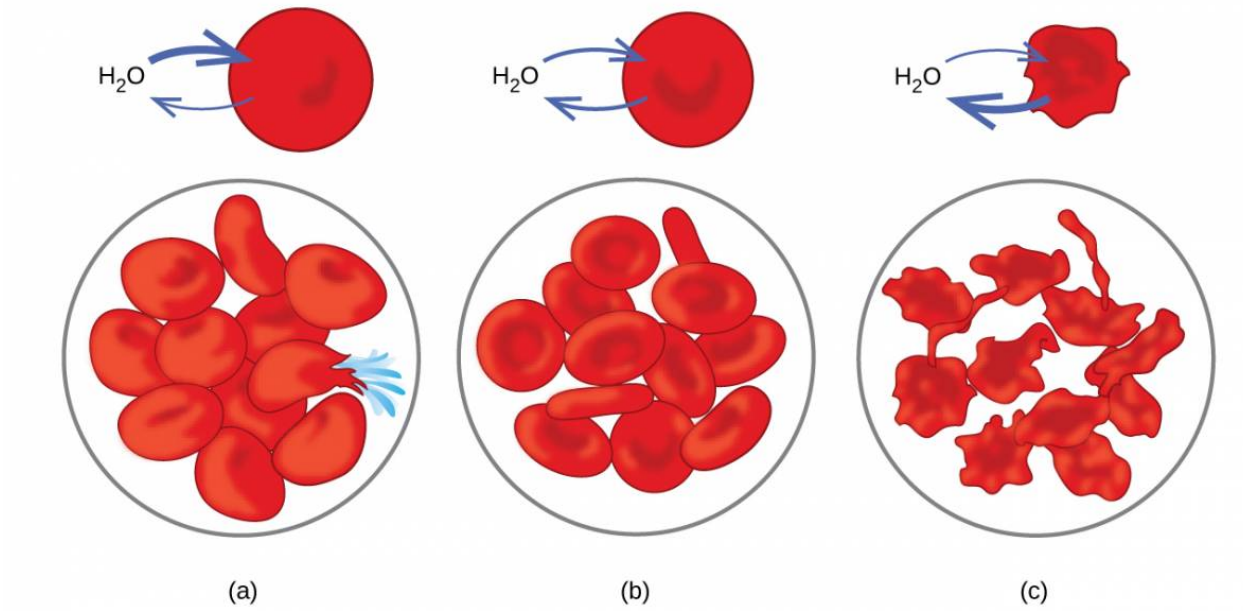
(a)

(b)

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a less concentrated solution, a hypotonic solution is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called hemolysis. When a more concentrated solution, a hypertonic solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called crenation. These effects are illustrated in Figure 3.14.

Figure 3.14

Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by "LadyofHats"/Wikimedia commons)



3.2.8 Determination of Molar Masses

Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the number of solute species present in a given amount of solution. Consequently, measuring one of these properties for a solution prepared using a known mass of solute permits determination of the solute's molar mass.

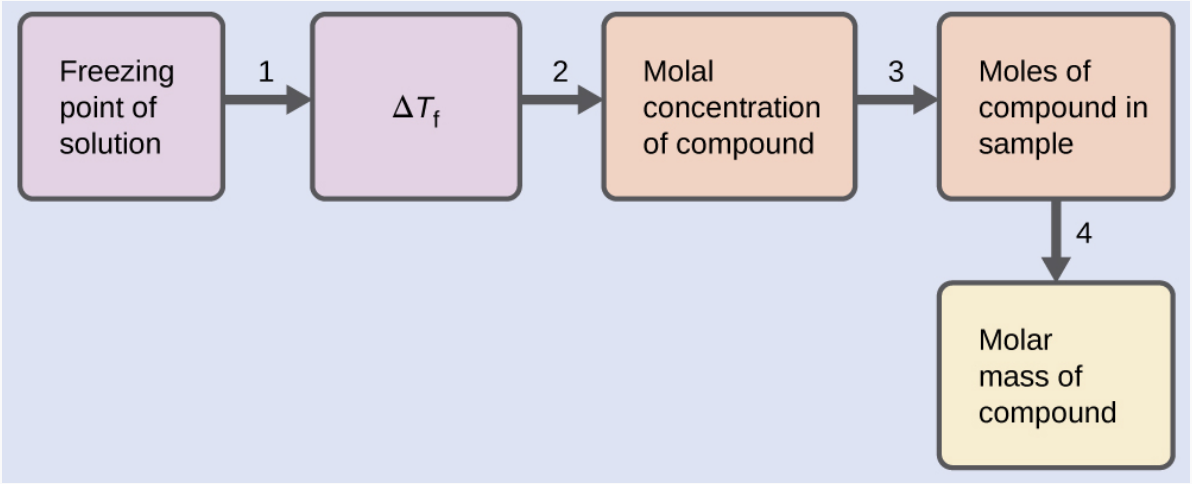
EXAMPLE 3.2.9

Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

Solution

Solve this problem using the following steps.



1. Step 1. *Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene* (Table 11.2).

$$\Delta T_f = 5.5\ °C - 2.32\ °C = 3.2\ °C$$

2. Step 2. *Determine the molal concentration from K_f, the freezing point depression constant for benzene* (Table 11.2), *and* ΔT_f.

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2\ °C}{5.12\ °C\ m^{-1}} = 0.63\ m$$

3. Step 3. *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*

$$\text{Moles of solute} = \frac{0.63\ \text{mol solute}}{1.00\ \text{kg solvent}} \times 0.0550\ \text{kg solvent} = 0.035\ \text{mol}$$

4. Step 4. *Determine the molar mass from the mass of the solute and the number of moles in that mass.*

$$\text{Molar mass} = \frac{4.00\ \text{g}}{0.035\ \text{mol}} = 1.1 \times 10^2\ \text{g/mol}$$

Check Your Learning

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

Answer

1.8

\(\times \)

10^2 g/mol

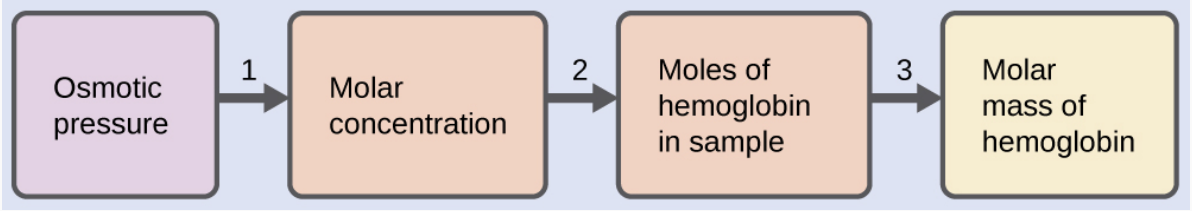
EXAMPLE 3.2.10

Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. Assuming ideal solution behavior, what is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. Step 1. *Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.*

$$\Pi = \frac{5.9 \text{ torr} \times 1 \text{ atm}}{760 \text{ torr}} = 7.8 \times 10^{-3} \text{ atm}$$

$$\Pi = \text{MRT}$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L atm/mol K})(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$$

2. Step 2. *Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.*

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L solution}} \times 0.500 \text{ L solution} = 1.6 \times 10^{-4} \text{ mol}$$

3. Step 3. *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^{4} \text{ g/mol}$$

Check Your Learning

Assuming ideal solution behavior, what is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

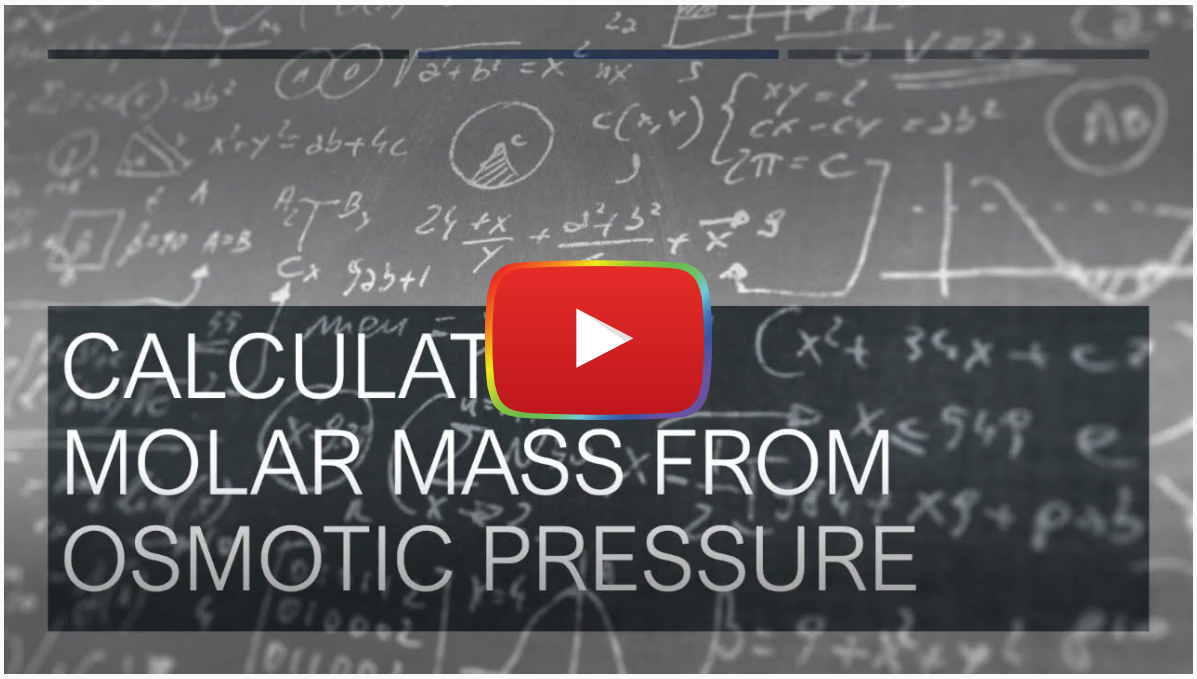
Answer

3

\(\times \)

10^4 g/mol

3.2.11 Calculating Molar Mass from Osmotic Pressure



Watch on YouTube

3.2.12 Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number not on the identity of solute species dissolved. The concentration terms in the equations for various colligative properties (freezing point depression, boiling point elevation, osmotic pressure) pertain to *all solute species present in the solution*. For the solutions considered thus far in this chapter, the solutes have been nonelectrolytes that dissolve physically without dissociation or any other accompanying process. Each molecule that dissolves yields one dissolved solute molecule. The dissolution of an electroyte, however, is not this simple, as illustrated by the two common examples below:

$$\begin{array}{ll} \text{dissociation} & \mathrm{NaCl(s)} \longrightarrow \mathrm{Na^+(aq) + Cl^-(aq)} \\ \text{ionization} & \mathrm{HCl(aq) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)} \end{array}$$

Considering the first of these examples, and assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86 \text{ °C kg water/mol ion} = 3.7 \text{ °C}.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The van't Hoff factor (*i*) is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table 3.1.

Table 3.15

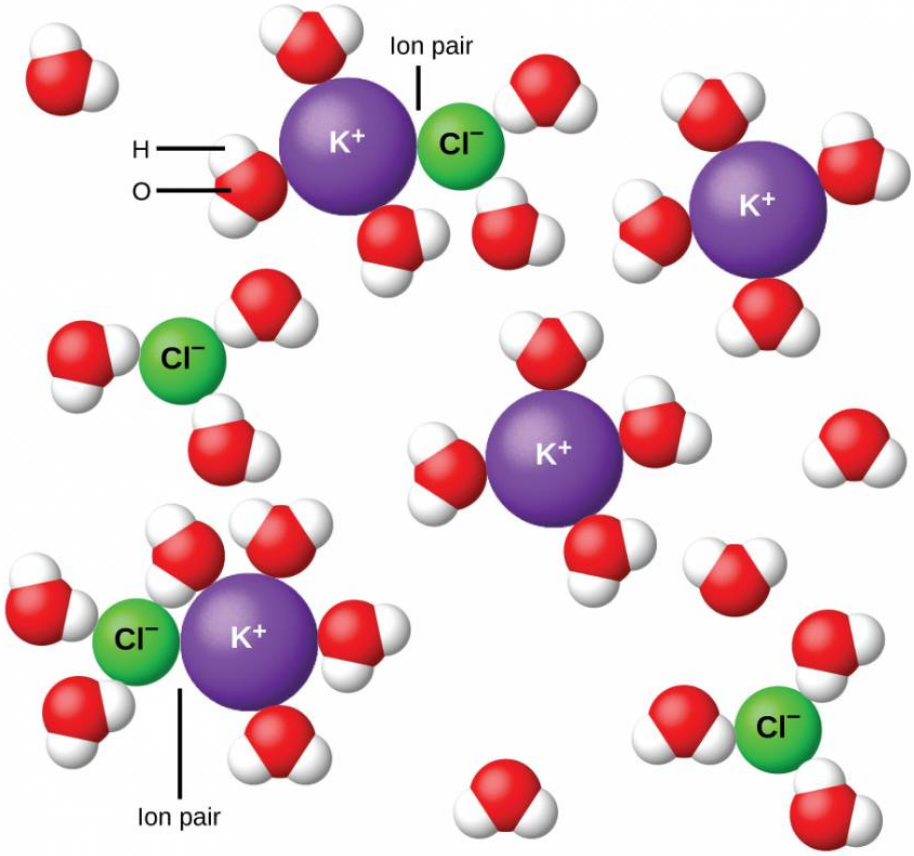
Predicated and Measured van't Hoff Factors for Several 0.050 m Aqueous Solutions

Formula unit	Classification	Dissolution products	*i* (predicted)	*i* (measured)
$C_{12}H_{22}O_{11}$ (glucose)	Nonelectrolyte	$C_{12}H_{22}O_{11}$	1	1.0
NaCl	Strong electrolyte	Na^+, Cl^-	2	1.9
HCl	Strong electrolyte (acid)	H_3O^+, Cl^-	2	1.9
$MgSO_4$	Strong electrolyte	Mg^{2+}, SO_4^{2-},	2	1.3
$MgCl_2$	Strong electrolyte	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Strong electrolyte	Fe^{3+}, $3Cl^-$	4	3.4

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure 3.15). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity or the effective concentration of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table 3.1 are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

Figure 3.16

Dissociation of ionic compounds in water is not always complete due to the formation of ion pairs.



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4

Vapor Pressure

Vapor pressure is defined as the pressure at which a gas coexists with its solid or liquid phase. This pressure can be lowered by dissolving a nonvolatile substance in a volatile liquid. Vapor pressure lowering is an example of a colligative property, as this property depends only on the concentration of solute particles. Raoult's law defines the relationship between a solution's vapor pressure and the vapor pressures and concentrations of its components. Distillation is a selective vaporization process by which solutions whose components have significantly different vapor pressures can be separated.

4.1 Phase Transitions

Learning Objectives

By the end of this section, you will be able to:

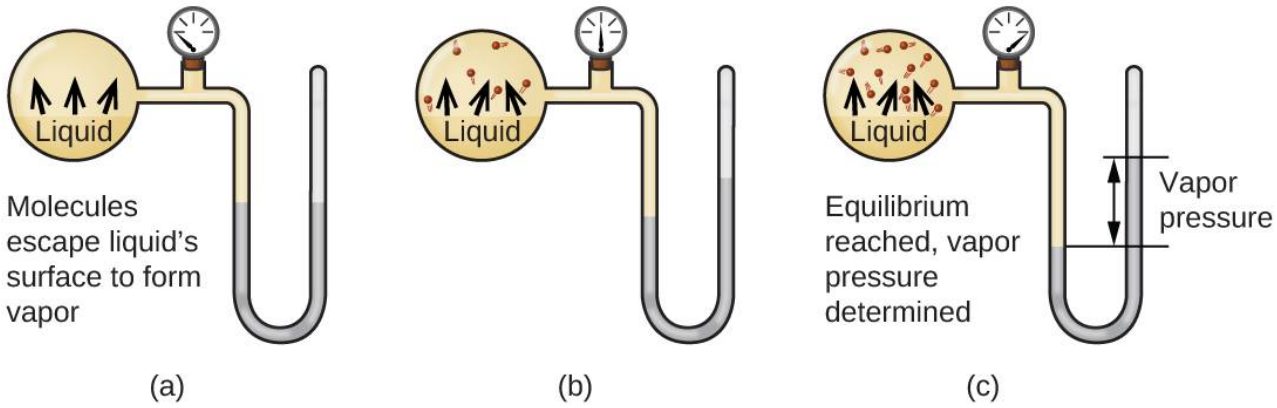
- Explain the relation between phase transition temperatures and intermolecular attractive forces
- Describe the process of distillation and its practical applications

4.1.1 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 4.1, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.

Figure 4.1

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.

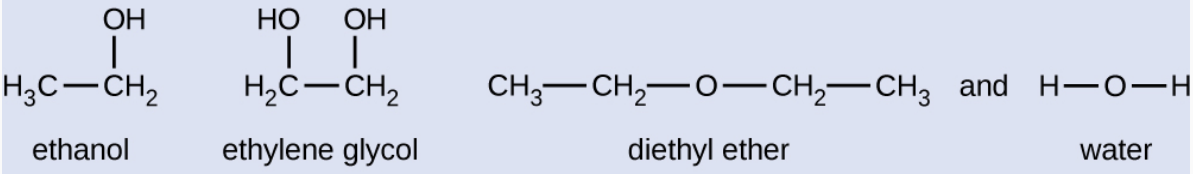


The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization 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 4.1.2

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 the lowest.

Check Your Learning

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

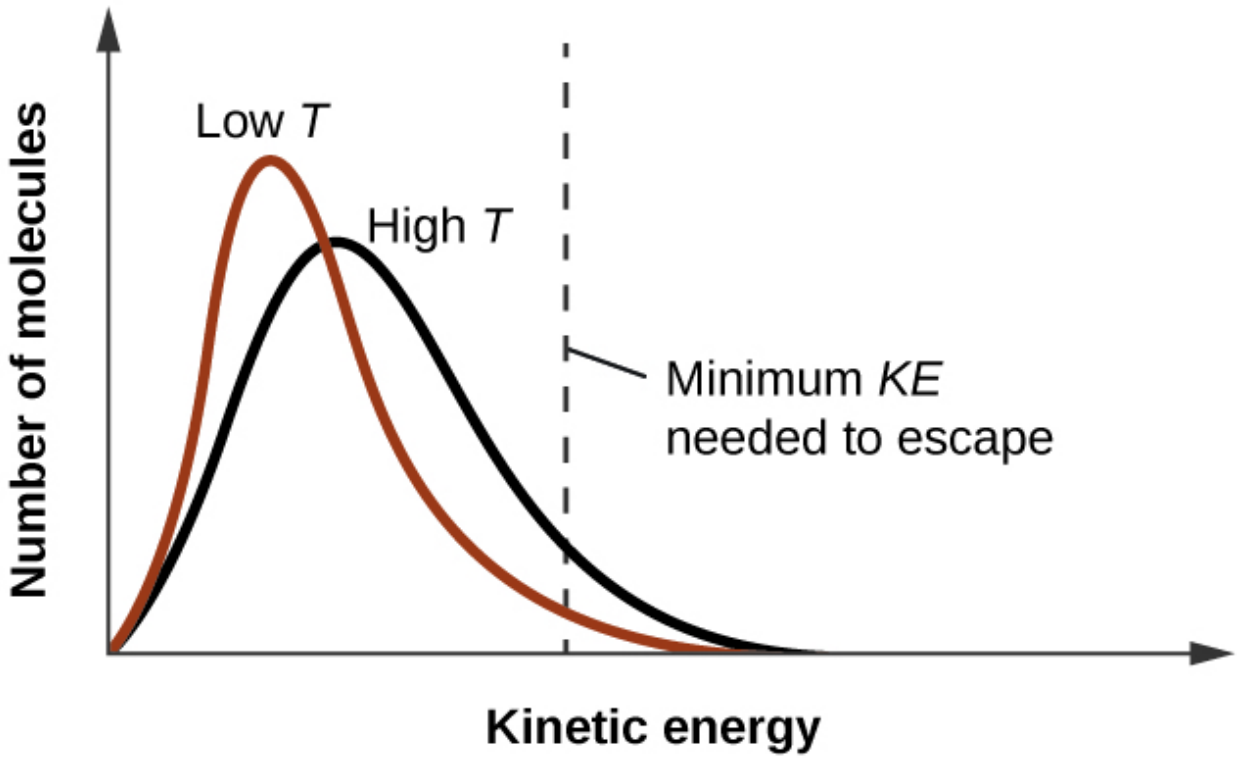
Answer

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 4.2. 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 4.2

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.



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

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

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and A is a constant whose value depends on the chemical identity of the substance. Temperature T must be in Kelvin in this equation. This equation is often rearranged 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 example exercises that follow. If at temperature T_1, the vapor pressure is P_1, and at temperature T_2, the vapor pressure is P_2, the corresponding linear equations are:

$$\ln P_1 = -\frac{\Delta H_{vap}}{RT_1} + \ln A \qquad \text{and} \qquad \ln P_2 = -\frac{\Delta H_{vap}}{RT_2} + \ln A$$

Since the constant, 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 into:

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

EXAMPLE 4.1.3

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:

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

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:

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

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.

Check Your Learning

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

41,360 J/mol or 41.4 kJ/mol

EXAMPLE 4.1.4

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:

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

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:

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

Check Your Learning

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

4.1.5 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:

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

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

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

EXAMPLE 4.1.6

Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 4.3). 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); ΔH_{vap} = 43.46 kJ/mol at 37 °C.

Figure 4.3

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:

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

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

Check Your Learning

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

4.1.7 Vapor Pressure Lowering

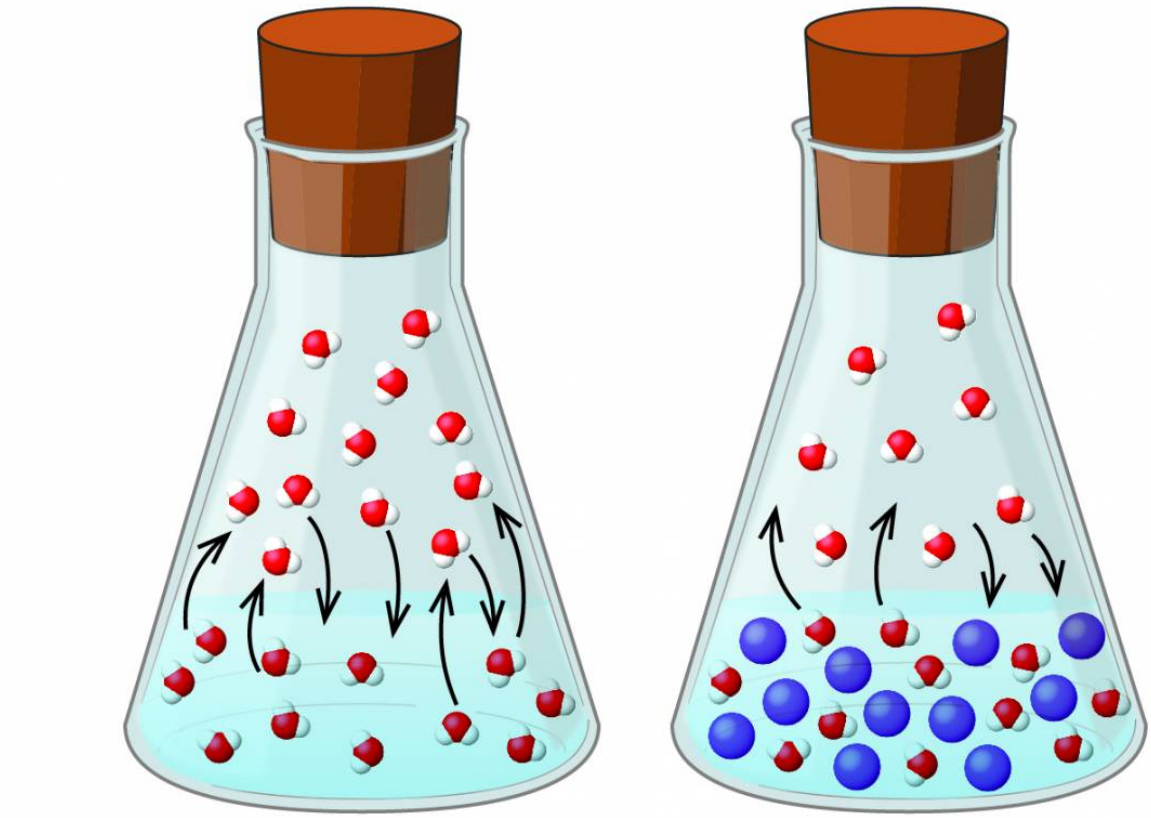
As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

$$\text{liquid} \rightleftharpoons \text{gas}$$

Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) (Figure 4.4). While this interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the more dispersed nature of matter in a solution, compared to separate solvent and solute phases serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.

Figure 4.4

The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.



(a) Pure water (b) Aqueous solution

The relationship between the vapor pressures of solution components and the concentrations of those components is described by Raoult's law: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

$$P_{\mathrm{A}} = X_{\mathrm{A}} P_{\mathrm{A}}^{*}$$

where P_{A} is the partial pressure exerted by component A in the solution, P_{A}^{*} is the vapor pressure of pure A, and X_{A} is the mole fraction of A in the solution.

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapor pressure exerted by a solution containing *i* components is

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^{*}$$

A nonvolatile substance is one whose vapor pressure is negligible ($P^{*} \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{*}$$

EXAMPLE 4.1.8

Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $C_3H_5(OH)_3$, and 184.4 g of ethanol, C_2H_5OH, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult's law as:

$$P_{\text{solution}} = X_{\text{solvent}} P^*_{\text{solvent}}$$

First, calculate the molar amounts of each solution component using the provided mass data.

$$92.1\ \text{g}\ C_3H_5(OH)_3 \times \frac{1\ \text{mol}\ C_3H_5(OH)_3}{92.094\ \text{g}\ C_3H_5(OH)_3} = 1.00\ \text{mol}\ C_3H_5(OH)_3$$
$$184.4\ \text{g}\ C_2H_5OH \times \frac{1\ \text{mol}\ C_2H_5OH}{46.069\ \text{g}\ C_2H_5OH} = 4.000\ \text{mol}\ C_2H_5OH$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapor pressure.

$$X_{C_2H_5OH} = \frac{4.000\ \text{mol}}{(1.00\ \text{mol} + 4.000\ \text{mol})} = 0.800$$
$$P_{\text{solv}} = X_{\text{solv}} P^*_{\text{solv}} = 0.800 \times 0.178\ \text{atm} = 0.142\ \text{atm}$$

Check Your Learning

A solution contains 5.00 g of urea, $CO(NH_2)_2$ (a nonvolatile solute) and 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 assuming ideal behavior?

Answer

23.4 torr

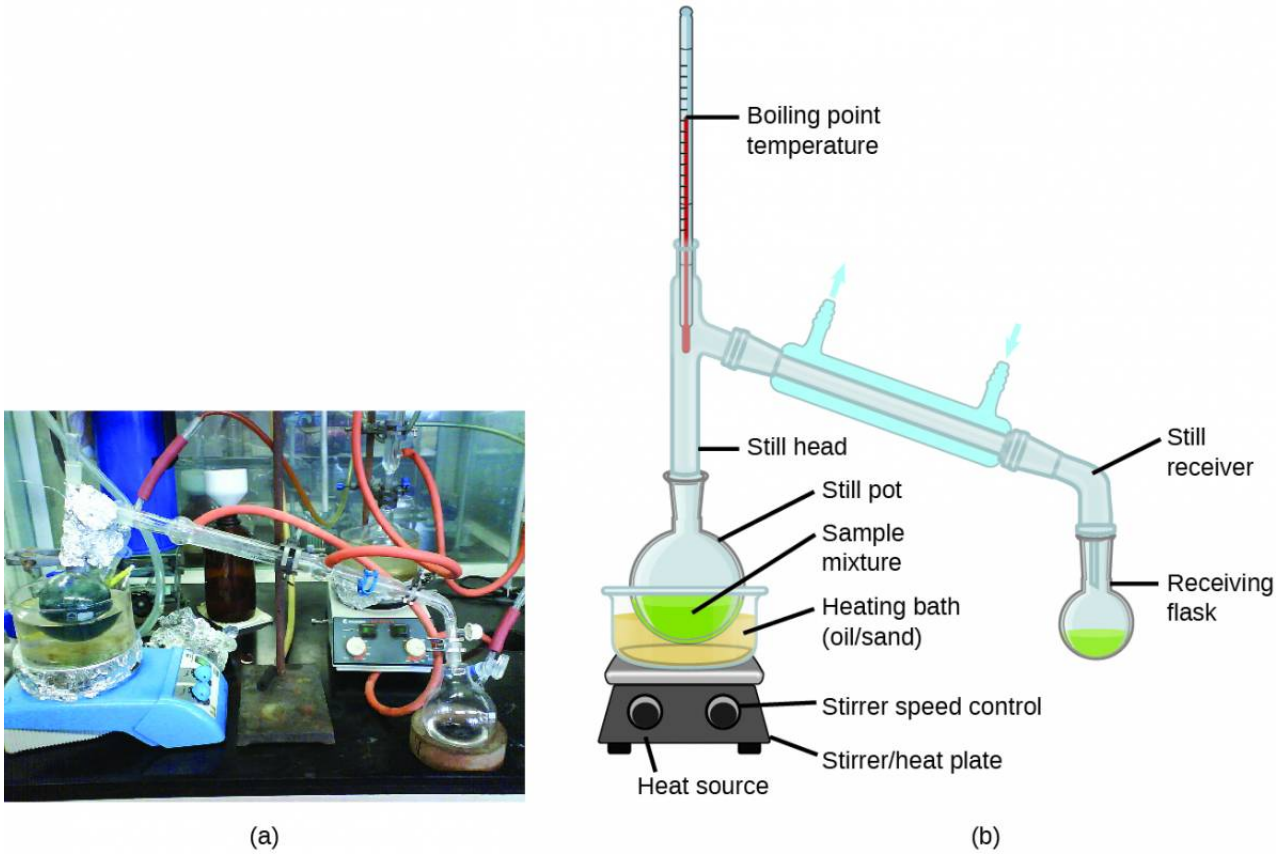
4.1.9 Distillation of Solutions

Solutions whose components have significantly different vapor pressures may be separated by a selective vaporization process known as distillation. Consider the simple case of a mixture of two volatile liquids A and B, with A being the more volatile liquid. Raoult's law can be used to show that the vapor above the solution is enriched in component A, that is, the mole fraction of A in the vapor is greater than the mole fraction of A in the liquid (see end-of-chapter Exercise 65). By appropriately heating the mixture, component A may be vaporized, condensed, and collected—effectively separating it from component B.

Distillation is widely applied in both laboratory and industrial settings, being used to refine petroleum, to isolate fermentation products, and to purify water. A typical apparatus for laboratory-scale distillations is shown in Figure 4.5.

Figure 4.5

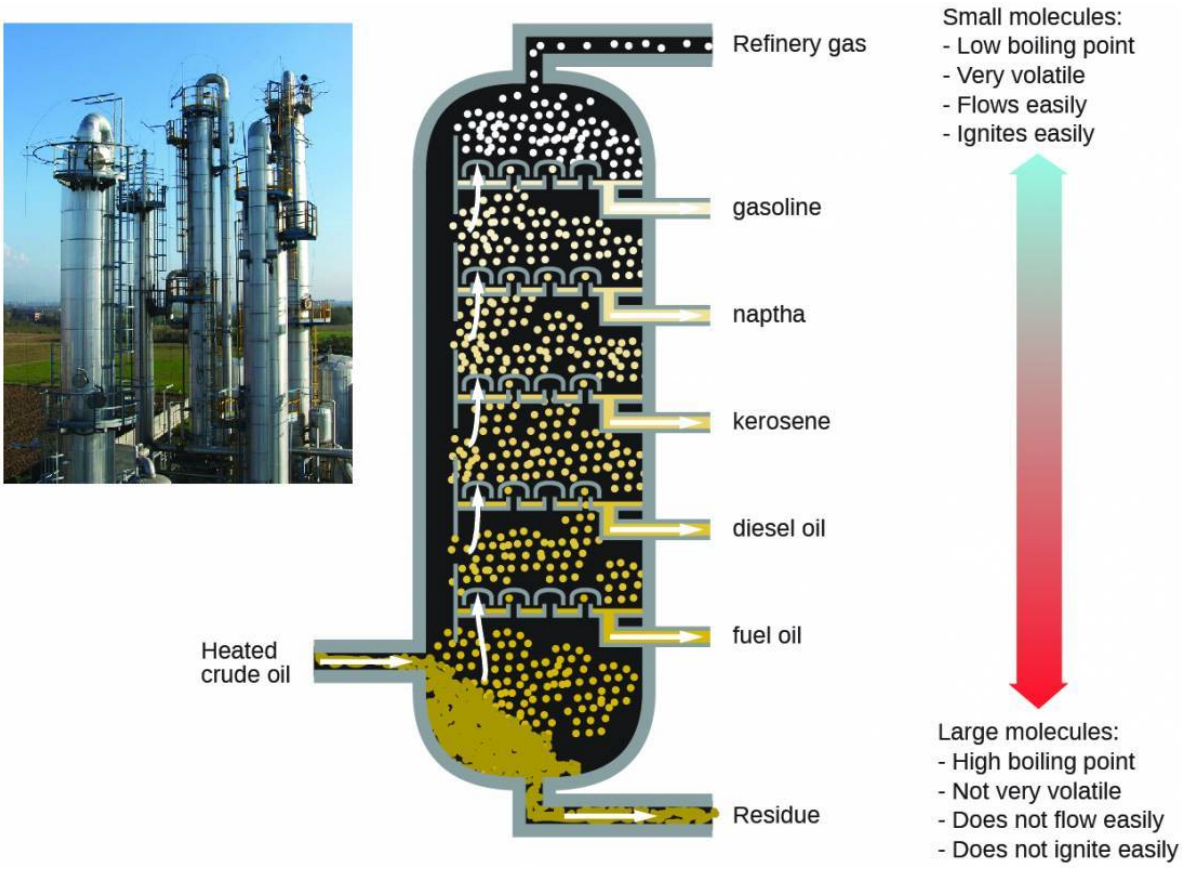
A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by "Rifleman82"/Wikimedia commons; credit b: modification of work by "Slashme"/Wikimedia Commons)



Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column* vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in Figure 4.6.

Figure 4.6

Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.



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5

Melting/Boiling

Phase transitions are processes that convert matter from one physical state into another. 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. Boiling point elevation and freezing point depression are examples of colligative properties that occur due to the addition of a non-volatile solute to a volatile solvent.

5.1 Phase Transitions

Learning Objectives

By the end of this section, you will be able to:

- 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

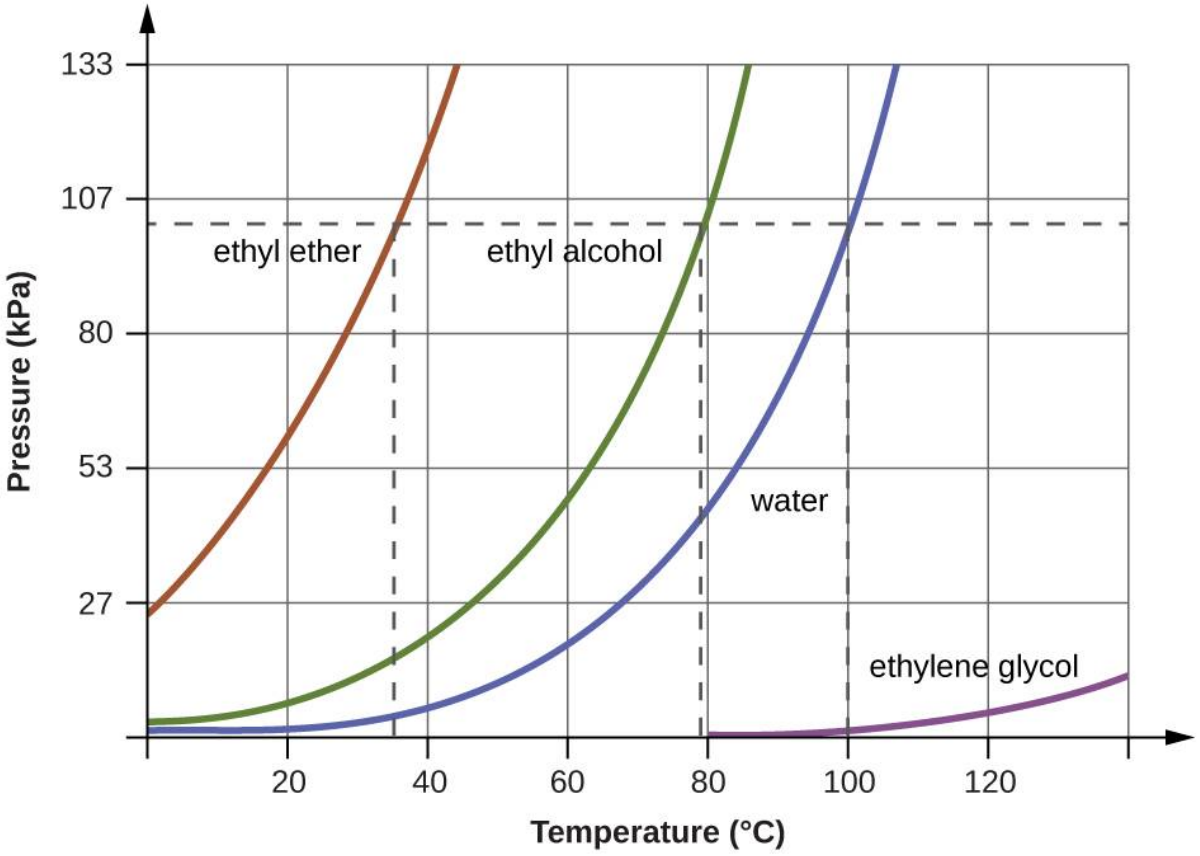
We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other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

5.1.1 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 5.1 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 5.1

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 5.1.2

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 5.1 to determine the boiling point of water at this elevation.

Solution

The graph of the vapor pressure of water versus temperature in Figure 5.1 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.

Check Your Learning

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use figure Figure5.1 to determine the approximate atmospheric pressure at the camp.

Answer:

Approximately 40 kPa (0.4 atm)

5.1.3 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 5.2).

Figure 5.2

(a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the a 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)

(a) (b) (c) (d)

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 occu 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, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endotherm process:

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l) \qquad \Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$$

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

$$\Delta T_{\text{b}} = K_{\text{b}} m$$

5.1.4 Boiling Point Elevation

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Vapor pressure increases with temperature, and so a solution will require a higher temperature than will pure solvent t achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_{b}, is called boiling point elevation and is directly proportional to the molal concentration of solute species:

$$\text{Boiling temperature} = 80.1\ ^\circ\text{C} + 0.83\ ^\circ\text{C} = 80.9\ ^\circ\text{C}$$

where K_{b} is the boiling point elevation constant, or the *ebullioscopic constant* and m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_{b} for several solvents are listed in Table 5.1.

Table 5.3

Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	Boiling Point (°C at 1 atm)	K_{b} (°Cm^{-1})	Freezing Point (°C at 1 atm)	K_{f} (°Cm^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68

Solvent	Boiling Point (°C at 1 atm)	K_b (°Cm^{-1})	Freezing Point (°C at 1 atm)	K_f (°Cm^{-1})
nitrobenzene	210.9	5.24	5.67	8.1

The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) wi exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

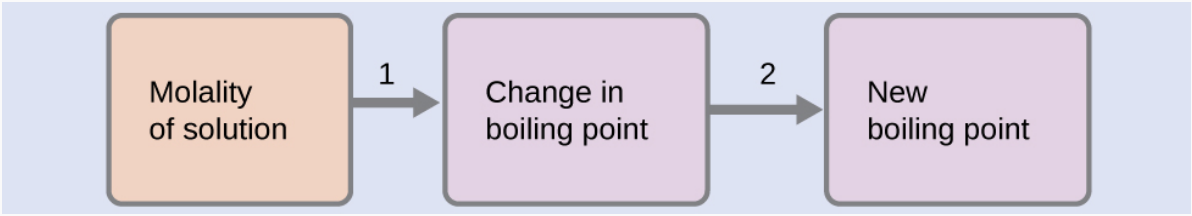
EXAMPLE 5.1.5

Calculating the Boiling Point of a Solution

Assuming ideal solution behavior, what is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



1. Step 1. *Calculate the change in boiling point.*

$$\Delta T_f = K_f m = 5.12\ °C\ m^{-1} \times 0.33\ m = 1.7\ °C$$

2. Step 2. *Add the boiling point elevation to the pure solvent's boiling point.*

$$\text{Boiling temperature} = 80.1\ °C + 0.83\ °C = 80.9\ °C$$

Check Your Learning

Assuming ideal solution behavior, what is the boiling point of the antifreeze described in Example 11.3?

Answer

109.2 °C

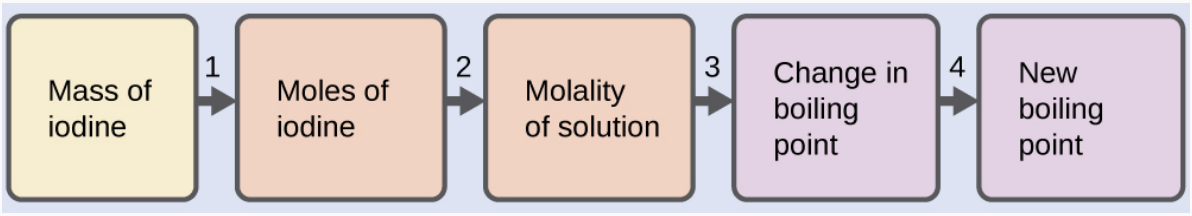
EXAMPLE 5.1.6

The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2, in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

A four-step approach to solving this problem is outlined below.



1. Step 1. *Convert from grams to moles of I_2 using the molar mass of I_2 in the unit conversion factor.*
   Result: 0.363 mol
2. Step 2. *Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.*
   Result: 0.454 *m*
3. Step 3. *Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.*
   Result: 1.65 °C
4. Step 4. *Determine the new boiling point from the boiling point of the pure solvent and the change.*
   Result: 62.91 °C
   Check each result as a self-assessment.

Check Your Learning

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Answer

100.12 °C

5.1.7 Freezing Point Depression

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt (Figure 5.3), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).

Figure 5.4

Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the freezing poin depression and is directly proportional to the molal concentration of the solute

$$\text{Freezing Temperature} = 5.5\ ^\circ\text{C} - 1.7\ ^\circ\text{C} = 3.8\ ^\circ\text{C}$$

where m is the molal concentration of the solute and K_f is called the freezing point depression constant (or *cryoscopi constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on th chemical identity of the solvent. Values of K_f for several solvents are listed in Table 5.1.

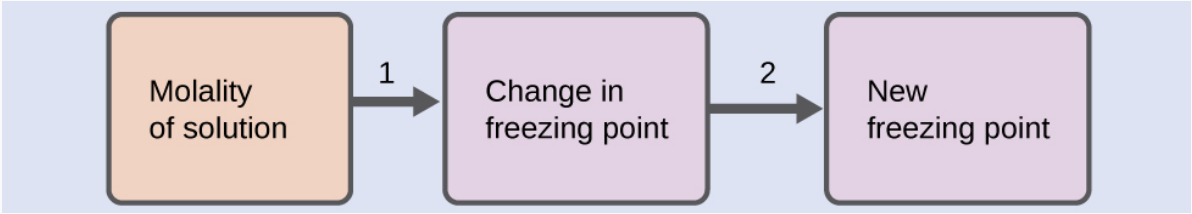
EXAMPLE 5.1.8

Calculation of the Freezing Point of a Solution

Assuming ideal solution behavior, what is the freezing point of the 0.33 *m* solution of a nonvolatile nonelectrolyte solute in benzene described in Example 11.4?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



1. Step 1. *Calculate the change in freezing point.*

2. Step 2. *Subtract the freezing point change observed from the pure solvent's freezing point.*

Check Your Learning

Assuming ideal solution behavior, what is the freezing point of a 1.85 *m* solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer

−9.3 °C

5.1.9 CHEMISTRY IN EVERYDAY LIFE

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Figure 5.4).

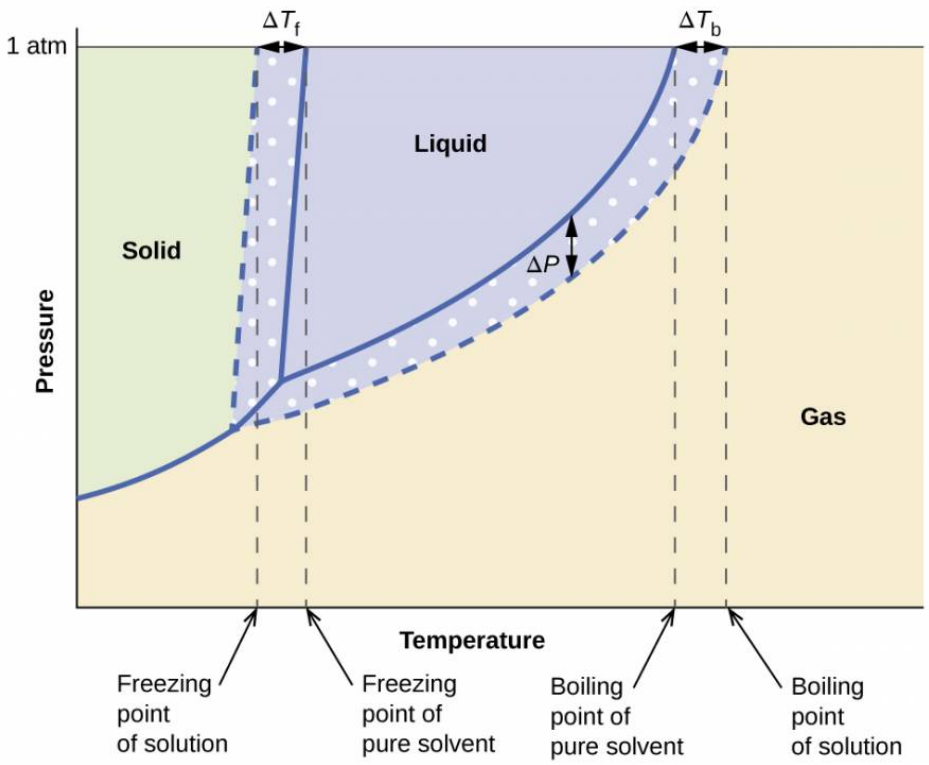
Figure 5.5

Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid (Figure 5.5).

Figure 5.6

Phase diagrams for a pure solvent (solid curves) and a solution formed by dissolving nonvolatile solute in the solvent (dashed curves).



The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, ΔP, that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b, associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced le of that for the pure solvent, representing the freezing point depression, ΔT_f, that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed of solvent only, and so transitions between these phases are not subject to colligative effects.

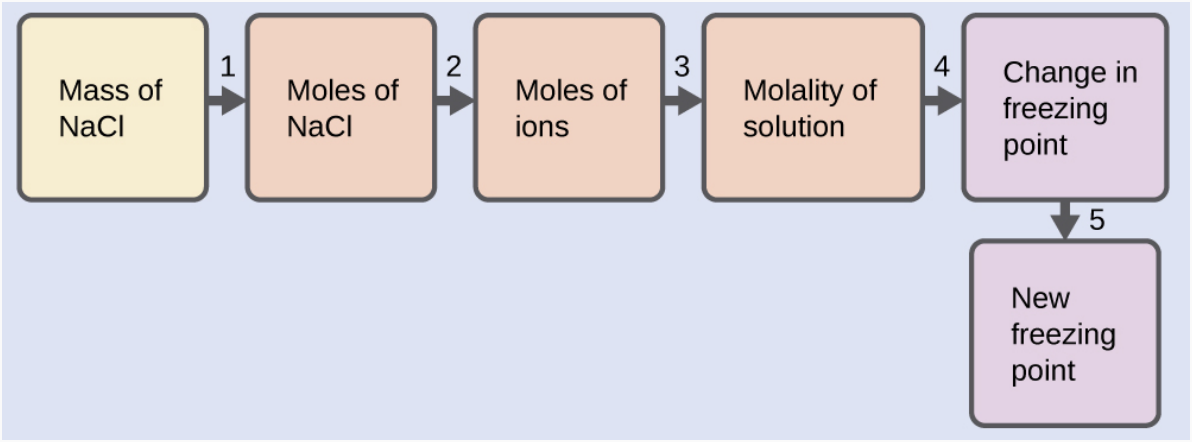
EXAMPLE 5.1.10

The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Use this information and a predicted value for the van't Hoff factor (Table 11.3) to determine the freezing temperature the solution (assume ideal solution behavior).

Solution

Solve this problem using the following series of steps.



1. Step 1. *Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor.*
   Result: 0.072 mol NaCl
2. Step 2. *Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl).*
   Result: 0.14 mol ions
3. Step 3. *Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms.*
   Result: 1.2 *m*
4. Step 4. *Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes.*
   Result: 2.1 °C
5. Step 5. *Determine the new freezing point from the freezing point of the pure solvent and the change.*
   Result: −2.1 °C
   Check each result as a self-assessment, taking care to avoid rounding errors by retaining guard digits in each step's result for computing the next step's result.

Check Your Learning

Assuming complete dissociation and ideal solution behavior, calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

Answer

−0.208 °C

Files

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Unit 2

Kinetics

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- Reaction Rates
- Experimental Rate Laws
- Integrated Rate Laws
- Temperature and Rate
- Reaction Mechanisms and Catalysis

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6

Reaction Rates

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction. The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway with a lower activation energy.

6.1 Chemical Reaction Rates

Learning Objectives

By the end of this section, you will be able to:

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

Figure 6.1

An agama lizard basks in the sun. As its body warms the chemical reactions of its metabolism speed up.

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. A cold lizard is a slower lizard and an easier meal for predators.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed and the quantitative techniques used to describe the rates at which reactions occur.

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration as shown here:

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in species concentration over time is the rate expression for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates “change in.” Thus,

$[H_2O_2]_{t_1}$

represents the molar concentration of hydrogen peroxide at some time t_1; likewise,

$[H_2O_2]_{t_2}$

represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. Figure 6.2 provides an example of data collected during the decomposition of H_2O_2.

Figure 6.2

The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\ \text{mol/L} - 1.000\ \text{mol/L})}{(6.00\ \text{h} - 0.00\ \text{h})} = 0.0833\ \text{mol}\ L^{-1}\ h^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

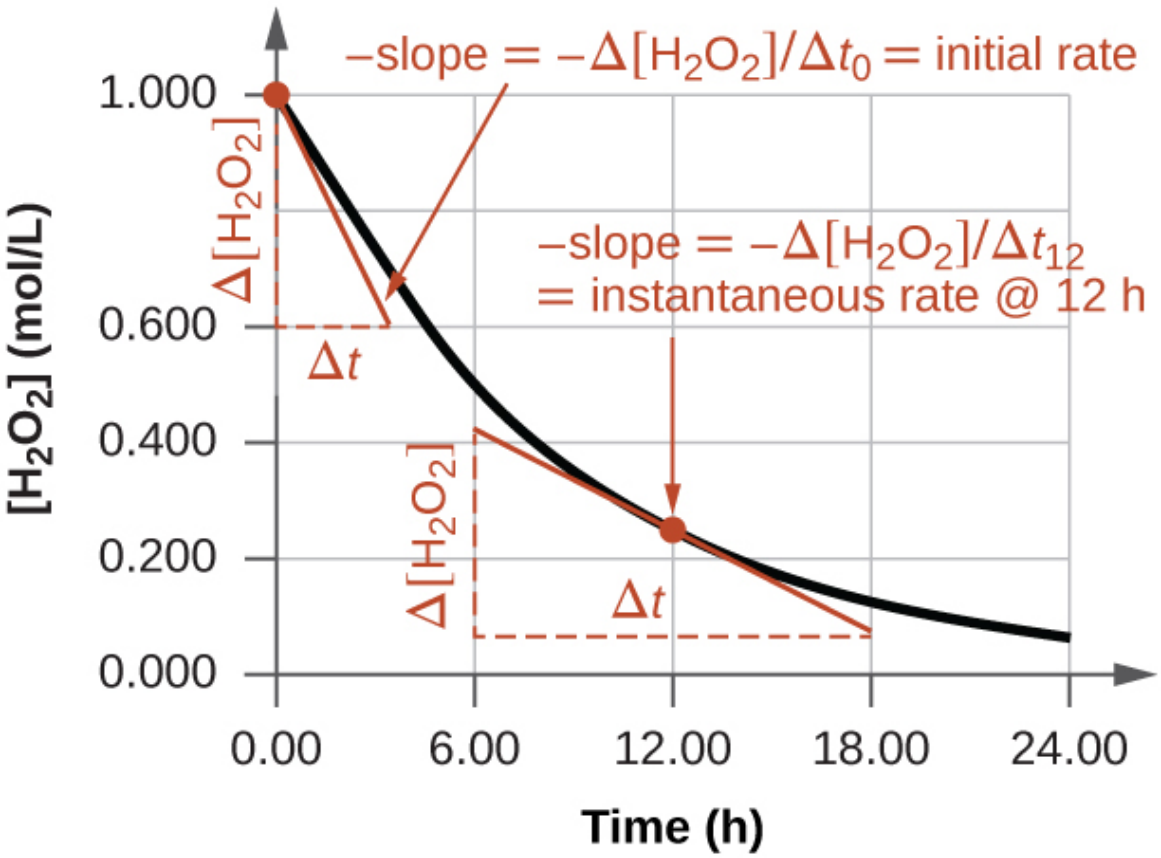
$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.0625\ \mathrm{mol/L} - 0.125\ \mathrm{mol/L})}{(24.00\ \mathrm{h} - 18.00\ \mathrm{h})} = 0.010\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an average rate for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its instantaneous rate. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its initial rate. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 6.3). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

Figure 6.3

This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at 12 h).


−slope = −Δ[H2O2]/Δt0 = initial rate
−slope = −Δ[H2O2]/Δt12
= instantaneous rate @ 12 h
Δ[H2O2]
Δt
Δ[H2O2]
Δt
1.000
0.600
0.400
0.200
0.000
[H2O2] (mol/L)
0.00
6.00
12.00
18.00
24.00
Time (h)

6.1.1 CHEMISTRY IN EVERYDAY LIFE

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 6.4). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

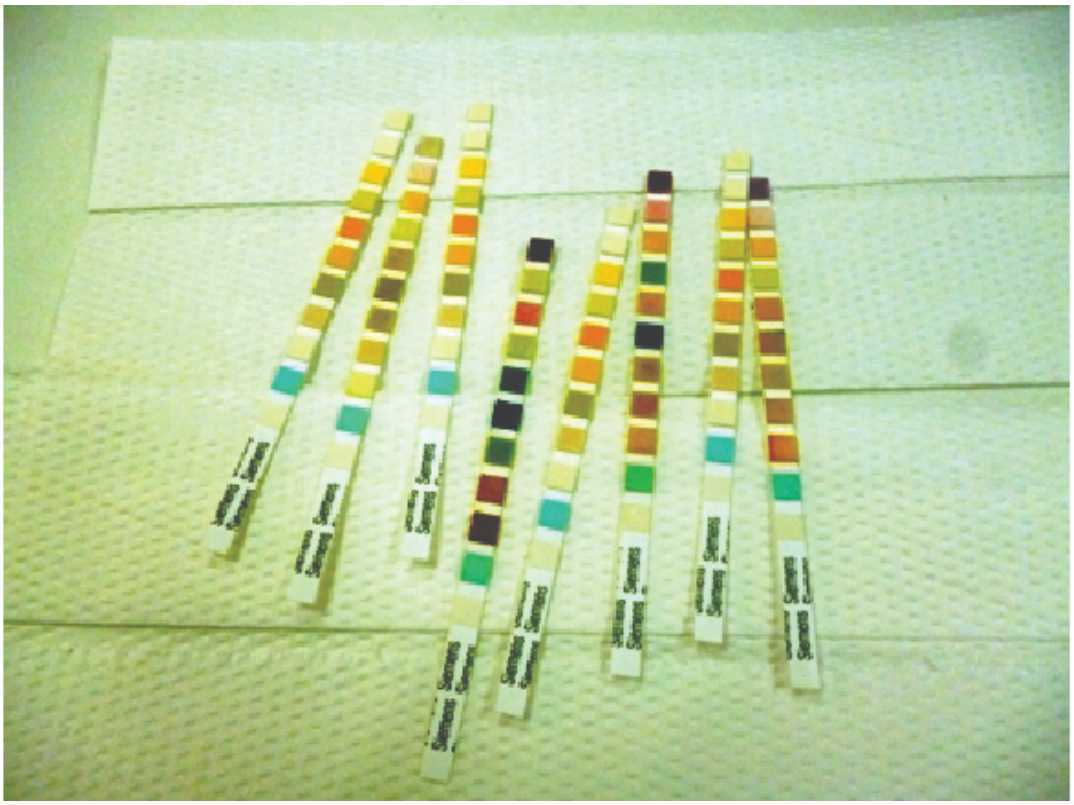
$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

Figure 6.4

Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)



6.1.2 Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$\mathrm{aA} \longrightarrow \mathrm{bB}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate} = -\left(\frac{1}{\mathrm{a}}\right)\left(\frac{\Delta \mathrm{A}}{\Delta t}\right) = \left(\frac{1}{\mathrm{b}}\right)\left(\frac{\Delta \mathrm{B}}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

$$2\mathrm{NH_3}\,(g) \longrightarrow \mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

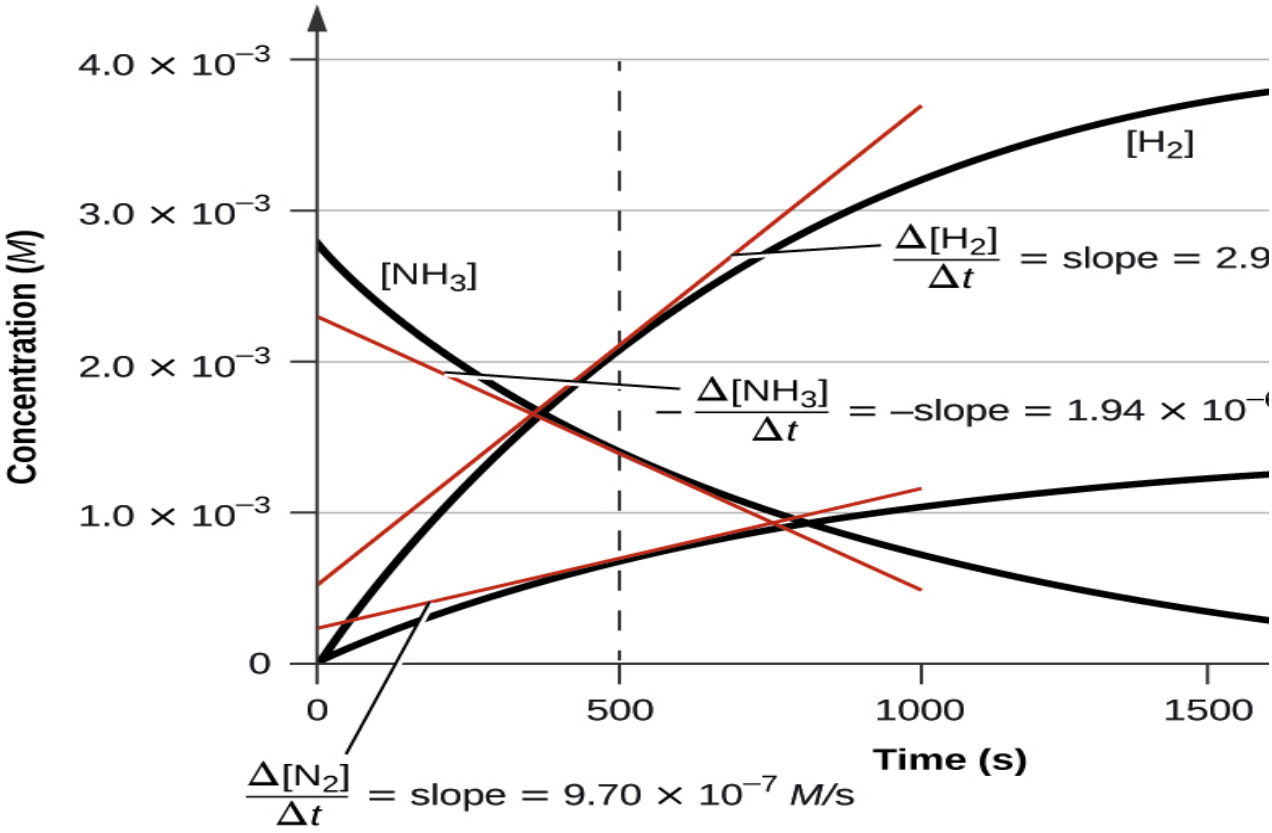
$$\frac{1}{3}\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t}$$

Figure 6.5 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\text{s}}{9.70 \times 10^{-7}\ M/\text{s}} \approx 3$$

Figure 6.5

Changes in concentrations of the reactant and products for the reaction $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$. *The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.*



6.2 Factors Affecting Reaction Rates

Learning Objectives

By the end of this section, you will be able to:

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

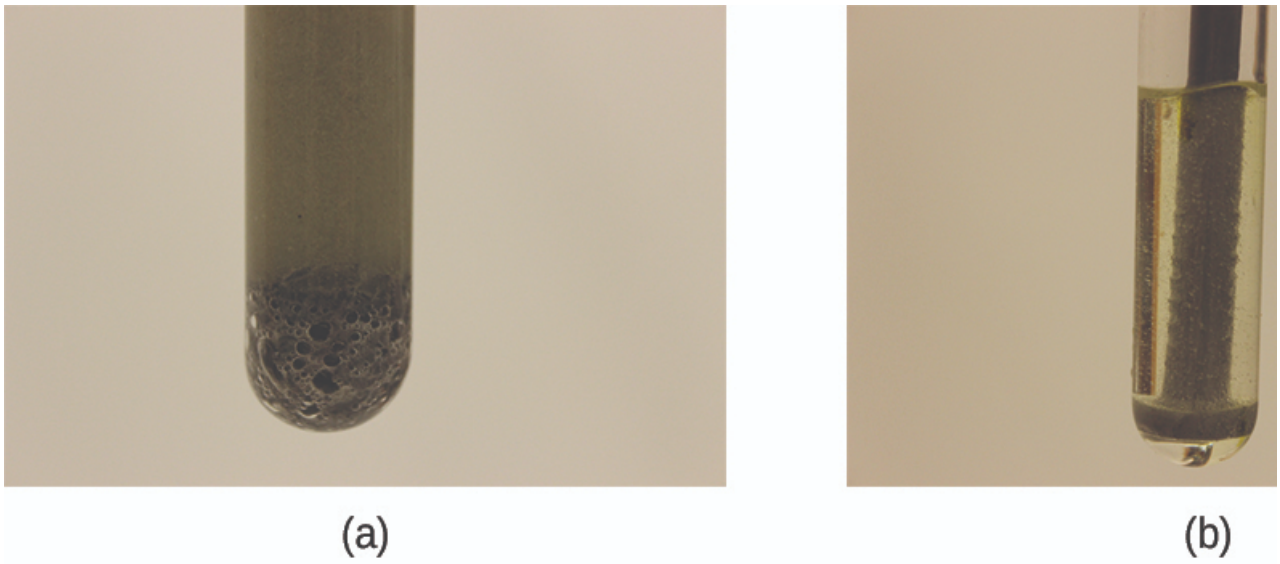
6.2.1 The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

6.2.2 The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 6.6). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.

Figure 6.6 (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.



LINK TO LEARNING

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

6.2.3 Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

6.2.4 Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 6.7). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$SO_2(g) + H_2O(g) \longrightarrow H_2SO_3(aq)$$

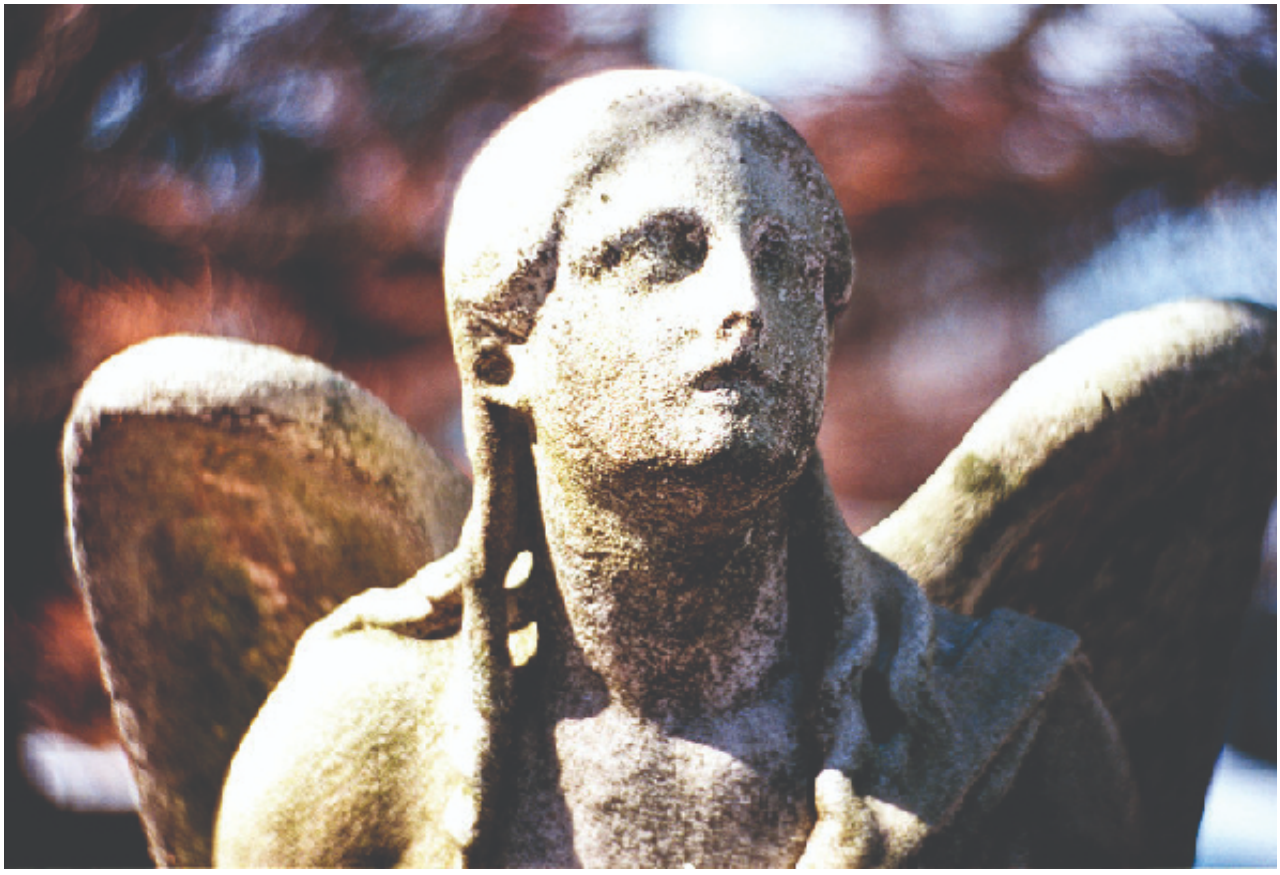
Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_3(s) + H_2SO_3(aq) \longrightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

Figure 6.6

Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)



LINK TO LEARNING

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

6.2.5 The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, H_2O_2, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

Under typical conditions, this decomposition occurs very slowly. When dilute H_2O_2(aq) is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called catalysts, a topic treated in greater detail later in this chapter.

LINK TO LEARNING

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

Files

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7

Experimental Rate Laws

Rate laws (differential rate laws) provide a mathematical description of how changes in the concentration of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the concentration of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Learning Objectives

By the end of this section, you will be able to:

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. Rate laws (sometimes called *differential rate laws*) or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow products$$

where *a* and *b* are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate} = k[A]^m [B]^n$$

in which [*A*] and [*B*] represent the molar concentrations of reactants, and *k* is the rate constant, which is specific for a particular reaction at a particular temperature. The exponents *m* and *n* are the reaction orders and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

EXAMPLE: 7.0.1 Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

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:

$$\text{rate} = k[NO_2]^m[CO]^n$$

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:

$$\text{rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

Check Your Learning

The rate law for the reaction:

$$H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

has been 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

Check Your Learning

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:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k[CH_3OH]$$

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

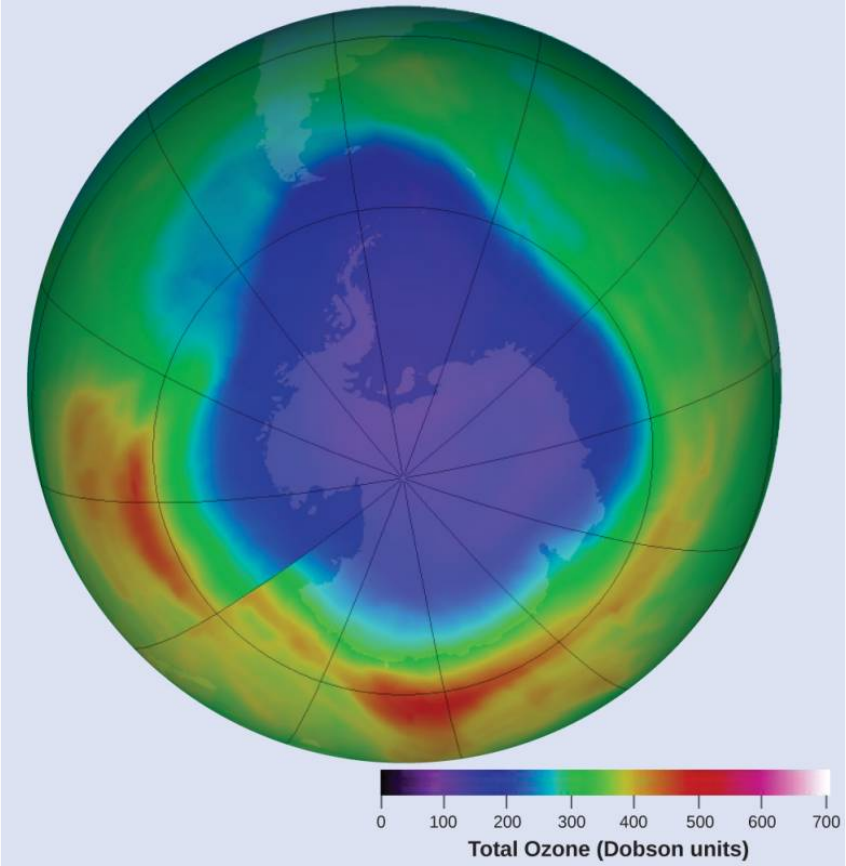
A common experimental approach to the determination of rate laws is the method of initial rates. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

EXAMPLE: 7.0.2 Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 7.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

Figure 7.1

A contour map showing stratospheric ozone concentration and the "ozone hole" that occurs over Antarctica during its spring months. (credit: modification of work by NASA)



$$\mathrm{NO(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}$ $(\mathrm{mol\ L^{-1}\ s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}

Trial	[NO] (mol/L)	$[O_3]$ (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}$ $(\text{mol L}^{-1}\ \text{s}^{-1})$
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\text{NO}]^m [\text{O}_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. Step 1.
   Determine the value of m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

2. Step 2.
   Determine the value of n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\text{NO}]^1 [\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

3. Step 3.
   Determine the value of k *from one set of concentrations and the corresponding rate.* The data from trial 1 are used below:

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \text{mol L}^{-1})(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

Check Your Learning

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO(g)} \longrightarrow \text{CH}_4\text{(g)} + \text{CO(g)}$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	$[CH_3CHO]$ (mol/L)	$-\frac{\Delta[CH_3CHO]}{\Delta t}$ $(\text{mol L}^{-1}\ \text{s}^{-1})$
1	1.75×10^{-3}	2.06×10^{-11}

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[CH_3CHO]}{\Delta t}\ (\text{mol L}^{-1}\ \text{s}^{-1})$
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

$$\text{rate} = k[CH_3CHO]^2$$

with k = 6.73

×

10^{-6} L/mol/s

EXAMPLE: 7.0.3 Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{NO}]}{\Delta t}$ $(\text{mol L}^{-1}\ \text{s}^{-1})$
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in Example 7.2, approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of *m* and *n*:

1. Step 1.
   Determine the value of m *from the data in which [NO] varies and [Cl_2] is constant*. Write the ratios with the subscripts *x* and *y* to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m [\text{Cl}_2]_x^n}{k[\text{NO}]_y^m [\text{Cl}_2]_y^n}$$

   Using the third trial and the first trial, in which [Cl_2] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m (0.10)^n}{k(0.10)^m (0.10)^n}$$

   Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

   which simplifies to:

$$2.25 = (1.5)^m$$

   Use logarithms to determine the value of the exponent *m*:

$$\begin{array}{ccc} \ln(2.25) & = & m\ln(1.5) \\ \frac{\ln(2.25)}{\ln(1.5)} & = & m \\ 2 & = & m \end{array}$$

   Confirm the result

$$1.5^2 = 2.25$$

2. Step 2.
   Determine the value of n *from data in which [Cl_2] varies and [NO] is constant.*

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m (0.15)^n}{k(0.10)^m (0.10)^n}$$

   Cancelation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

   which simplifies to:

$$1.5 = (1.5)^n$$

Thus *n* must be 1, and the form of the rate law is:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2]$$

3. Step 3.
   Determine the numerical value of the rate constant k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for *k* are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be $\text{mol}^{-2}\ \text{L}^2/\text{s}$ so that the rate is in terms of mol/L/s.

   To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

$$\begin{aligned} 0.00300\ \text{mol L}^{-1}\ \text{s}^{-1} &= k(0.10\ \text{mol L}^{-1})^2(0.10\ \text{mol L}^{-1})^1 \\ k &= 3.0\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1} \end{aligned}$$

Check Your Learning

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\text{OCl}^-(aq) + \text{I}^-(aq) \longrightarrow \text{OI}^-(aq) + \text{Cl}^-(aq)$$

Trial	$[\text{OCl}^-]$ (mol/L)	$[\text{I}^-]$ (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant *k* with appropriate units for this reaction.

Answer

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$2.00 = 2.00^y$
$y = 1$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$
\begin{aligned}
2.00 &= \frac{2^x}{2^y} \\
2.00 &= \frac{2^x}{2^1} \\
4.00 &= 2^x \\
x &= 2
\end{aligned}
$$

Substituting the concentration data from trial 1 and solving for *k* yields:

$$
\begin{aligned}
\text{rate} &= k[\text{OCl}^-]^2[\text{I}^-]^1 \\
0.00184 &= k(0.0040)^2(0.0020)^1 \\
k &= 5.75 \times 10^4\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}
\end{aligned}
$$

7.0.4 Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$
\begin{aligned}
\text{NO}_2 + \text{CO} &\longrightarrow \text{NO} + \text{CO}_2 & \text{rate} &= k[\text{NO}_2]^2 \\
\text{CH}_3\text{CHO} &\longrightarrow \text{CH}_4 + \text{CO} & \text{rate} &= k[\text{CH}_3\text{CHO}]^2 \\
2\text{N}_2\text{O}_5 &\longrightarrow \text{NO}_2 + \text{O}_2 & \text{rate} &= k[\text{N}_2\text{O}_5] \\
2\text{NO}_2 + \text{F}_2 &\longrightarrow 2\text{NO}_2\text{F} & \text{rate} &= k[\text{NO}_2][\text{F}_2] \\
2\text{NO}_2\text{Cl} &\longrightarrow 2\text{NO}_2 + \text{Cl}_2 & \text{rate} &= k[\text{NO}_2\text{Cl}]
\end{aligned}
$$

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example 7.2 was determined to be

$$\text{L mol}^{-1}\ \text{s}^{-1}\ .$$

For the third-order reaction described in Example 7.3, the unit for *k* was derived to be

$$\text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}\ .$$

Dimensional analysis requires the rate constant unit for a reaction whose overall order is *x* to be

$L^{x-1}\ mol^{1-x}\ s^{-1}$.

Table 7.1 summarizes the rate constant units for common reaction orders.

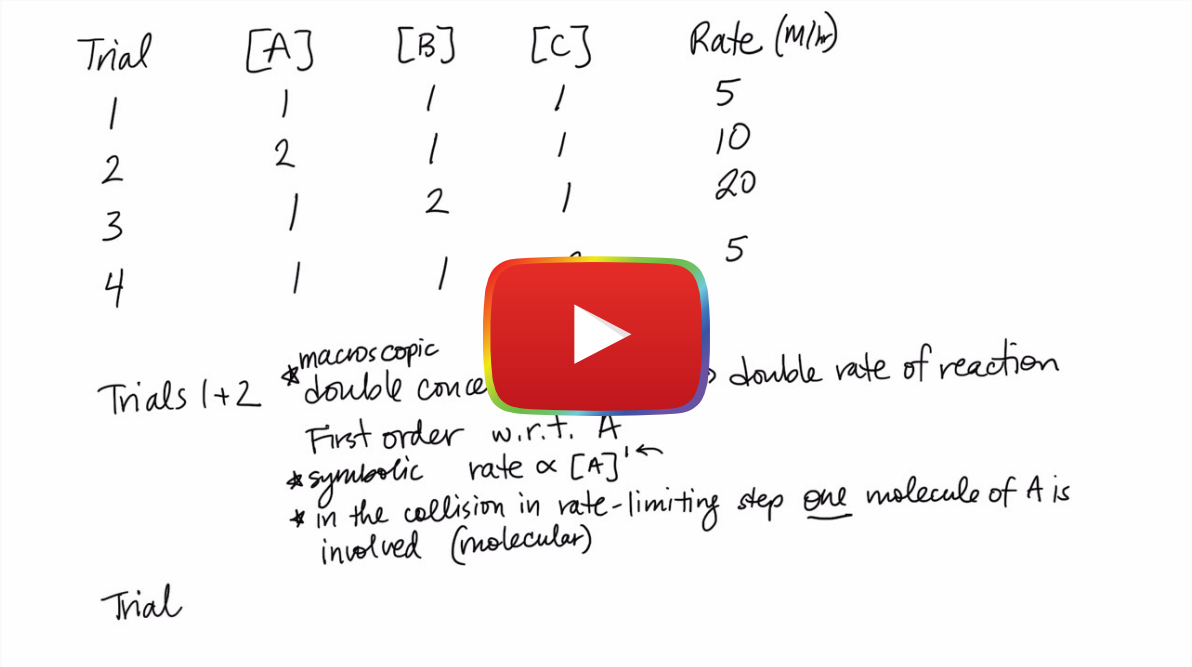
Table 7.2

Rate Constant Units for Common Reaction Orders

Overall Reaction Order (*x*)	**Rate Constant Unit ($L^{x-1}\ mol^{1-x}\ s^{-1}$)**
0 (zero)	mol $L^{-1}\ s^{-1}$
1 (first)	s^{-1}
2 (second)	L $mol^{-1}\ s^{-1}$
3 (third)	$L^2\ mol^{-2}\ s^{-1}$

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

7.0.5 Order with Respect to a Reactant



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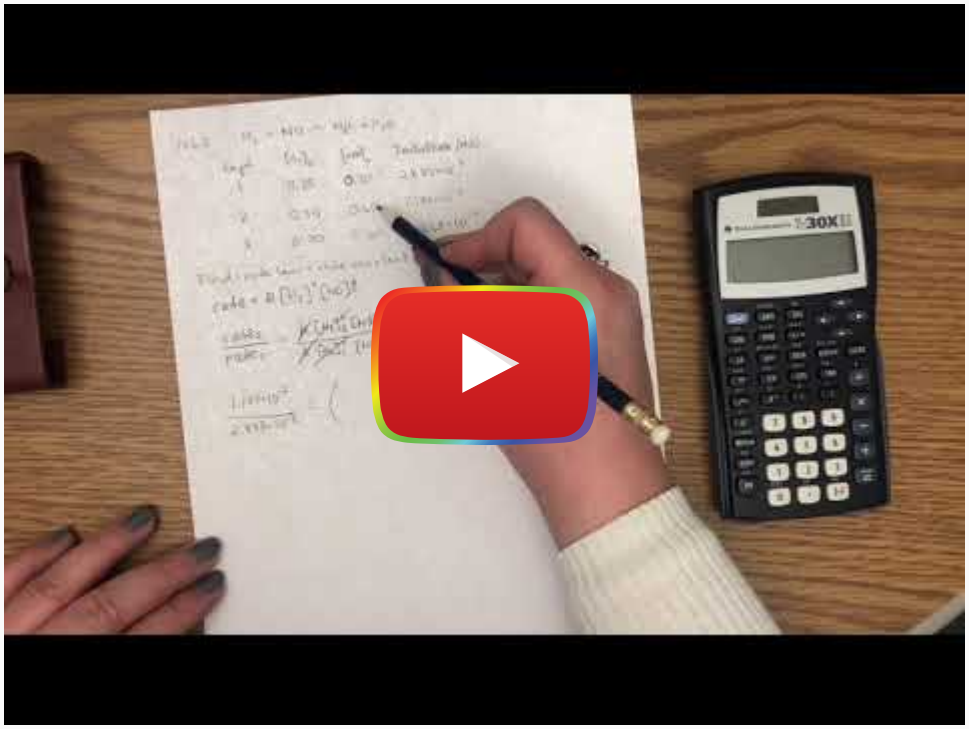
Example: 7.0.6 Determination of Order



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8

Integrated Rate Laws

Integrated rate laws are mathematically derived from differential rate laws, and they describe the time dependence of reactant and product concentrations. The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. A reaction's half-life varies with rate constant and, for some reaction orders, reactant concentration. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

Learning Objectives

By the end of this section, you will be able to:

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws discussed thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called integrated rate laws. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

8.0.1 First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

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

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \qquad \text{or} \qquad \ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

and a format showing a linear dependence of concentration in time:

$$\ln[A]_t = \ln[A]_0 - kt$$

EXAMPLE 8.0.2

The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2

×

10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or 0.200x. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln\frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.7 \times 10^2\ \text{s} \end{aligned}$$

Check Your Learning

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine−131 in a 0.500 *M* solution of this substance to decay to Xe-131?

Answer

16.7 days

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $\ln[A]_t$ versus t for a first-order reaction is a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A.

EXAMPLE 8.0.3

Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure 6.2 can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

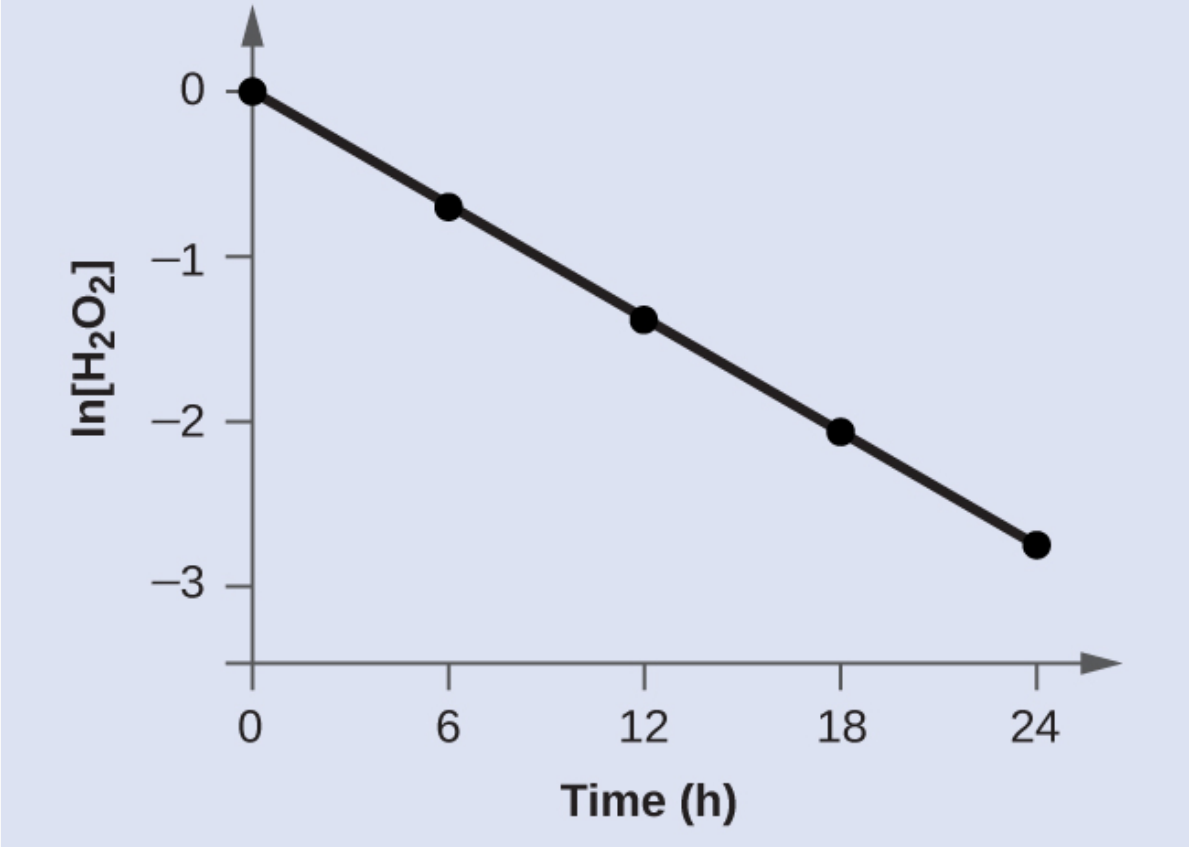
Solution

The data from Figure 6.2 are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure 8.1.

Time (h)	**$[H_2O_2]$ (M)**	**$\ln[H_2O_2]$**
0.00	1.000	0.000
6.00	0.500	−0.693
12.00	0.250	−1.386
18.00	0.125	−2.079
24.00	0.0625	−2.772

Figure 8.1

A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.



The plot of $\ln[H_2O_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[\mathrm{H_2O_2}]}{\Delta t}$$

The slope of this line may be derived from two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 0.00 h is 0.000; the value when t = 24.00 h is −2.772

$$\begin{aligned} \text{slope} &= \frac{-2.772-0.000}{24.00-0.00\ \text{h}} \\ &= \frac{-2.772}{24.00\ \text{h}} \\ &= -0.116\ \text{h}^{-1} \\ k &= -\text{slope} = -(-0.116\ \text{h}^{-1}) = 0.116\ \text{h}^{-1} \end{aligned}$$

Check Your Learning

Graph the following data to determine whether the reaction

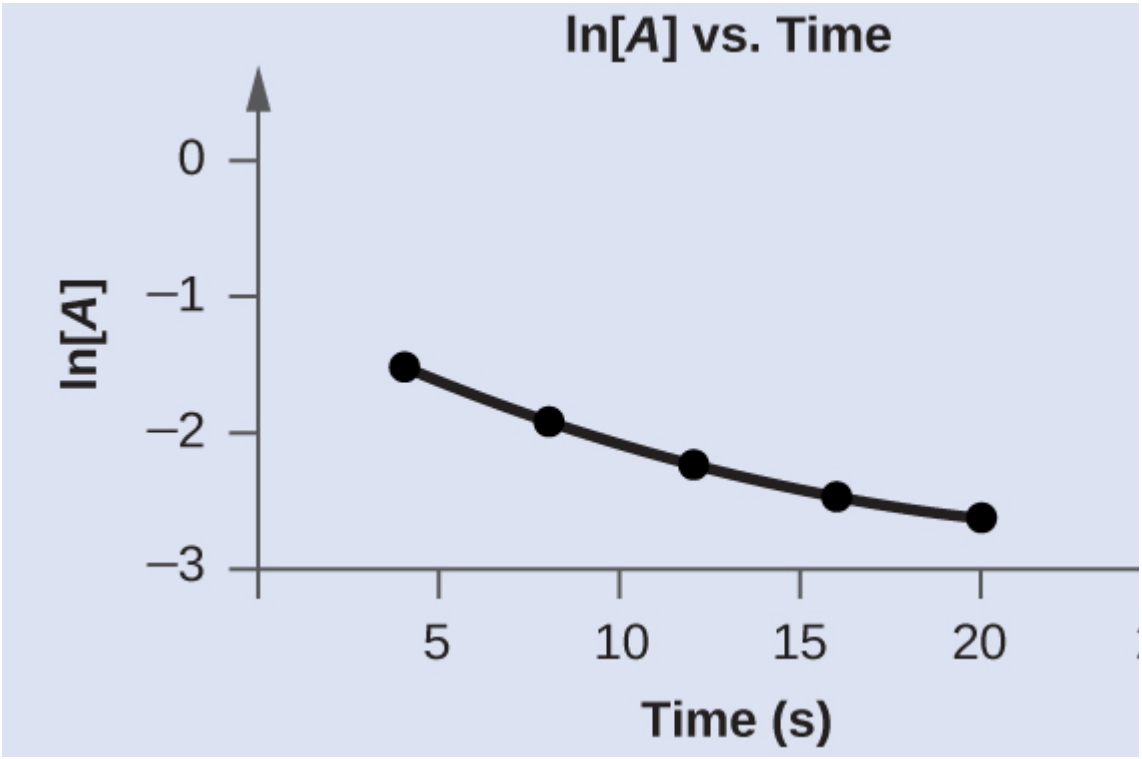
$$A \longrightarrow B + C$$

is first order.

Time (s)	[A]
4.0	0.220
8.0	0.144
12.0	0.110
16.0	0.088
20.0	0.074

Answer

The plot of $\ln[A]_t$ vs. t is not linear, indicating the reaction is not first order:



8.0.4 Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate} = k[A]^2$$

For the

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

EXAMPLE 8.0.5

The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This "dimerization" reaction is second order with a rate constant equal to 5.76

×

10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, k = 5.76

×

10^{-2} L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\begin{aligned}
\frac{1}{[A]_t} &= (5.76 \times 10^{-2}\ \text{L mol}^{-1}\ \text{min}^{-1})\,(10\ \text{min}) + \frac{1}{0.200\ \text{mol}^{-1}} \\
\frac{1}{[A]_t} &= (5.76 \times 10^{-1}\ \text{L mol}^{-1}) + 5.00\ \text{L mol}^{-1} \\
\frac{1}{[A]_t} &= 5.58\ \text{L mol}^{-1} \\
[A]_t &= 1.79 \times 10^{-1}\ \text{mol L}^{-1}
\end{aligned}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Check Your Learning

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0195 mol/L

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$\begin{aligned} \frac{1}{[A]_t} &= kt + \frac{1}{[A]_0} \\ y &= mx + b \end{aligned}$$

A plot of

$\frac{1}{[A]_t}$

versus t for a second-order reaction is a straight line with a slope of k and a y-intercept of

$\frac{1}{[A]_0}$.

If the plot is not a straight line, then the reaction is not second order.

EXAMPLE 8.0.6

Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 8.3. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

Time (s)	**$[C_4H_6]$ (*M*)**
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus t and compare it to a plot of

$$\frac{1}{[C_4H_6]_t}$$

versus t. The values needed for these plots follow.

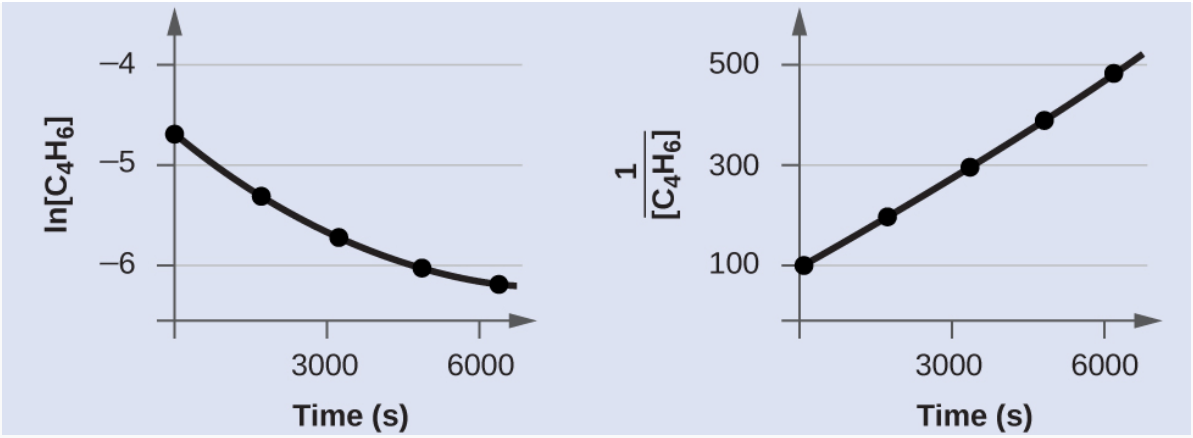
Time (s)	$\frac{1}{[C_4H_6]}$ (M^{-1})	**$\ln[C_4H_6]$**
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure 8.2, which clearly shows the plot of $\ln[C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of

$$\frac{1}{[C_4H_6]_t}$$

versus t is linear, indicating that the reaction is second order.

Figure 8.2
These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.



According to the second-order integrated rate law, the rate constant is equal to the slope of the

$\frac{1}{[A]_t}$

versus *t* plot. Using the data for *t* = 0 *s* and *t* = 6200 *s*, the rate constant is estimated as follows:

$$k = \text{slope} = \frac{(481\ M^{-1} - 100\ M^{-1})}{(6200\ \text{s} - 0\ \text{s})} = 0.0614\ \text{M}^{-1}\ \text{s}^{-1}$$

Check Your Learning

Do the following data fit a second-order rate law?

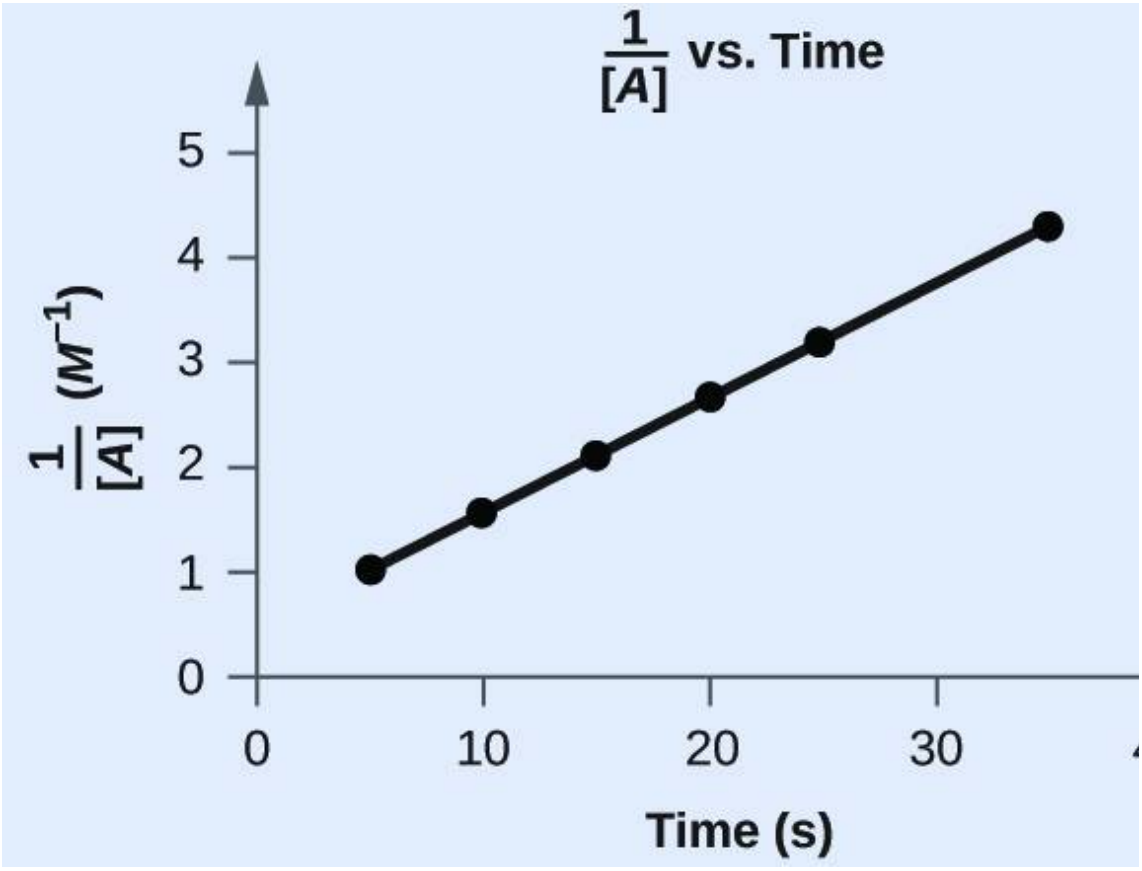
Time (s)	**[*A*] (*M*)**
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

Answer

Yes. The plot of

$\frac{1}{[A]_t}$

vs. *t* is linear:



8.0.7 Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate} = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$\begin{aligned} [A]_t &= -kt + [A]_0 \\ y &= mx + b \end{aligned}$$

A plot of [*A*] versus *t* for a zero-order reaction is a straight line with a slope of −*k* and a *y*-intercept of $[A]_0$. Figure 8.3 shows a plot of $[NH_3]$ versus *t* for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially

decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

EXAMPLE 8.0.8

Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure 8.3 to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, t, with a slope equal to the negative of the rate constant, $-k$. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at $t = 0$ and $t = 1000$ s:

$$k = -\text{slope} = -\frac{(0.0015 \text{ mol L}^{-1} - 0.0028 \text{ mol L}^{-1})}{(1000 \text{ s} - 0 \text{ s})} = 1.3 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

Check Your Learning

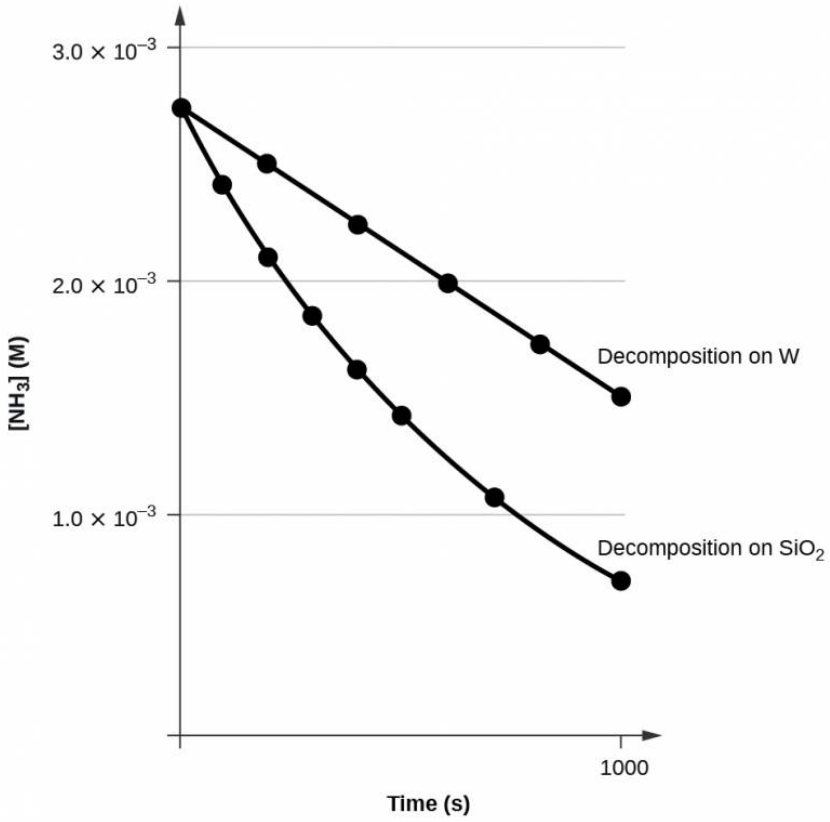
The zero-order plot in Figure 8.3 shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer

35 min

Figure 8.3

The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.



8.0.9 The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide (Figure 6.2) as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

8.0.9.1 First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

Invoking the definition of half-life, symbolized

$t_{1/2}$,

requires that the concentration of *A* at this point is one-half its initial concentration:

$t = t_{1/2}$,

$[A]_t = \frac{1}{2}[A]_0$.

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$\begin{aligned} t_{1/2} &= \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k} \\ &= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k} \\ t_{1/2} &= \frac{0.693}{k} \end{aligned}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

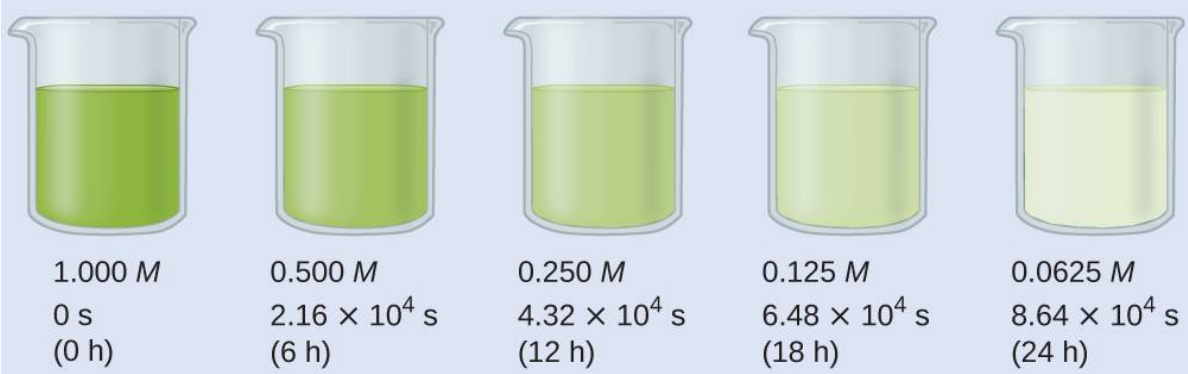
EXAMPLE 8.0.10

Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 8.4.

Figure 8.4

The decomposition of H_2O_2 ($2H_2O_2 \rightarrow 2H_2O + O_2$) at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.



Solution

Inspecting the concentration/time data in Figure 8.4 shows the half-life for the decomposition of H_2O_2 is 2.16

×

10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4\ \text{s}} = 3.21 \times 10^{-5}\ \text{s}^{-1}$$

Check Your Learning

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

8.0.10.1 Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\begin{aligned} \frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k[A]_0} \end{aligned}$$

For a second-order reaction,

$t_{1/2}$

is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life:

$t = t_{1/2}$

and

$[A] = \frac{[A]_0}{2}$.

Substituting these terms into the zero-order integrated rate law yields:

$$\begin{aligned} \frac{[\mathrm{A}]_0}{2} &= -kt_{1/2} + [\mathrm{A}]_0 \\ kt_{1/2} &= \frac{[\mathrm{A}]_0}{2} \\ t_{1/2} &= \frac{[A]_0}{2k} \end{aligned}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, the half-life of a zero-order reaction increases as the initial concentration increases.

Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table 8.1.

Table 8.5

Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	**First-Order**	**Second-Order**
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M\,s^{-1}$	s^{-1}	$M^{-1}\,s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + (\frac{1}{[A]_0})$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

EXAMPLE 8.0.11

Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example 8.3?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{[(0.0576\ \text{L mol}^{-1}\ \text{min}^{-1})(0.200\ \text{mol L}^{-1})]} = 18\ \text{min}$$

Check Your Learning

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure 8.3)?

Answer

87 min

Files

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Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (17.3-17.4)

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9

Temperature and Rate

Chemical reactions typically require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant, activation energy, temperature, and dependence on collision orientation.

9.1 Collision Theory

Learning Objectives

By the end of this section, you will be able to:

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\,\text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.

3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient amounts, the reaction will occur at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

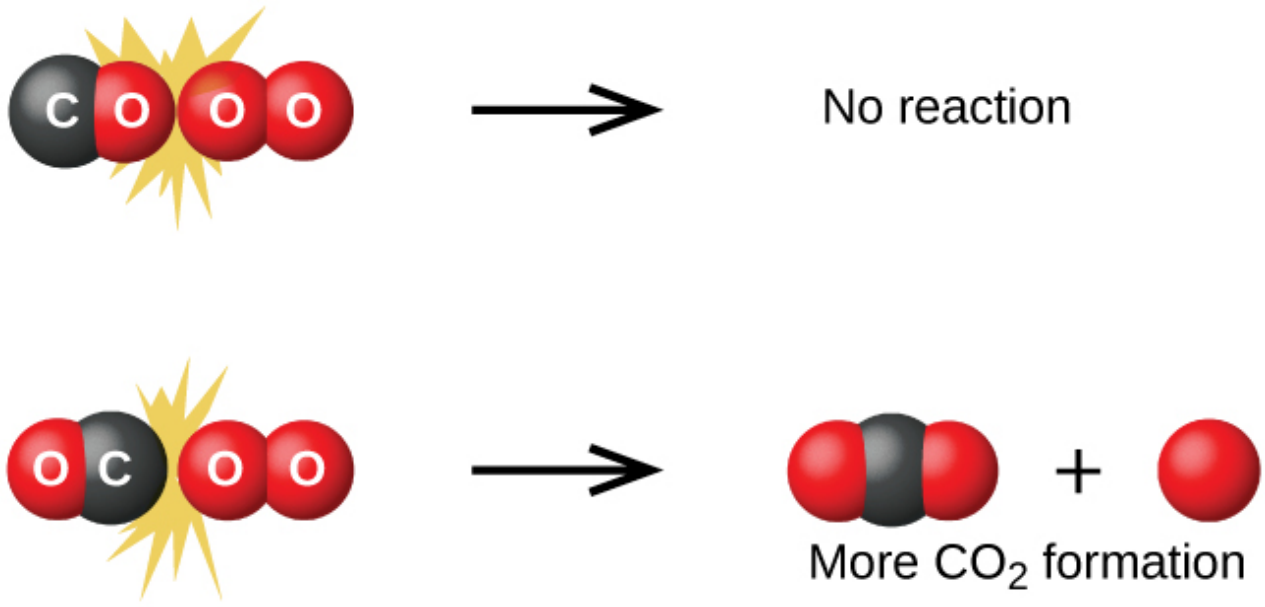
Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 9.1. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms

$(O = C = O)$.

This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

Figure 9.1

Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.



If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to

form an unstable species called an activated complex or a transition state. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

9.1.1 Activation Energy and the Arrhenius Equation

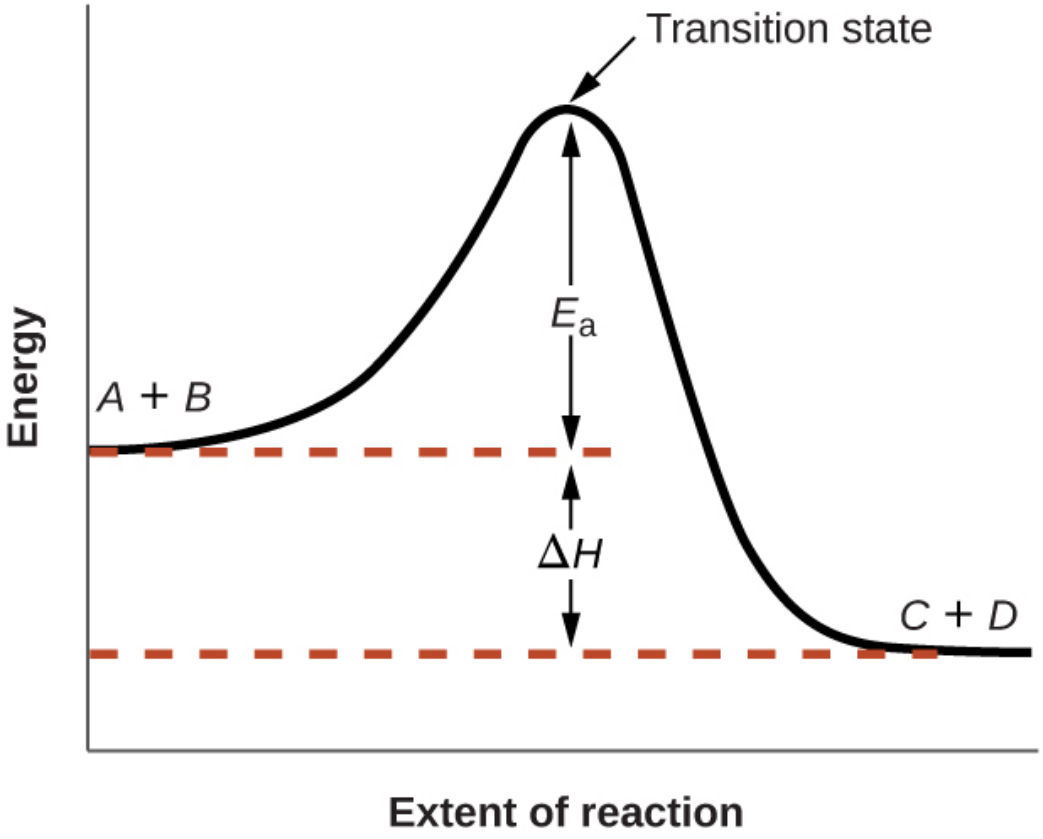
The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure 9.2 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$A + B \longrightarrow C + D$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, *A* + *B*. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, *C* + *D*. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

Figure 9.2
Reaction diagram for the exothermic reaction $A + B \longrightarrow C + D$.



The Arrhenius equation relates the activation energy and the rate constant, *k*, for many chemical reactions:

$$k = Ae^{-E_a/RT}$$

In this equation, *R* is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, *e* is the constant 2.7183, and *A* is a constant called the frequency factor, which is related to the frequency of collisions and the orientation of the reacting molecules.

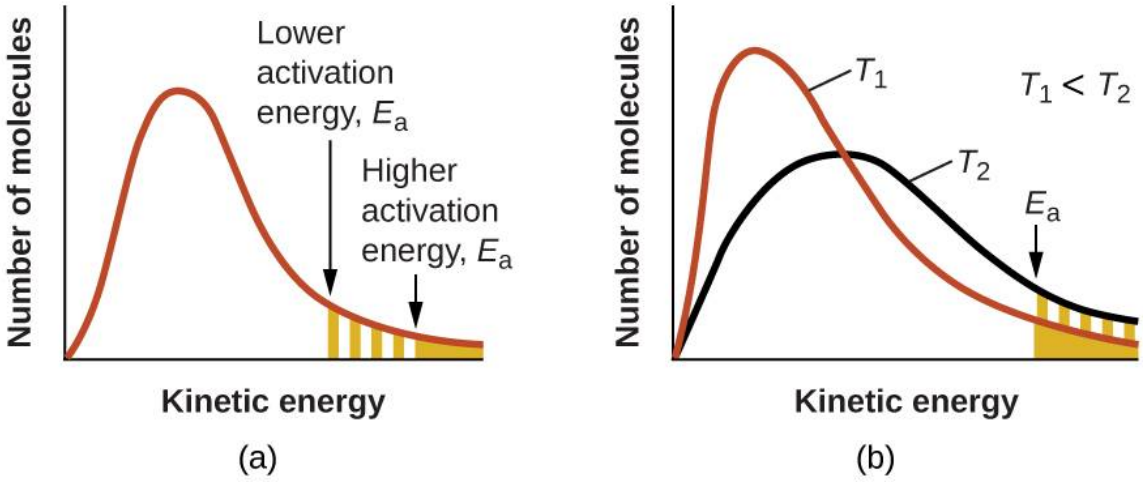
Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in Figure 9.3(**a**). Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in Figure 9.3(**b**). This yields a greater value for the rate constant and a correspondingly faster reaction rate.

Figure 9.3

Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.



A convenient approach for determining E_a for a reaction involves the measurement of k at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\begin{aligned} \ln k &= \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \\ y &= mx + b \end{aligned}$$

A plot of ln k versus

$\frac{1}{T}$

is linear with a slope equal to

$\frac{-E_a}{R}$

and a y-intercept equal to ln A.

EXAMPLE 9.1.2

Determination of E_a

The variation of the rate constant with temperature for the decomposition of HI(g) to H_2(g) and I_2(g) is given here. What is the activation energy for the reaction?

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

T **(K)**	***k*** **(L/mol/s)**
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}

T (K)	k (L/mol/s)
781	3.95×10^{-2}

Solution

Use the provided data to derive values of

$\frac{1}{T}$

and ln k:

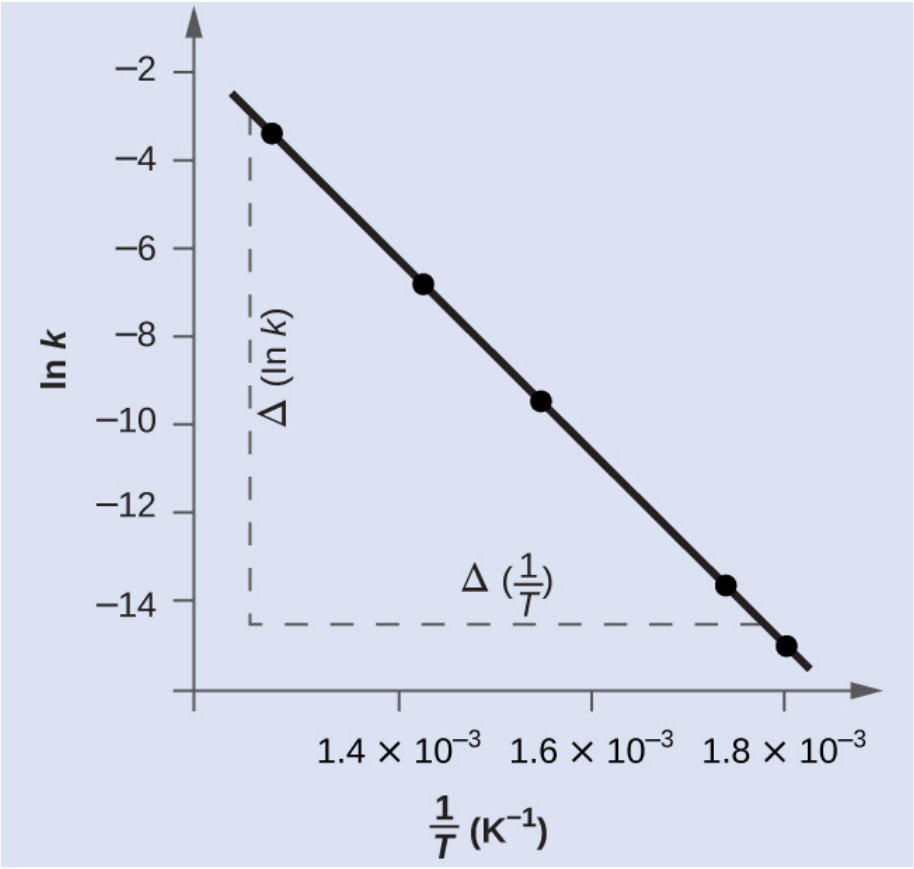
$\frac{1}{T}$ (K^{-1})	ln k
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 9.4 is a graph of ln k versus

$\frac{1}{T}$.

In practice, the equation of the line (slope and y-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

Figure 9.4
This graph shows the linear relationship between ln k and $\frac{1}{T}$ for the reaction $2\mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}$ according to the Arrhenius equation.



$$\begin{aligned}
\text{Slope} &= \frac{\Delta(\ln k)}{\Delta(\frac{1}{T})} \\
&= \frac{(-14.860) - (-3.231)}{(1.80 \times 10^{-3}\ \text{K}^{-1}) - (1.28 \times 10^{-3}\ \text{K}^{-1})} \\
&= \frac{-11.629}{0.52 \times 10^{-3}\ \text{K}^{-1}} = -2.2 \times 10^{4}\ \text{K} \\
&= -\frac{E_a}{R} \\
E_a &= -\text{slope} \times R = -(-2.2 \times 10^{4}\ \text{K} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \\
&\quad 1.8 \times 10^{5}\ \text{J mol}^{-1} \text{ or } 180\ \text{kJ mol}^{-1}
\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_a = -R \left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_a = -8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\left(\frac{-3.231-(-14.860)}{1.28\times10^{-3}\ \text{K}^{-1}\ -\ 1.80\times10^{-3}\ \text{K}^{-1}}\right)$$

and the result is E_a = 1.8

×

10^5 J mol^{-1} or 180 kJ mol^{-1}

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

Check Your Learning

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\text{N}_2\text{O}_5(g) \longrightarrow 4\text{NO}(g) + 3\text{O}_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

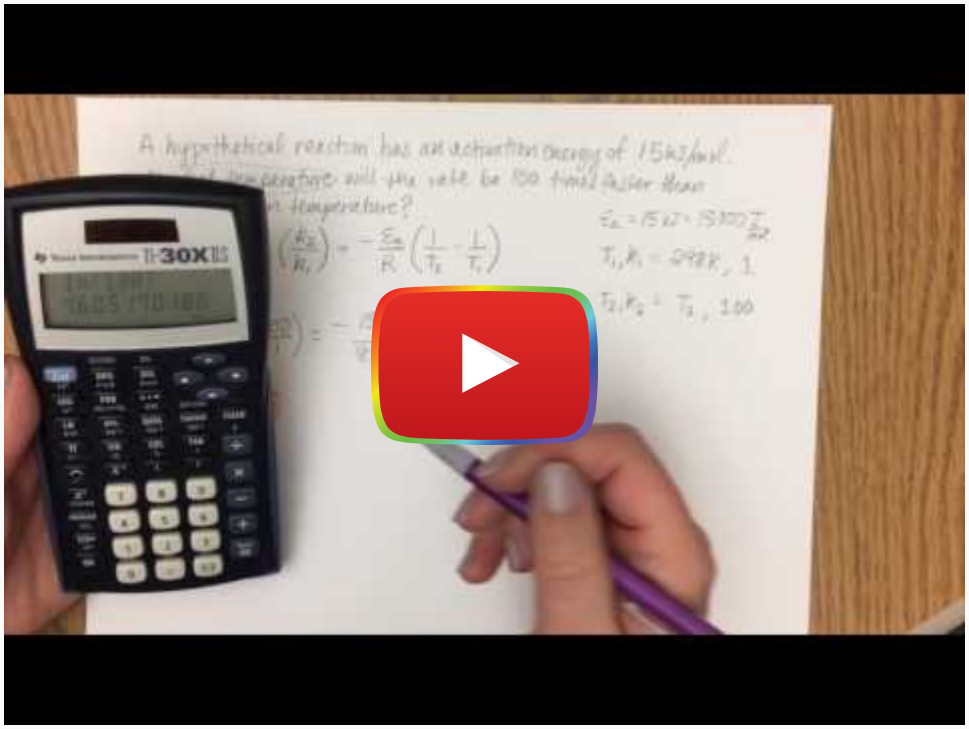
Answer

1.1

×

10^5 J mol^{-1} or 110 kJ mol^{-1}

Example: 9.1.3 Arrhenius Equation



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10

Reaction Mechanisms and Catalysis

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The molecularity of an elementary reaction is the number of reactant species involved, typically one (unimolecular), two (bimolecular), or, less commonly, three (termolecular). The overall rate of a reaction is determined by the rate of the slowest in its mechanism, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible. Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy, but they do not affect equilibrium. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

10.1 Reaction Mechanisms

Learning Objectives

By the end of this section, you will be able to:

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$\begin{aligned} \mathrm{O_3(g)} &\longrightarrow \mathrm{O_2(g) + O} \\ \mathrm{O + O_3(g)} &\longrightarrow \mathrm{2O_2(g)} \end{aligned}$$

Each of the steps in a reaction mechanism is an elementary reaction. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$A \longrightarrow \text{products}$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction *does not involve the direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

10.1.1 Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the reaction of a *single* reactant species to produce one or more molecules of product:

$$O_3 \longrightarrow O_2 + O$$

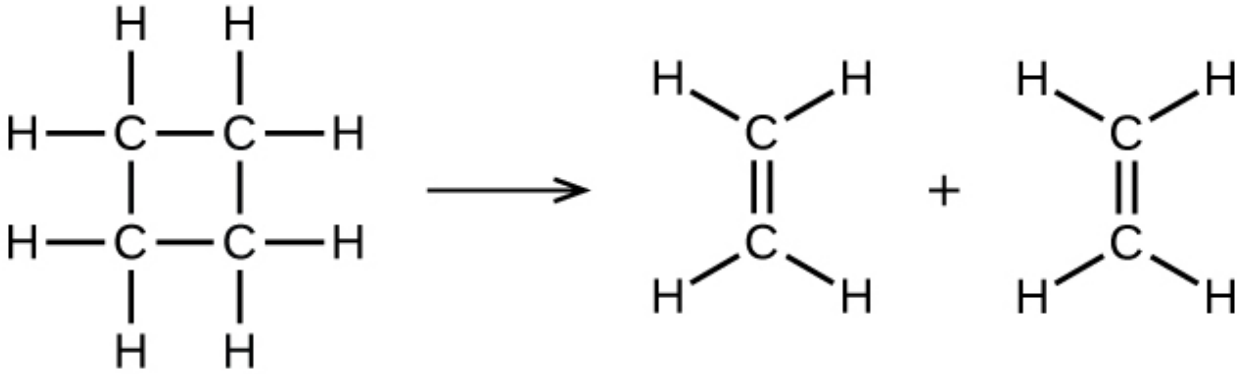
The rate law for a unimolecular reaction is first order:

$$A + B \longrightarrow \text{products}$$
$$\text{and}$$
$$2A \longrightarrow \text{products}$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$\text{rate} = k[A][A] = k[A]^2$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an "overall" reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

10.1.2 Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$2NO + Cl_2 \longrightarrow 2NOCl$$
$$\text{rate} = k[NO]^2[Cl_2]$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B* (second-order overall):

$$\text{rate} = k[NO_2][CO]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)\ (\text{slow})$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)\ (\text{fast})$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

(see Figure 10.1)

Figure 10.1

The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$$

10.1.3 Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$\begin{aligned} \text{rate}_1 &= \text{rate}_{-1} \\ k_1[\text{NO}][\text{Cl}_2] &= k_{-1}[\text{NOCl}_2] \\ [\text{NOCl}_2] &= \left(\frac{k_1}{k_{-1}}\right)[\text{NO}][\text{Cl}_2] \end{aligned}$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$\text{F}_2(g) \rightleftharpoons 2\text{F}(g) \text{ fast}$$

10.1.4 Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure 10.2.

Figure 10.2

A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$$

For temperatures above 225 °C, the rate law has been found to be:

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{diagram (a): } E_\mathrm{a} = 32\ \mathrm{kJ} - 6\ \mathrm{kJ} = 26\ \mathrm{kJ}$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$\mathrm{3O_2(g) \xrightarrow{h\nu} 2O_3(g)}$$

The rate-determining (slower) step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2. When this reaction is at equilibrium:

$$\begin{gathered}\mathrm{NO}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g) \\ \mathrm{O_3}(g) \longrightarrow \mathrm{O_2}(g) + \mathrm{O}(g) \\ \mathrm{NO_2}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{O_2}(g)\end{gathered}$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\mathrm{CH_3Cl} + \mathrm{OH} \longrightarrow \mathrm{Cl} + \text{other products}$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

EXAMPLE 10.1.5

Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$C_2H_4 + H_2 \longrightarrow C_2H_6 .$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$A \rightleftharpoons B$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\text{Rate}(r) = k(r)[B]$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, [$NOCl_2$]. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\text{Rate}_f = \text{Rate}_r \text{ so } k(f)[A] = k(r)[B]$$

Substituting this expression into the rate law for step 2 yields:

$$K = \frac{[B]}{[A]}$$

Check Your Learning

The first step of a proposed multistep mechanism is:

$$F_2(g) \rightleftharpoons 2F(g) \text{ fast}$$

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

10.2 Catalysis

Learning Objectives

By the end of this section, you will be able to:

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

10.2.1 Catalysts Do Not Affect Equilibrium

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

$$\text{diagram (a): } E_a = 32\ \text{kJ} - 6\ \text{kJ} = 26\ \text{kJ}$$

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.

10.2.2 PORTRAIT OF A CHEMIST

Fritz Haber

In the early 20th century, German chemist Fritz Haber (Figure 10.3) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient, to ammonia, a form of nitrogen that is easiest for plants to absorb.

$$\begin{aligned} O_3 &\longrightarrow O_2 + O \\ O + O_3 &\longrightarrow 2O_2 \end{aligned}$$

The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (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).

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. 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. 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.

Figure 10.3

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.

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.

$$CH_3Cl + OH \longrightarrow Cl + \text{other products}$$

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:

$$2NO_2(g) \longrightarrow N_2(g) + 2O_2(g)$$
$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$
$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

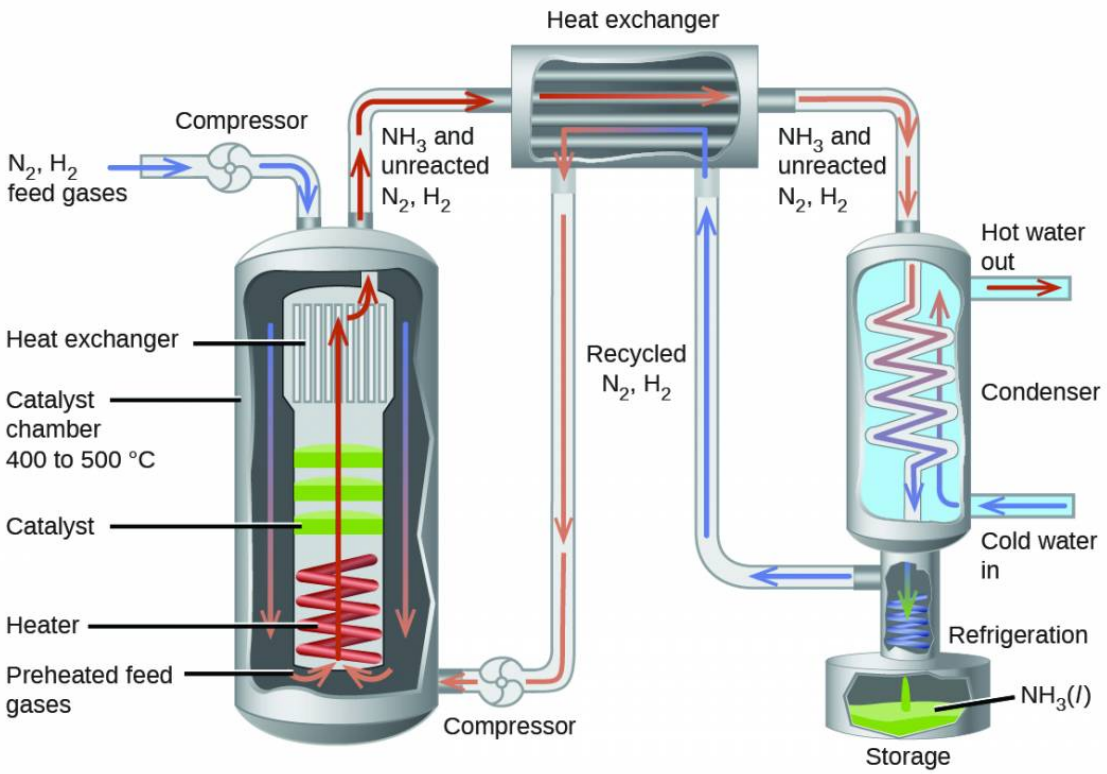
Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

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 10.4).

Figure 10.4

Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.



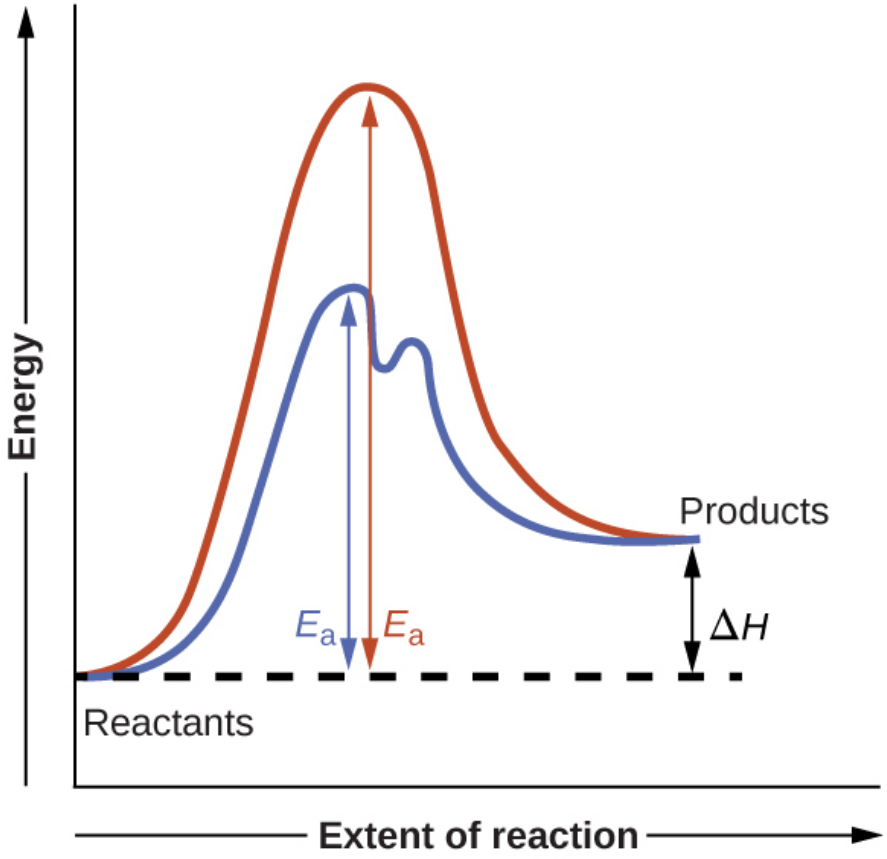
Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the

previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 10.5 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

Figure 10.5

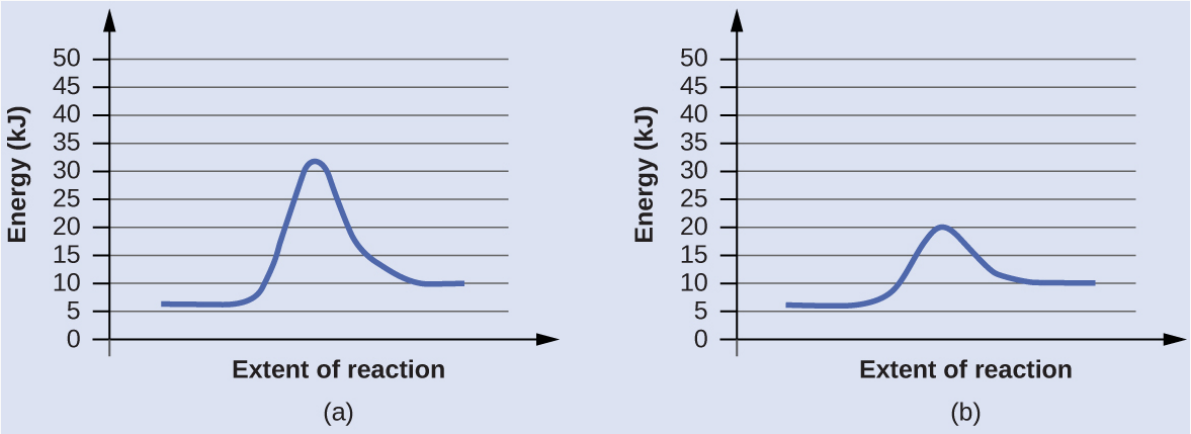
Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).



EXAMPLE 10.2.3

Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

Activation energies are calculated by subtracting the reactant energy from the transition state energy.

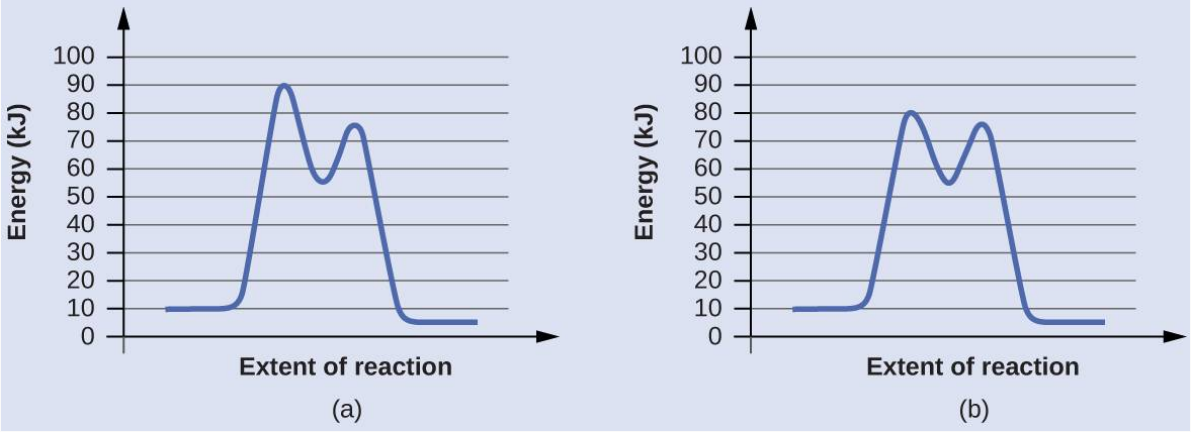
$$\text{Rate}(r) = k(r)[B]$$

$$\frac{k(f)}{k(r)} = \frac{[B]}{[A]}$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram (b).

Check Your Learning

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

10.2.4 Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following two-step mechanism:

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide -catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

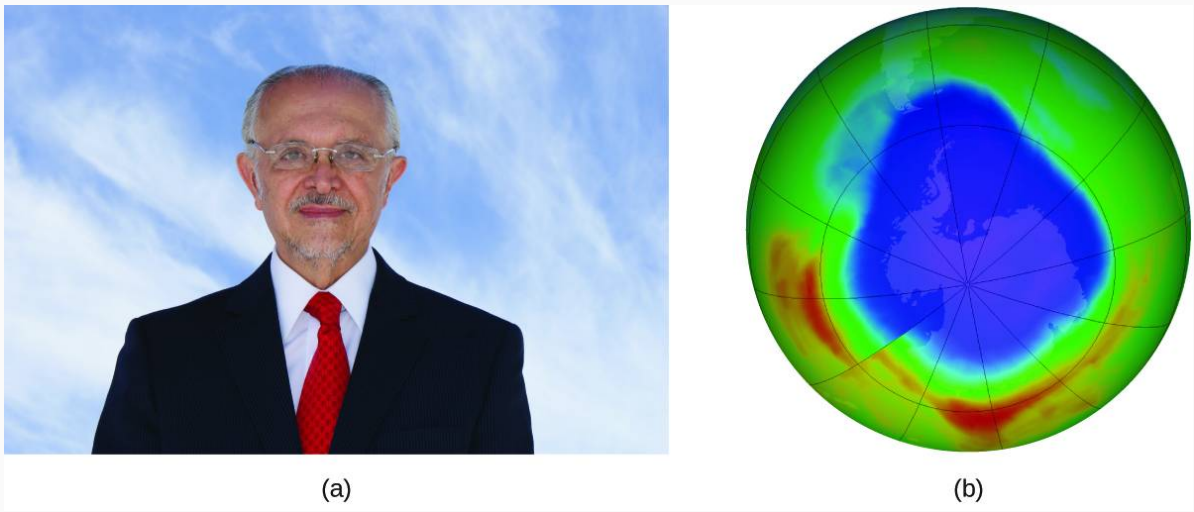
10.2.5 PORTRAIT OF A CHEMIST

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 10.6), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[2] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).

Figure 10.6

(a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)



(a) (b)

In 1974, Molina and Rowland published a paper in the journal *Nature* detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

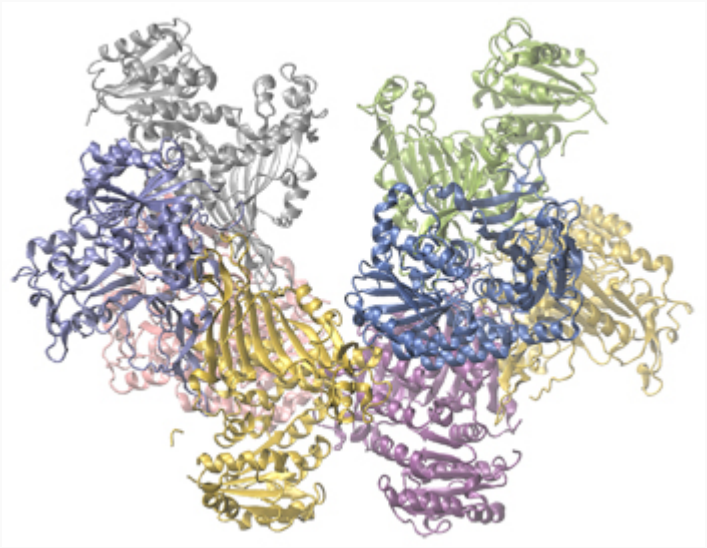
10.2.6 HOW SCIENCES INTERCONNECT

Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 10.7, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 10.8).

Figure 10.7

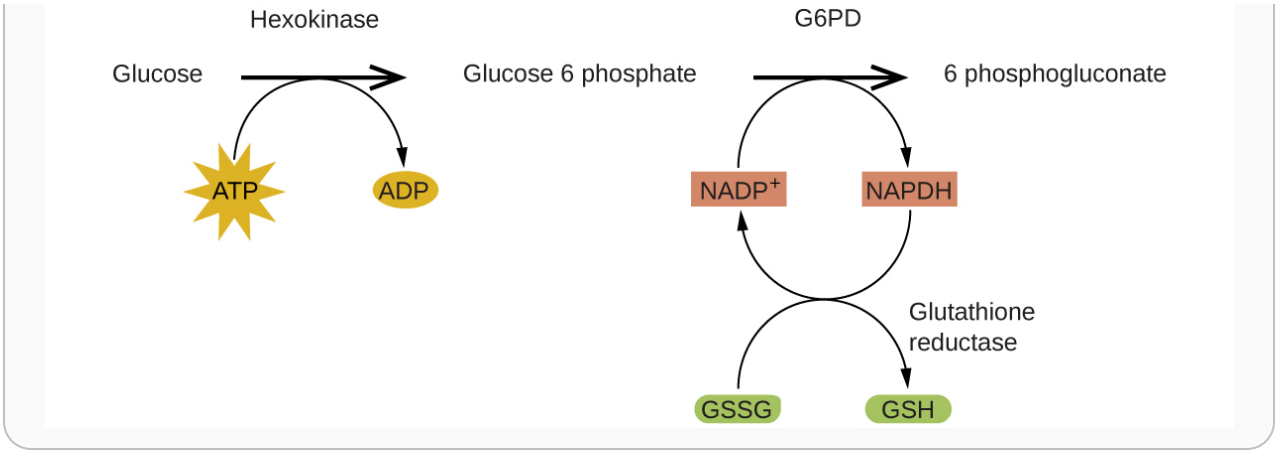
Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.



A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

Figure 10.8

In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.



10.2.7 Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

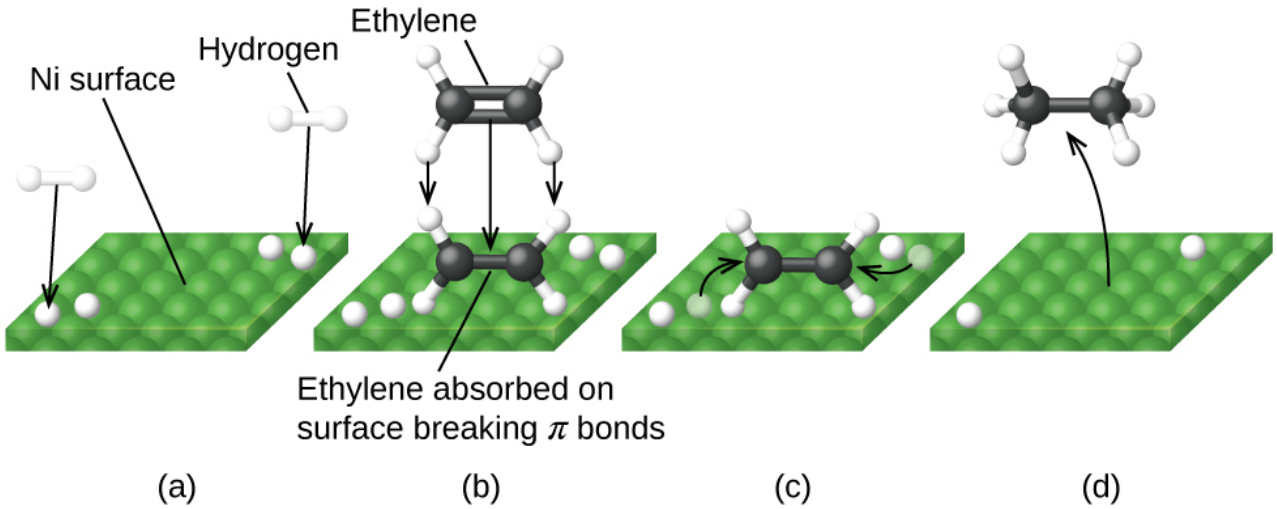
Heterogeneous catalysis typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)
4. Desorption of product(s) from the surface of the catalyst

Figure 10.9 illustrates the steps of a mechanism for the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

Figure 10.9

Mechanism for the Ni-catalyzed reaction (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C-C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.



Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 10.10).

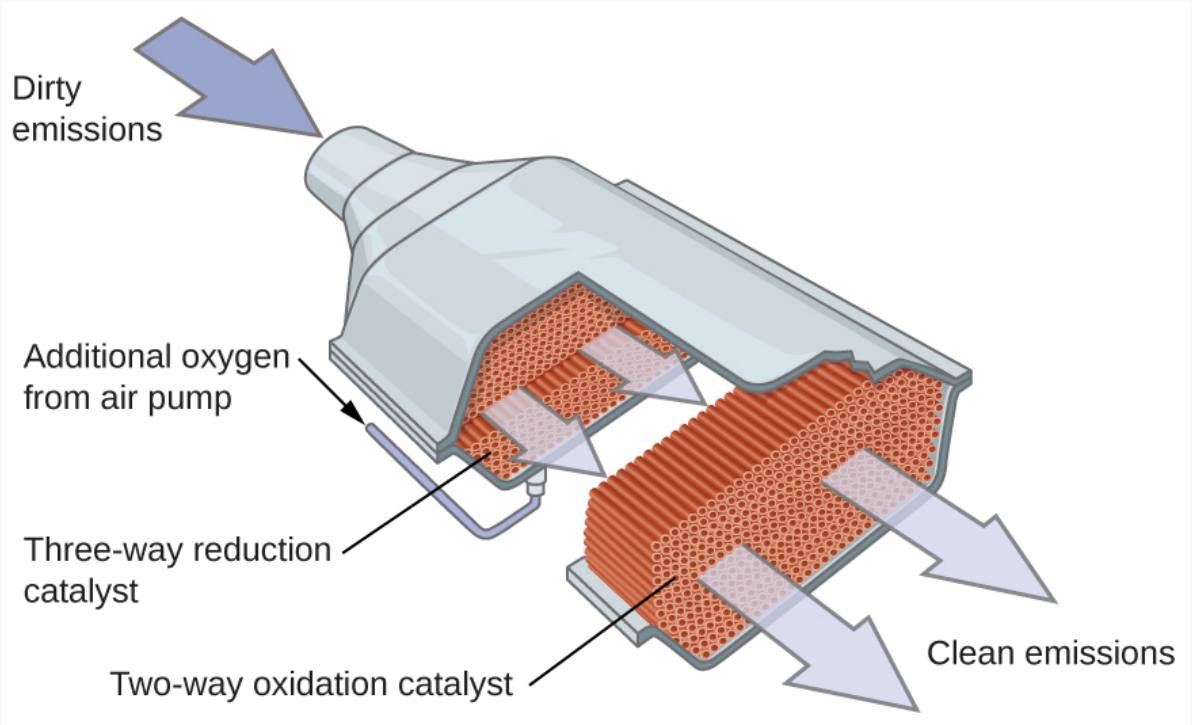
10.2.8 CHEMISTRY IN EVERYDAY LIFE

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 10.10).

Figure 10.10

A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.



Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

LINK TO LEARNING

The University of California at Davis' "ChemWiki" provides a thorough explanation of how catalytic converters work.

10.2.9 HOW SCIENCES INTERCONNECT

Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 10.1.

Table 10.11

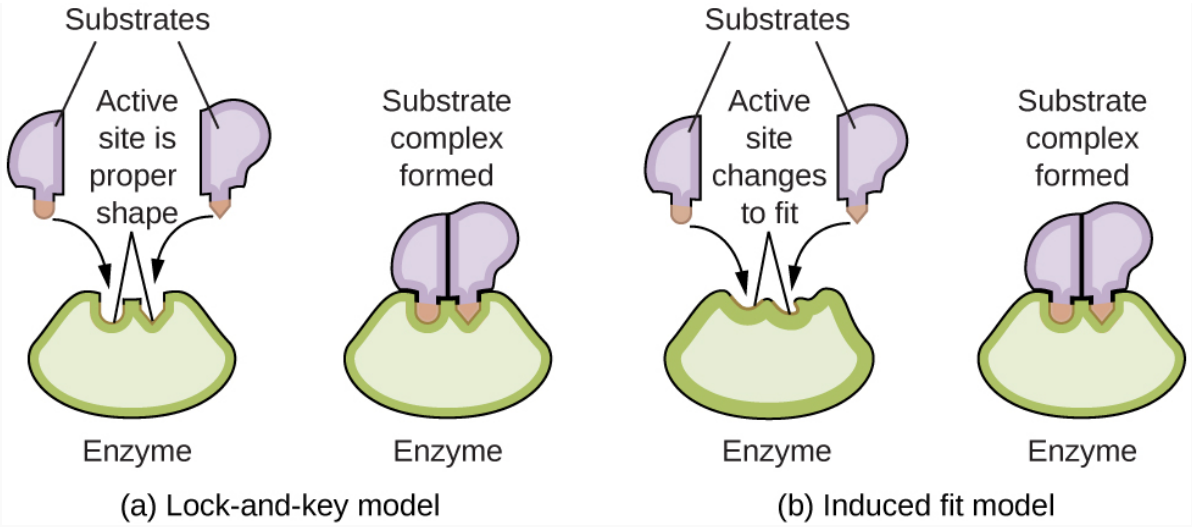
Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 10.11).

Figure 10.12

(a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.



LINK TO LEARNING

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

The connection between the rate of a reaction and its equilibrium constant is one we can easily determine with just a bit of algebraic substitution. For a reaction where substance A forms B (and the reverse)

The rate of the forward reaction is

And the rate of the reverse reaction is

Once equilibrium is established, the rates of the forward and reverse reactions are equal:

Rearranging a bit, we get

Also recall that the equilibrium constant is simply the ratio of product to reactant concentration at equilibrium:

So the equilibrium constant turns out to be the ratio of the forward to the reverse rate constants. This relationship also helps cement our understanding of the nature of a catalyst. That is, a catalyst does not change the fundamental equilibrium (or the underlying thermodynamics) of a reaction. Rather, what it does is alter the rate constant for the reaction – that is, both rate constants, forward and reverse, equally. In doing so, catalysts usually speed up the rate at which reactions attain equilibrium (though they can be used to slow down the rate of reaction as well!).

Files

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Unit 3

Nuclear Chemistry

Welcome to your new content! Start typing here to get started!

- Radioactive Decay
- Rates of Decay, Radiodating
- Fission and Fusion
- Biological Effects

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11

Radioactive Decay

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged. Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope.

11.1 Structure and Stability

Learning Objectives

By the end of this section, you will be able to:

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of

$^{1}_{1}\mathrm{H}$,

neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation

$$^{A}_{Z}\mathrm{X},$$

where X is the symbol for the element, A is the mass number, and Z is the atomic number (for example,

$$^{14}_{6}\mathrm{C}) .$$

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example,

$$^{14}_{6}\mathrm{C}$$

is called “carbon-14.”

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8

$\times$

10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth’s density were equal to the average nuclear density, the earth’s radius would be only about 200 meters (earth’s actual radius is approximately 6.4

$\times$

10^6 meters, 30,000 times larger). Example 11.1 demonstrates just how great nuclear densities can be in the natural world.

EXAMPLE 11.1

Density of a Neutron Star

Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass =

$M_\odot$

= mass of the sun = 1.99

$\times$

10^{30} kg) and a diameter of 26 km.
(a) What is the density of this neutron star?

(b) How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution

We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

$$d = \frac{m}{V} \qquad \text{with} \qquad V = \frac{4}{3}\pi r^3$$

(a) The radius of the neutron star is

$$\tfrac{1}{2} \times 26 \text{ km} = \tfrac{1}{2} \times 2.6 \times 10^4 \text{ m} = 1.3 \times 10^4 \text{ m},$$

so the density of the neutron star is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{2.4(1.99 \times 10^{30} \text{ kg})}{\frac{4}{3}\pi(1.3 \times 10^4 \text{ m})^3} = 5.2 \times 10^{17} \text{ kg/m}^3$$

(b) The radius of the U-235 nucleus is

$$\tfrac{1}{2} \times 15 \times 10^{-15} \text{ m} = 7.5 \times 10^{-15} \text{ m},$$

so the density of the U-235 nucleus is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{235 \text{ amu}(\frac{1.66 \times 10^{-27} \text{kg}}{1 \text{ amu}})}{\frac{4}{3}\pi(7.5 \times 10^{-15} \text{ m})^3} = 2.2 \times 10^{17} \text{ kg/m}^3$$

These values are fairly similar (same order of magnitude), but the neutron star is more than twice as dense as the U-235 nucleus.

Check Your Learning

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of 1.75 fm (1 fm = 1

×

10^{-15} m).

Answer

The density of the neutron star is 3.4

×

10^{18} kg/m^3. The density of a hydrogen nucleus is 6.0

×

10^{17} kg/m^3. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the strong nuclear force. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

LINK TO LEARNING

Visit this website for more information about the four fundamental forces.

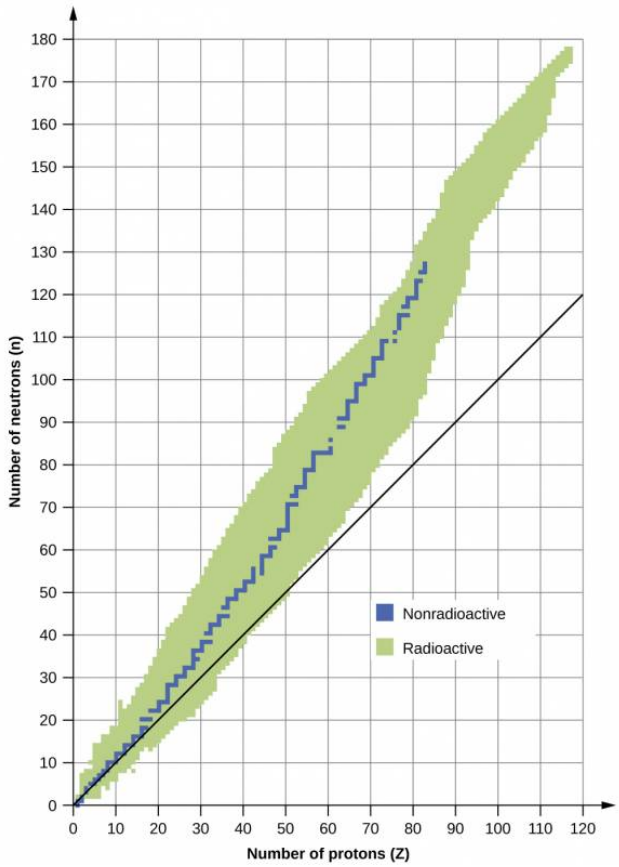
11.1.2 Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the band of stability (also called the belt, zone, or valley of stability). The straight line in Figure 11.1 represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and

neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

Figure 11.1

This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.



The nuclei that are to the left or to the right of the band of stability are unstable and exhibit radioactivity. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or radioisotope) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see Table 11.1). Nuclei with certain numbers of nucleons, known as magic numbers, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as

$^{4}_{2}\mathrm{He}$,

$^{16}_{8}\mathrm{O}$,

$^{40}_{20}\mathrm{Ca}$,

and

$^{208}_{82}\mathrm{Pb}$,

are called “double magic” and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Table 11.2

Stable Nuclear Isotopes

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

11.2 Nuclear Equations

Learning Objectives

By the end of this section, you will be able to:

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

11.2.1 Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure 11.2. Protons

$(^{1}_{1}\mathrm{p}$,

also represented by the symbol

$^{1}_{1}\mathrm{H})$

and neutrons

$(^{1}_{0}\mathrm{n})$

are the constituents of atomic nuclei, and have been described previously. Alpha particles

$(^{4}_{2}\mathrm{He},$

also represented by the symbol

$^{4}_{2}\alpha)$

are high-energy helium nuclei. Beta particles

$(^{0}_{-1}\beta,$

also represented by the symbol

$^{0}_{-1}\mathrm{e})$

are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. Positrons

$(^{0}_{+1}\mathrm{e},$

also represented by the symbol

$^{0}_{+1}\beta)$

are positively charged electrons (“anti-electrons”). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized

$^{4}_{2}\mathrm{He}\,.$

This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Figure 11.3

Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Name	Symbol(s)	Representation	Description
Alpha particle	^4_2He or $^4_2\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$^0_{-1}\text{e}$ or $^0_{-1}\beta$		(High-energy) electrons
Positron	$^0_{+1}\text{e}$ or $^0_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	^1_1H or ^1_1p		Nuclei of hydrogen atoms
Neutron	^1_0n		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of antimatter, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of gamma rays (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$$^0_{-1}\text{e} + ^0_{+1}\text{e} \longrightarrow \gamma + \gamma$$

As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are a type of high energy electromagnetic radiation produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

11.2.2 Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of nucleons (subatomic particles within the atoms' nuclei) rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that

$^{17}_{8}\mathrm{O}$

is a product of the nuclear reaction of

$^{14}_{7}\mathrm{N}$

and

$^{4}_{2}\mathrm{He}$

if we knew that a proton,

$^{1}_{1}\mathrm{H},$

was one of the two products. Example 11.2 shows how we can identify a nuclide by balancing the nuclear reaction.

EXAMPLE 11.2.3

Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25

$(^{25}_{12}\mathrm{Mg})$

produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\mathrm{Mg} + ^{4}_{2}\mathrm{He} \longrightarrow ^{1}_{1}\mathrm{H} + ^{A}_{Z}\mathrm{X}$$

where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = A + 1, \text{ or } A = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = Z + 1, \text{ and } Z = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is

$^{28}_{13}\mathrm{Al}$.

Check Your Learning

The nuclide

$^{125}_{53}\mathrm{I}$

combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$^{125}_{53}\mathrm{I} + ^{0}_{-1}\mathrm{e} \longrightarrow ^{125}_{52}\mathrm{Te}$$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

11.3 Radioactive Decay

Learning Objectives

By the end of this section, you will be able to:

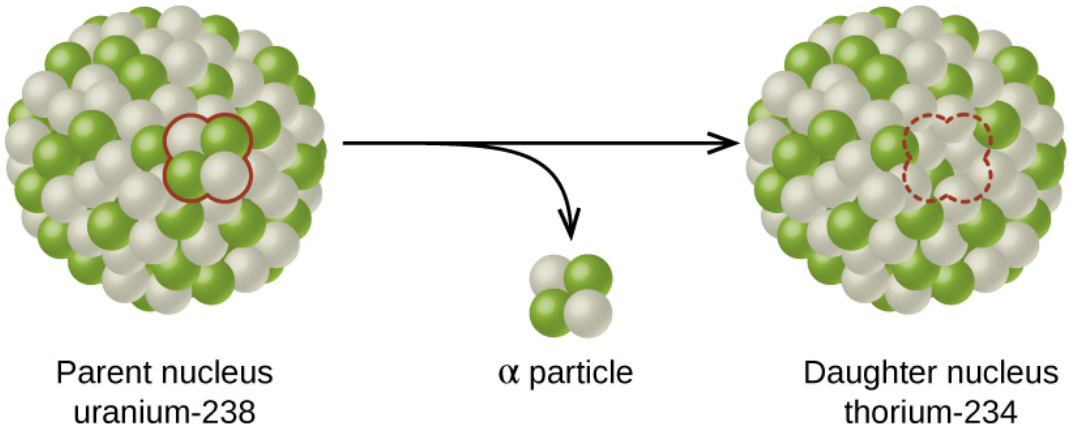
- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term “radioactivity,” and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is radioactive decay. The unstable nuclide is called the parent nuclide; the nuclide that results from the decay is known as the daughter nuclide. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure 11.3).

Figure 11.4

A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.



LINK TO LEARNING

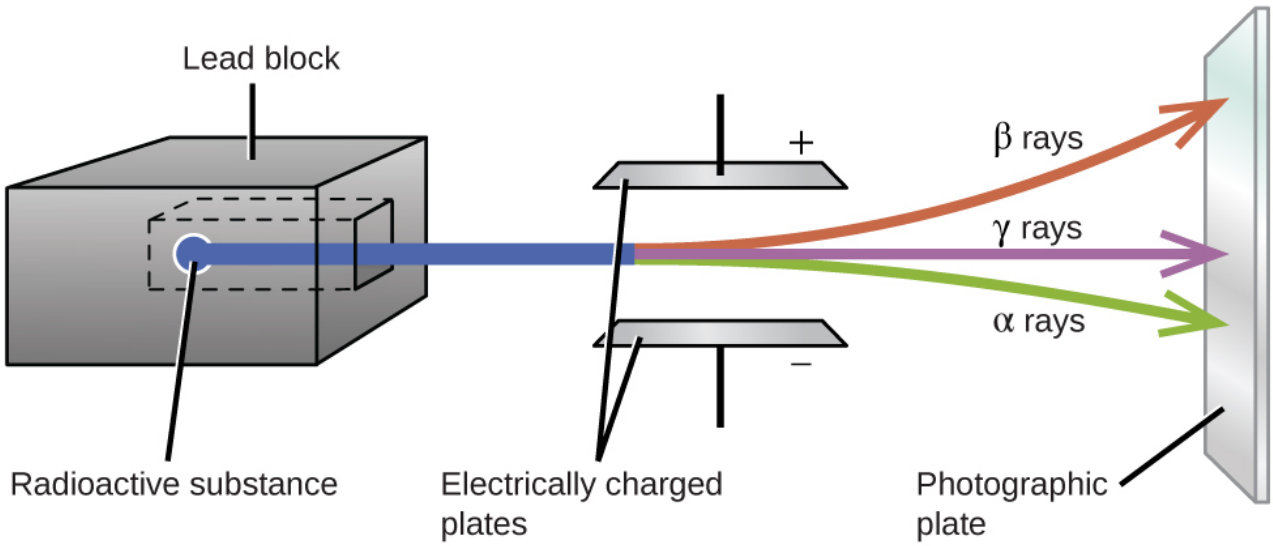
Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

11.3.1 Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 11.4) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

Figure 11.5

Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.



Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb} \qquad \text{or} \qquad {}^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\text{Pb}$$

Alpha decay occurs primarily in heavy nuclei (A > 200, Z > 83). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to Figure 11.1), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\text{e} + {}^{131}_{54}\text{Xe} \qquad \text{or} \qquad {}^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\text{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\text{Co}^{*} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\text{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^+ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\mathrm{e} + {}^{15}_{7}\mathrm{N} \qquad \text{or} \qquad {}^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}\mathrm{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

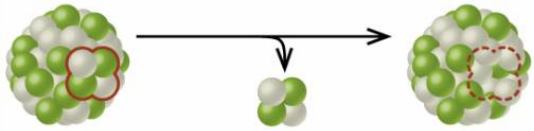
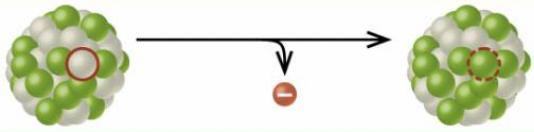
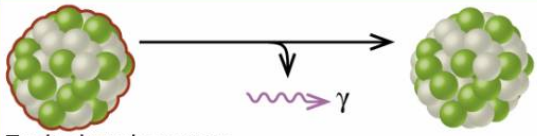
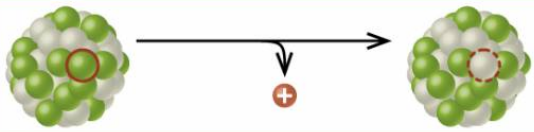
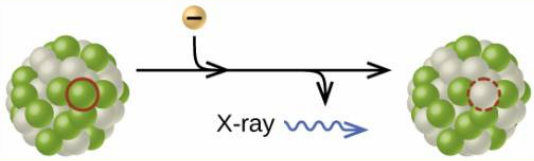
$$^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure 11.5 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

Figure 11.6

This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$	 Excited nuclear state	A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

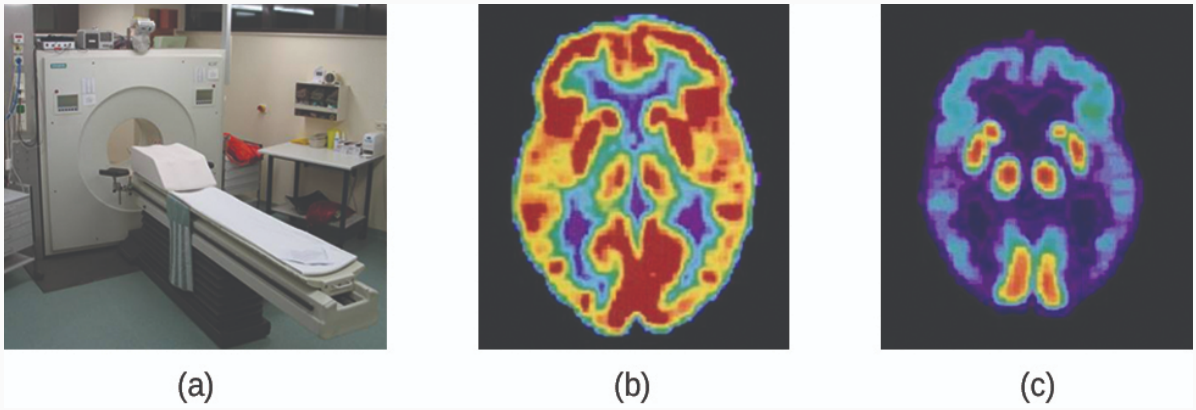
11.3.2 CHEMISTRY IN EVERYDAY LIFE

PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (Figure 11.6). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

Figure 12.7

A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)



(a) (b) (c)

For example, F-18 is produced by proton bombardment of ^{18}O

$$(^{18}_{8}\mathrm{O} + ^{1}_{1}\mathrm{p} \longrightarrow ^{18}_{9}\mathrm{F} + ^{1}_{0}\mathrm{n})$$

and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

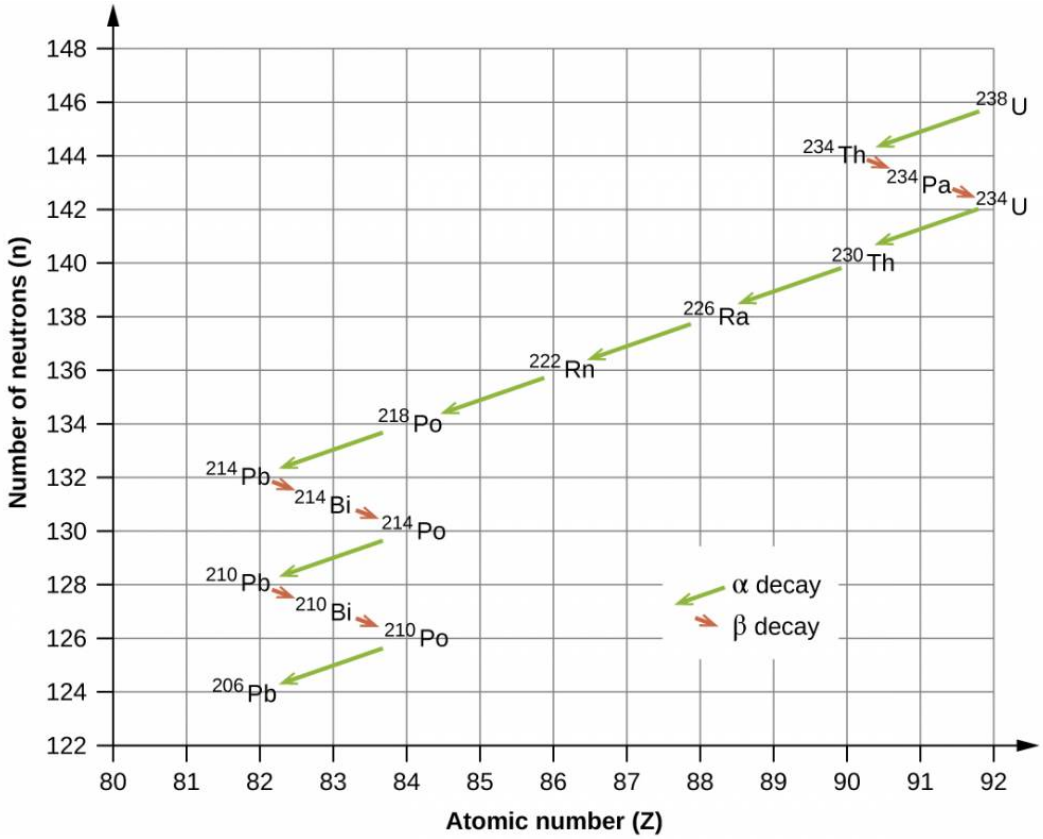
11.3.3 Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these

series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure 11.7). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

Figure 12.8

Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.



Example: 11.3.4 Radioactive Decay

Watch on YouTube

Files

Open in Google Drive

Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (20.1-20.3)

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12

Rates of Decay, Radiodating

All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more. It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

12.1 Radioactive Decay

Learning Objectives

- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

12.1.1 Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure 12.1). In a given cobalt-60 source, since half of the

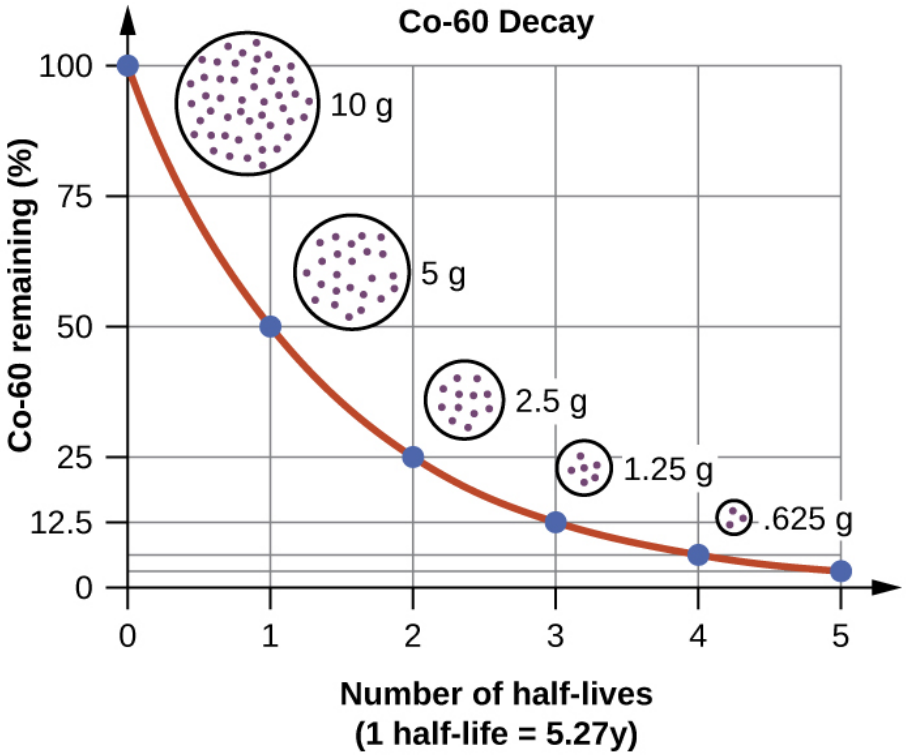
$$^{60}_{27}\text{Co}$$

nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order

kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

Figure 12.1

For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.



Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, *N*, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is:

decay rate = λN with λ = the decay constant for the particular radioisotope

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \qquad \text{or} \qquad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, *N*, and time are:

$$N_t = N_0 e^{-\lambda t} \qquad \text{or} \qquad t = -\frac{1}{\lambda} \ln\left(\frac{N_t}{N_0}\right)$$

where N_0 is the initial number of nuclei or moles of the isotope, and N_t is the number of nuclei/moles remaining at time *t*. Example 12.1 applies these calculations to find the rates of radioactive decay for specific nuclides.

EXAMPLE 12.1.2

Rates of Radioactive Decay

$^{60}_{27}\text{Co}$

decays with a half-life of 5.27 years to produce

$^{60}_{28}\text{Ni}$.

(a) What is the decay constant for the radioactive disintegration of cobalt-60?

(b) Calculate the fraction of a sample of the

$^{60}_{27}\text{Co}$

isotope that will remain after 15 years.

(c) How long does it take for a sample of

$^{60}_{27}\text{Co}$

to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27\ \text{y}} = 0.132\ \text{y}^{-1}$$

(b) The fraction of

$^{60}_{27}\text{Co}$

that is left after time t is given by

$\frac{N_t}{N_0}$.

Rearranging the first-order relationship $N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15\times\text{y})} = 0.138$$

The fraction of

$^{60}_{27}\text{Co}$

that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the

$^{60}_{27}\text{Co}$

originally present will remain after 15 years.

(c) 2.00% of the original amount of

$^{60}_{27}\text{Co}$

is equal to 0.0200

×

N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\ \text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6\ \text{y}$$

Check Your Learning

Radon-222,

$^{222}_{86}\text{Rn},$

has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer

11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of

$^{209}_{83}\text{Bi}$

is 1.9×10^{19} years;

$^{239}_{94}\text{Ra}$

is 24,000 years;

$^{222}_{86}\text{Rn}$

is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 12.1, and others are listed in Appendix M.

Table 12.2

Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

12.1.3 Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is radiometric dating and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

12.1.3.1 Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called radiocarbon dating or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes:

$^{12}_{6}\text{C},$

which constitutes about 99% of the carbon on earth;

$^{13}_{6}\text{C},$

about 1% of the total; and trace amounts of

$^{14}_{6}\text{C}.$

Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\text{N} + {}^{1}_{0}\text{n} \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of

$$^{14}_{6}CO_2$$

to

$$^{12}_{6}CO_2$$

depends on the ratio of

$$^{14}_{6}CO$$

to

$$^{12}_{6}CO$$

in the atmosphere. The natural abundance of

$$^{14}_{6}CO$$

in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of

$$^{14}_{6}C^{14}_{6}CO_2$$

and

$$^{12}_{6}CO_2$$

into plants is a regular part of the photosynthesis process, which means that the

$$^{14}_{6}C:\ ^{12}_{6}C$$

ratio found in a living plant is the same as the

$$^{14}_{6}C:\ ^{12}_{6}C$$

ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because

$$^{12}_{6}C$$

is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

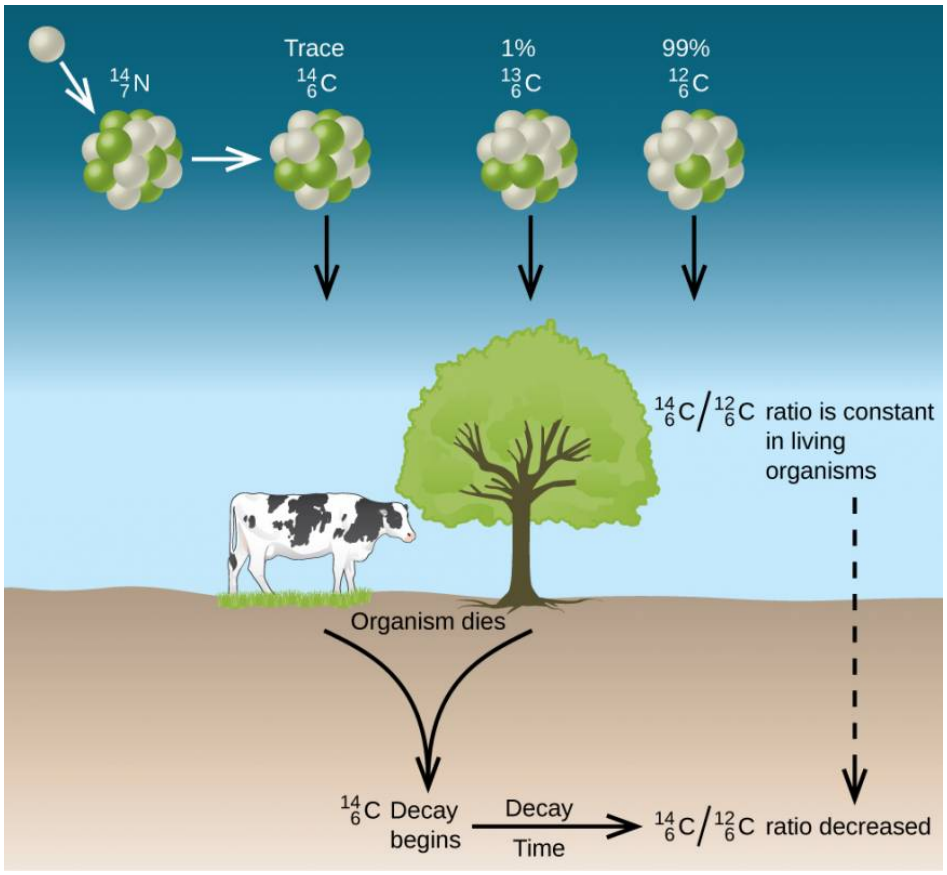
Thus, the

$^{14}_{6}\mathrm{C}:{}^{12}_{6}\mathrm{C}$

ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure 12.2 visually depicts this process.

Figure 12.3

Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).



For example, with the half-life of

$^{14}_{6}\mathrm{C}$

being 5730 years, if the

$^{14}_{6}\mathrm{C}:{}^{12}_{6}\mathrm{C}$

ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of

$^{14}_{6}\mathrm{C}$: $^{12}_{6}\mathrm{C}$

ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

LINK TO LEARNING

Visit this website to perform simulations of radiometric dating.

EXAMPLE 12.1.4

12.1.4.1 Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, *N*, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript *t* represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\ \text{y}} = 1.21 \times 10^{-4}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4}\ \text{y}^{-1}}\ln\left(\frac{10.8\ \text{dis/min/g C}}{13.6\ \text{dis/min/g C}}\right) = 1910\ \text{y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 12.3).

Figure 12.4

Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Check Your Learning

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer

about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the

$^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$

ratio. The accuracy of a straightforward application of this technique depends on the

$^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$

ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely

$^{12}_{6}\text{CO}_2$)

in the atmosphere caused by combustion of fossil fuels (in which essentially all of the

$^{14}_{6}\text{C}$

has decayed), the ratio of

$^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$

in the atmosphere may be changing. This manmade increase in

$^{12}_{6}\text{CO}_2$

in the atmosphere causes the

$^{14}_{6}\text{C}:\,^{12}_{6}\text{C}$

ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

12.1.4.2 Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is

indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

EXAMPLE 12.1.5

Radioactive Dating of Rocks

An igneous rock contains 9.58

×

10^{-5} g of U-238 and 2.51

×

10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.
The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5}\ \text{g U} \times \left(\frac{1\ \text{mol U}}{238\ \text{g U}}\right) = 4.03 \times 10^{-7}\ \text{mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5}\ \text{g Pb} \times \left(\frac{1\ \text{mol Pb}}{206\ \text{g Pb}}\right) \times \left(\frac{1\ \text{mol U}}{1\ \text{mol Pb}}\right) = 1.22 \times 10^{-7}\ \text{mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7}\ \text{mol} + 1.22 \times 10^{-7}\ \text{mol} = 5.25 \times 10^{-7}\ \text{mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda} \ln\left(\frac{N_t}{N_0}\right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9\ \text{y}} = 1.54 \times 10^{-10}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10}\ \text{y}^{-1}} \ln\left(\frac{4.03 \times 10^{-7}\ \text{mol U}}{5.25 \times 10^{-7}\ \text{mol U}}\right) = 1.7 \times 10^{9}\ \text{y}$$

Therefore, the rock is approximately 1.7 billion years old.

Check Your Learning

A sample of rock contains 6.14×10^{-4} g of Rb-87 and 3.51×10^{-5} g of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer

3.7

×

10^{9} y

12.2 Transmutation and Nuclear Energy

Learning Objectives

By the end of this section, you will be able to:

- Describe the synthesis of transuranium nuclides

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Scientists learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

12.2.1 Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

The

$^{17}_{8}\mathrm{O}$

and

$^{1}_{1}\mathrm{H}$

nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called particle accelerators are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

12.2.2 CHEMISTRY IN EVERYDAY LIFE

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 12.4). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.

Figure 12.5

A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

LINK TO LEARNING

Famous physicist Brian Cox talks about his work on the Large Hadron Collider at CERN, providing an entertaining and engaging tour of this massive project and the physics behind it.

View a short video from CERN, describing the basics of how its particle accelerators work.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U}$$

$$^{239}_{92}\text{U} \longrightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e} \qquad \text{half-life} = 23.5 \text{ min}$$

$$^{239}_{93}\text{Np} \longrightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e} \qquad \text{half-life} = 2.36 \text{ days}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the fission of U-235. Additional neutrons are released during this fission process (see the next section), some of which combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. These processes are summarized in the equation:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \xrightarrow{\beta^-} ^{239}_{93}\text{Np} \xrightarrow{\beta^-} ^{239}_{94}\text{Pu}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 12.2.

Table 12.6

Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + ^{1}_{0}\text{n} \longrightarrow ^{240}_{95}\text{Am} + ^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + ^{4}_{2}\text{He} \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + ^{4}_{2}\text{He} \longrightarrow ^{245}_{98}\text{Cf} + ^{1}_{0}\text{n}$
einsteinium	Es	99	$^{238}_{92}\text{U} + 15^{1}_{0}\text{n} \longrightarrow ^{253}_{99}\text{Es} + 7^{0}_{-1}\text{e}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + ^{4}_{2}\text{He} \longrightarrow ^{256}_{101}\text{Md} + ^{1}_{0}\text{n}$

Name	Symbol	Atomic Number	Reaction
nobelium	No	102	$^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4{}^{1}_{0}\mathrm{n}$
rutherfordium	Rf	104	$^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{257}_{104}\mathrm{Rf} + 4{}^{1}_{0}\mathrm{n}$
seaborgium	Sg	106	$^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3{}^{1}_{0}\mathrm{n}$ $^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4{}^{1}_{0}\mathrm{n}$
meitnerium	Mt	107	$^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

Footnotes

1) The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

Files

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13

Fission and Fusion

A nucleus has less mass than the total mass of its constituent nucleons. This "missing" mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein's mass-energy equivalence equation, $E = mc^2$. Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

13.1 Nuclear Binding Energy

Learning Objectives

- Calculate mass defect and binding energy for nuclei

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underset{\text{protons}}{(2 \times 1.0073 \text{ amu})} + \underset{\text{neutrons}}{(2 \times 1.0087 \text{ amu})} + \underset{\text{electrons}}{(2 \times 0.00055 \text{ amu})} = 4.0331 \text{ amu}$$

However, mass spectrometric measurements reveal that the mass of an

$^{4}_{2}\mathrm{He}$

atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the mass defect indicates a “loss” in mass of 4.0331 amu − 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The nuclear binding energy is the energy produced when the atoms’ nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the mass-energy equivalence equation as stated by Albert Einstein:

$$E = mc^2$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect, as demonstrated in Example 13.1. A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making 1 eV = 1.602×10^{-19} J.

EXAMPLE 13.1.1

Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide

$$^{4}_{2}\mathrm{He}$$

in:
(a) joules per mole of nuclei

(b) joules per nucleus

(c) MeV per nucleus

Solution

The mass defect for a

$$^{4}_{2}\mathrm{He}$$

nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).
(a) First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of 3.05×10^{-5} kg/mol. Substituting this quantity into the mass-energy equivalence equation yields:

$$E = mc^2 = \frac{3.05 \times 10^{-5}\ \text{kg}}{\text{mol}} \times \left(\frac{2.998 \times 10^{8}\ \text{m}}{\text{s}}\right)^2 = 2.74 \times 10^{12}\ \text{kg m}^2\,\text{s}^{-2}\,\text{mol}^{-1}$$
$$= 2.74 \times 10^{12}\ \text{J mol}^{-1} = 2.74\ \text{TJ mol}^{-1}$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

(b) The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12}\ \text{J mol}^{-1} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{nuclei}} = 4.55 \times 10^{-12}\ \text{J} = 4.55\ \text{pJ}$$

(c) Recall that 1 eV = 1.602×10^{-19} J. Using the binding energy computed in part (b):

$$E = 4.55 \times 10^{-12}\ \text{J} \times \frac{1\ \text{eV}}{1.602 \times 10^{-19}\ \text{J}} = 2.84 \times 10^{7}\ \text{eV} = 28.4\ \text{MeV}$$

Check Your Learning

What is the binding energy for the nuclide

$^{19}_{9}\text{F}$

(atomic mass: 18.9984 amu) in MeV per nucleus?

Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

The relative stability of a nucleus is correlated with its binding energy per nucleon, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, we saw in Example 13.1 that the binding energy for a

$^{4}_{2}\text{He}$

nucleus is 28.4 MeV. The binding energy *per nucleon* for a

$^{4}_{2}\text{He}$

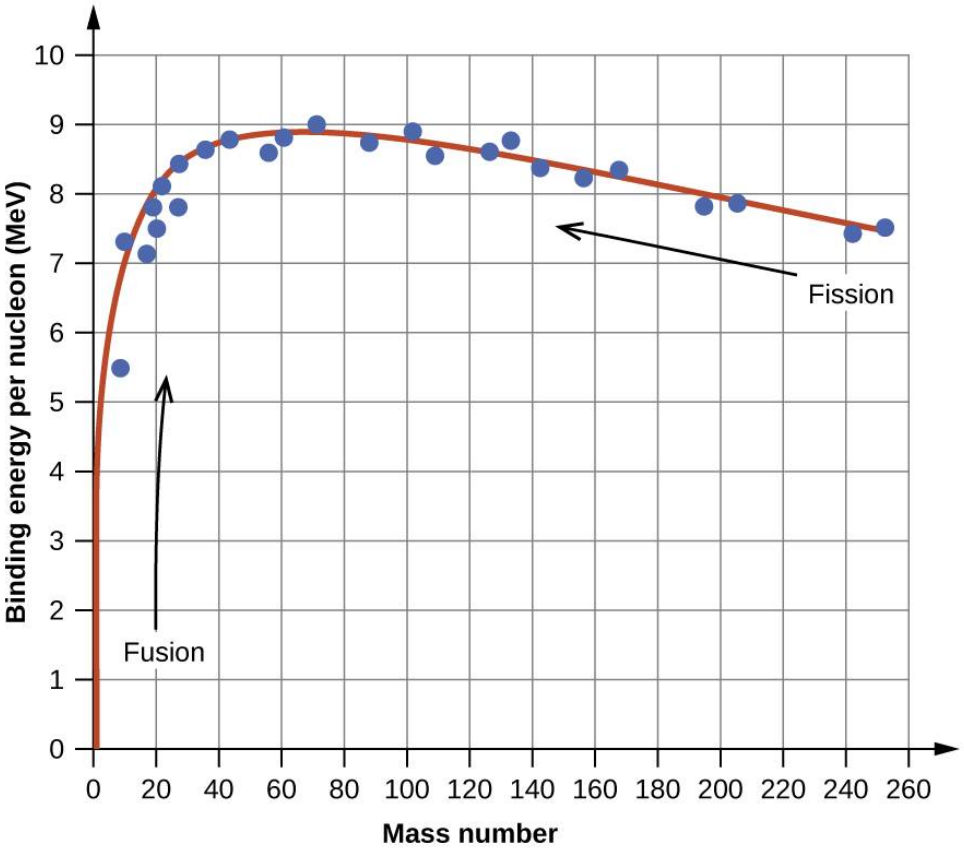
nucleus is therefore:

$$\frac{28.4\ \text{MeV}}{4\ \text{nucleons}} = 7.10\ \text{MeV/nucleon}$$

In Example 13.2, we learn how to calculate the binding energy per nucleon of a nuclide on the curve shown in Figure 13.1.

Figure 13.1

The binding energy per nucleon is largest for nuclides with mass number of approximately 56.


Binding energy per nucleon (MeV)
10
9
8
7
6
5
4
3
2
1
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
Mass number
Fusion
Fission

EXAMPLE 13.1.2

Calculation of Binding Energy per Nucleon

The iron nuclide

$^{56}_{26}\text{Fe}$

lies near the top of the binding energy curve (Figure 13.1) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide

$^{56}_{26}\text{Fe}$

(atomic mass of 55.9349 amu)?

Solution

As in Example 13.1, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an

$^{56}_{26}\text{Fe}$

atom:

$$\begin{aligned}\text{Mass defect} &= [(26 \times 1.0073\ \text{amu}) + (30 \times 1.0087\ \text{amu}) + (26 \times 0.00055\ \text{amu})] - 55.9349\ \text{a}\\ &= 56.4651\ \text{amu} - 55.9349\ \text{amu}\\ &= 0.5302\ \text{amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned}E = mc^2 &= 0.5302\ \text{amu} \times \frac{1.6605 \times 10^{-27}\ \text{kg}}{1\ \text{amu}} \times (2.998 \times 10^8\ \text{m/s})^2\\ &= 7.913 \times 10^{-11}\ \text{kg·m/s}^2\\ &= 7.913 \times 10^{-11}\ \text{J}\end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11}\ \text{J} \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = 493.9\ \text{MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

$$\text{Binding energy per nucleon} = \frac{493.9\ \text{MeV}}{56} = 8.820\ \text{MeV/nucleon}$$

Note that this is almost 25% larger than the binding energy per nucleon for

$^{4}_{2}\text{He}$.

(Note also that this is the same process as in Example 20.1, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

Check Your Learning

What is the binding energy per nucleon in

$^{19}_{9}\text{F}$

(atomic mass, 18.9984 amu)?

Answer

7.810 MeV/nucleon

13.2 Fission and Fusion

Learning Objectives

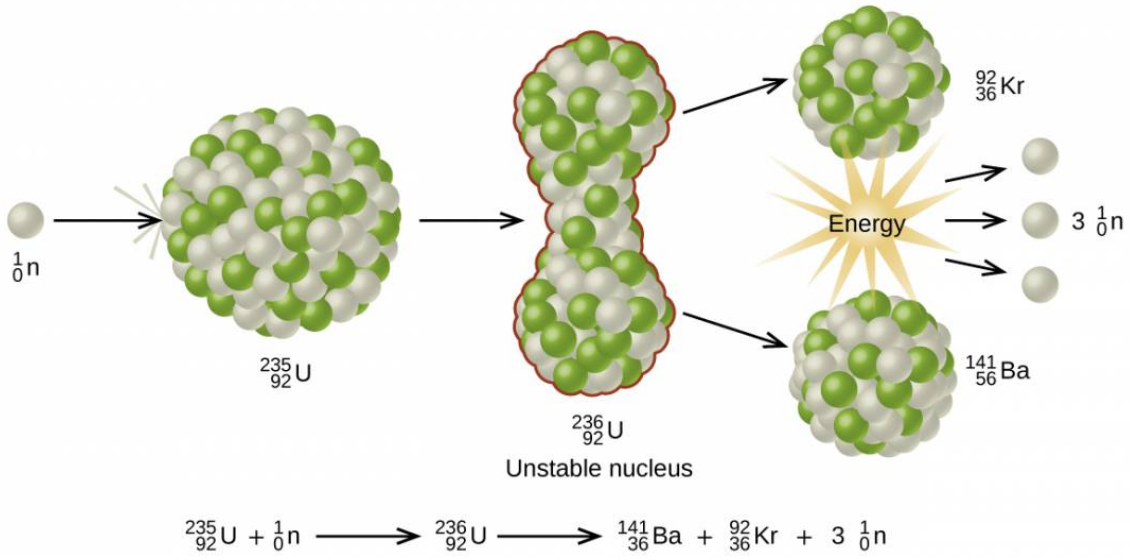
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

13.2.1 Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the “peak” of the binding energy graph near 56 (see Figure 13.1). Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 13.2.

Figure 13.2

When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.



$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{36}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 13.3. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

Figure 13.3

(a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\ {}^{1}_{0}n$$

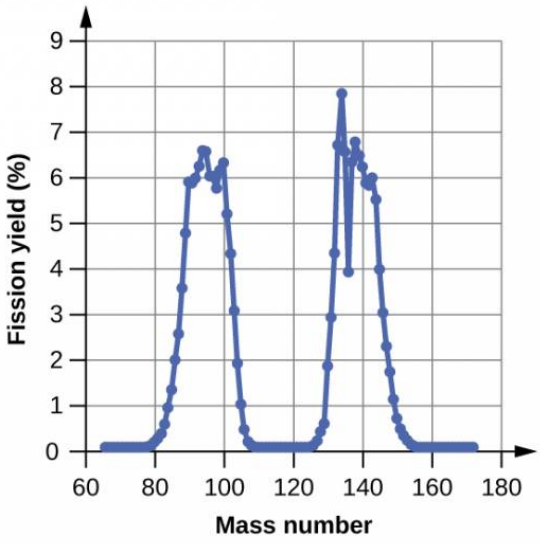
$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{96}_{37}Rb + {}^{137}_{55}Cs + 3\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$

(a)



(b)

LINK TO LEARNING

View this link to see a simulation of nuclear fission.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this “lost” mass is converted into a very large amount of energy, about 1.8

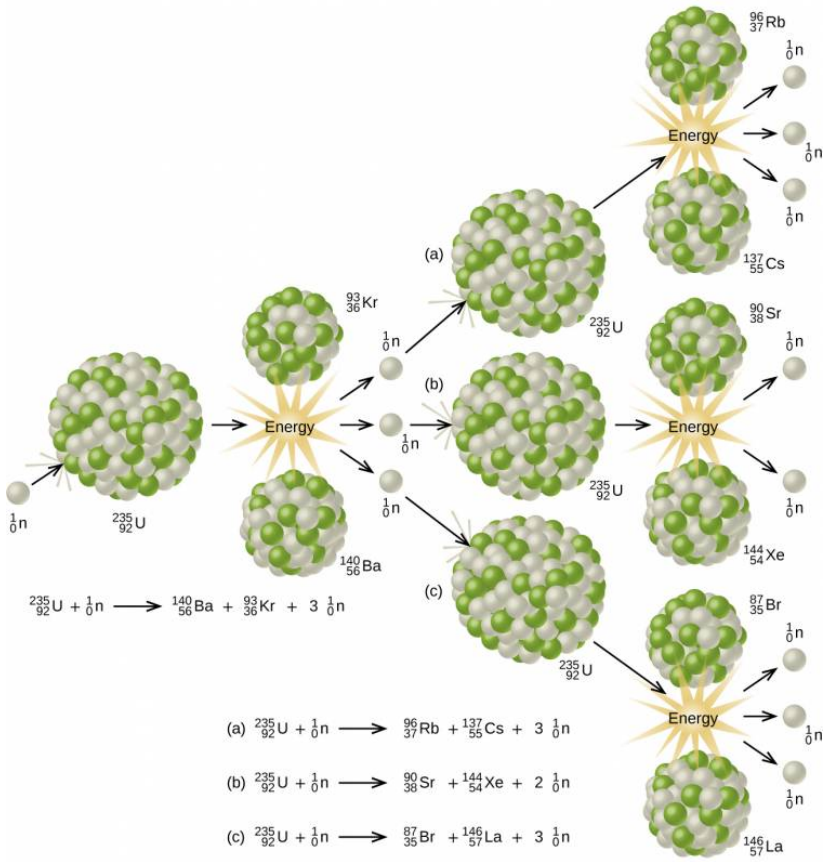
×

10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two “medium-sized” nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (see Figure 13.4). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

Figure 13.4

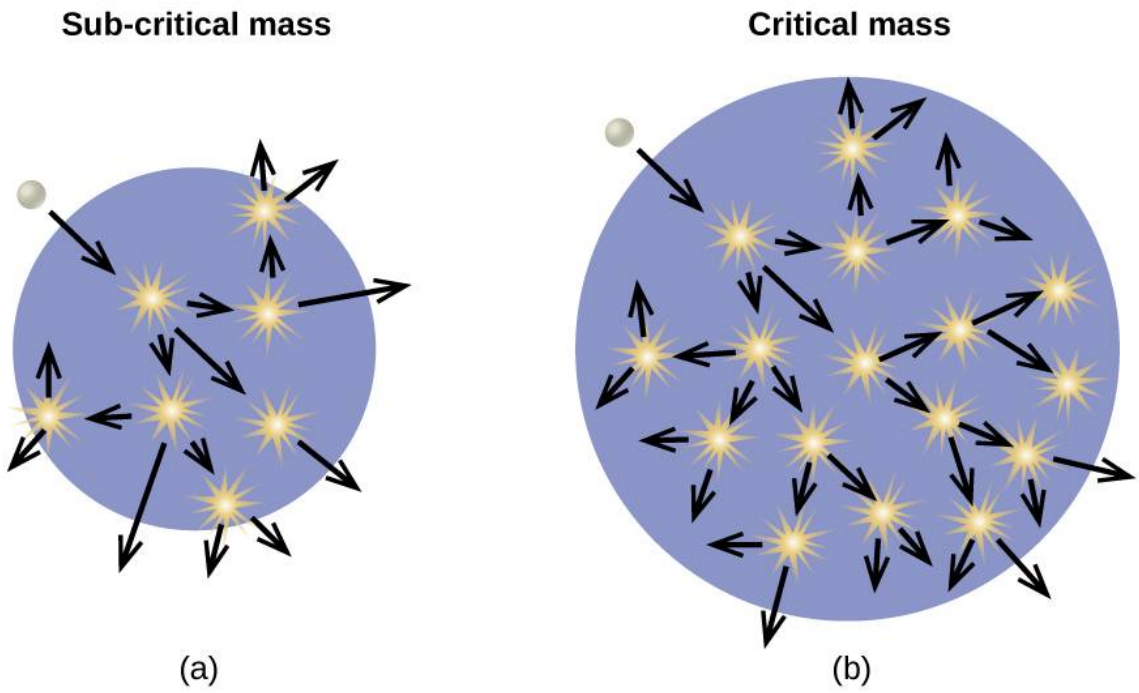
The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.



Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 13.5).

Figure 13.5

(a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.



An atomic bomb (Figure 13.6) contains several pounds of fissionable material,

$^{235}_{92}\mathrm{U}$

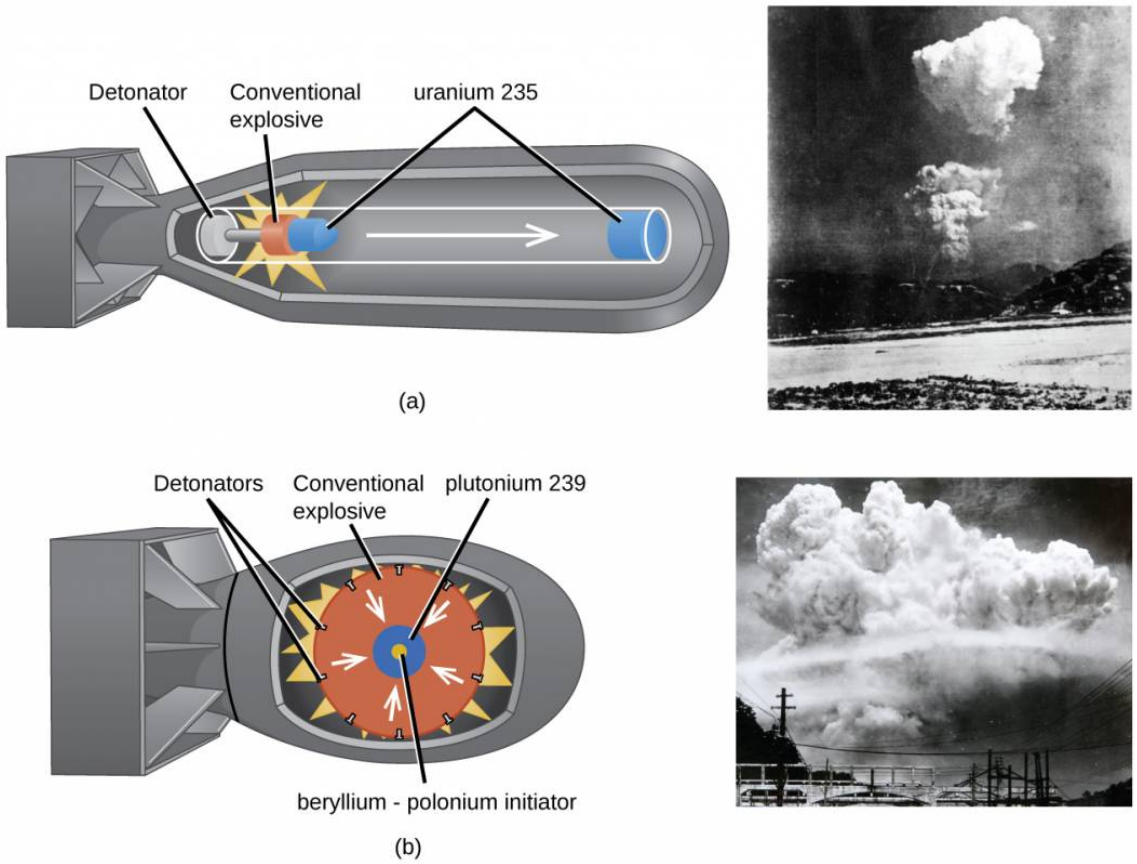
or

$^{239}_{94}\mathrm{Pu},$

a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

Figure 13.6

(a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 9, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

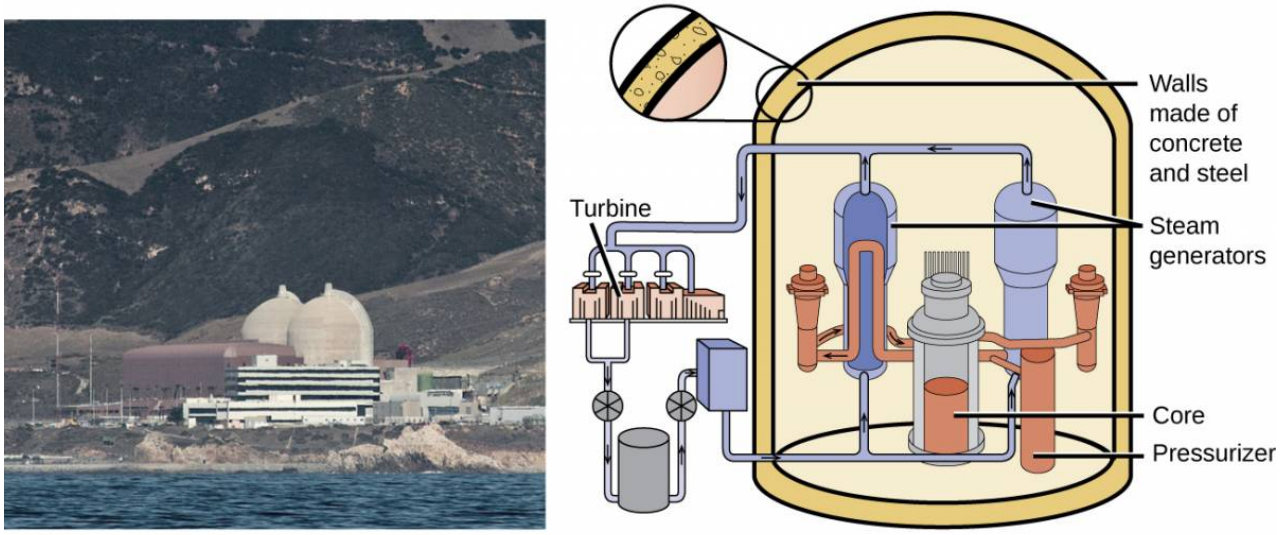


13.2.1.1 Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure 13.7). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

Figure 13.7

(a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by "Mike" Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)



13.2.2 Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham's law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

13.2.3 Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (refer back to Figure 13.5). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water

$$(^2_1H_2O)$$

or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

13.2.4 Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

13.2.5 Control Rods

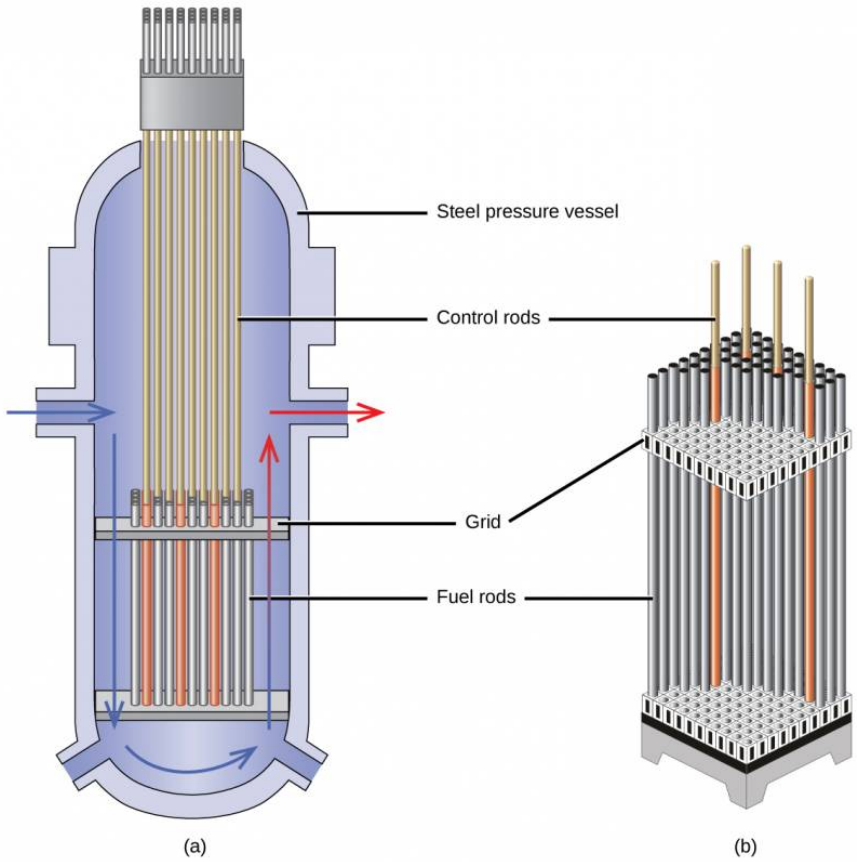
Nuclear reactors use control rods (Figure 13.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\mathrm{B} + ^{1}_{0}\mathrm{n} \longrightarrow ^{7}_{3}\mathrm{Li} + ^{4}_{2}\mathrm{He}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

Figure 13.8

The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossary.php?en=control+rod)



13.2.6 Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

LINK TO LEARNING

Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

13.2.7 CHEMISTRY IN EVERYDAY LIFE

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

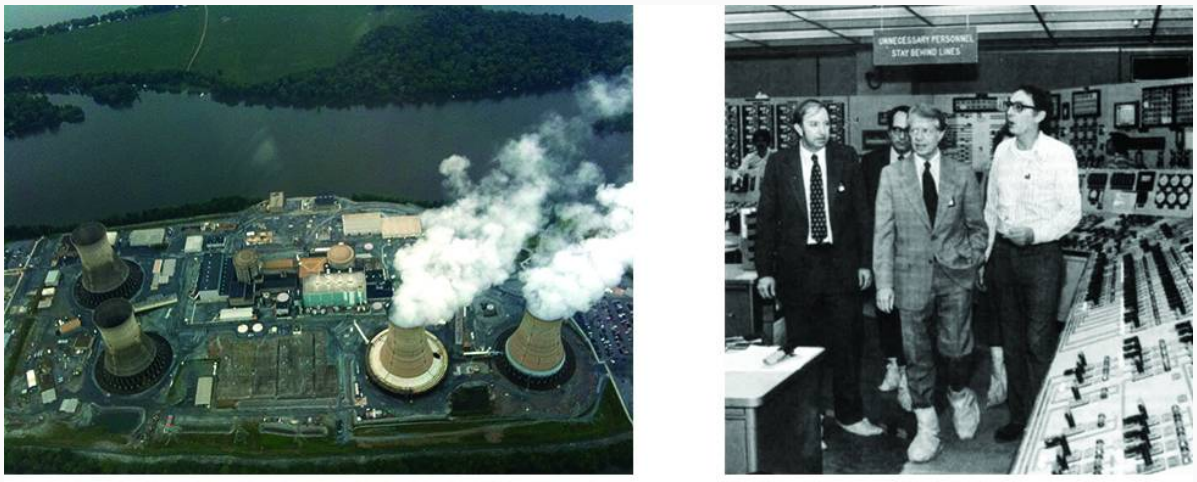
$$\mathrm{Zr}(s) + 2\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\mathrm{H_2}(g)$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 13.9).

Figure 13.9

(a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.



(a) (b)

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an

unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

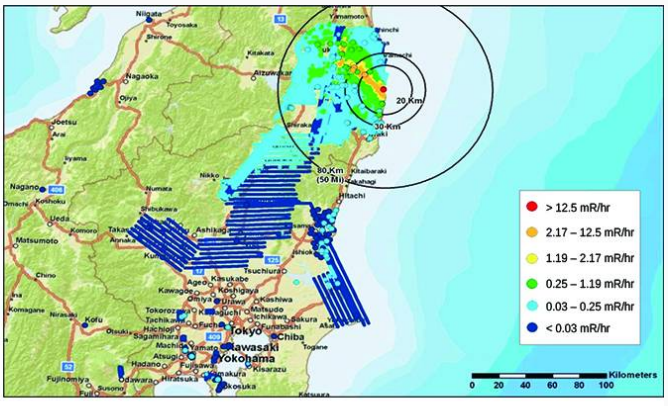
In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 13.10).

Figure 13.10

(a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

(a)



(b)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission

products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

LINK TO LEARNING

Explore the information in this link to learn about the approaches to nuclear waste management.

13.2.8 Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1}\mathrm{e}^{+}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of

$${}^{4}_{2}\mathrm{He}$$

produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron,

$${}^{2}_{1}\mathrm{H}$$

and a triton,

$${}^{3}_{1}\mathrm{H},$$

undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of

$${}^{4}_{2}\mathrm{He}$$

formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 20.23). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

Files

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14

Biological Effects

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating. Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

14.1 Biological Effects of Radiation

Learning Objectives

By the end of this section, you will be able to:

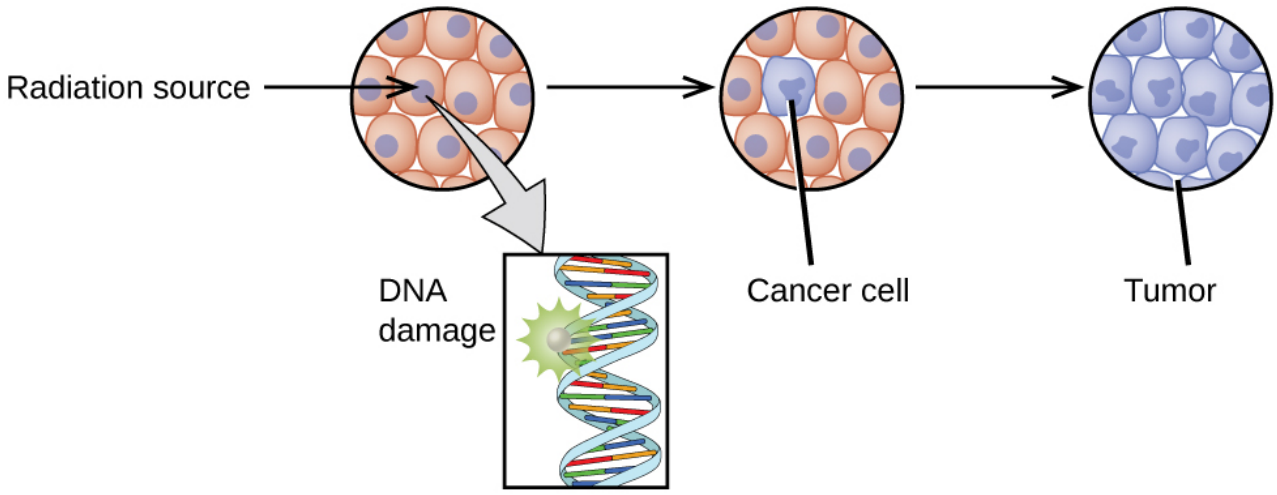
- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely

reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 14.1).

Figure 14.1

Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

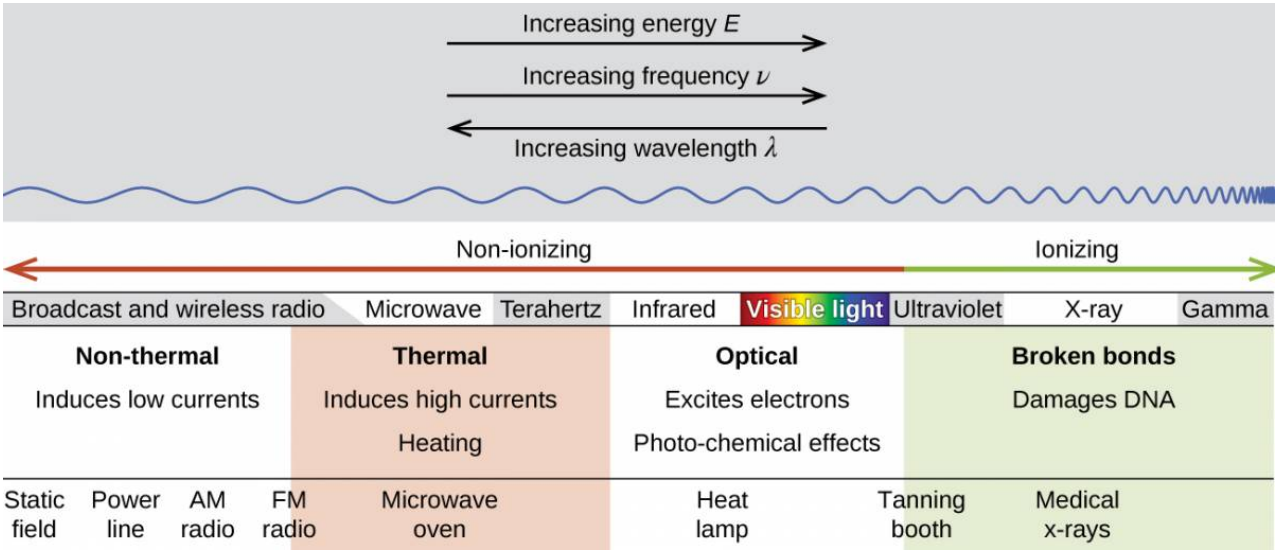


14.1.1 Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 14.2).

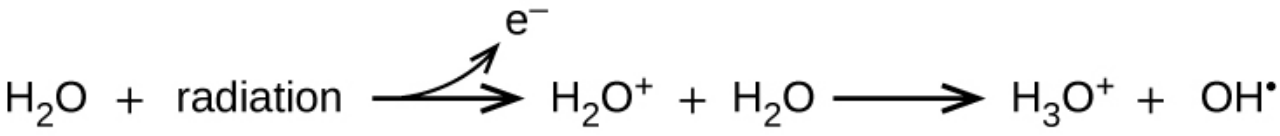
Figure 14.2

Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.



Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels

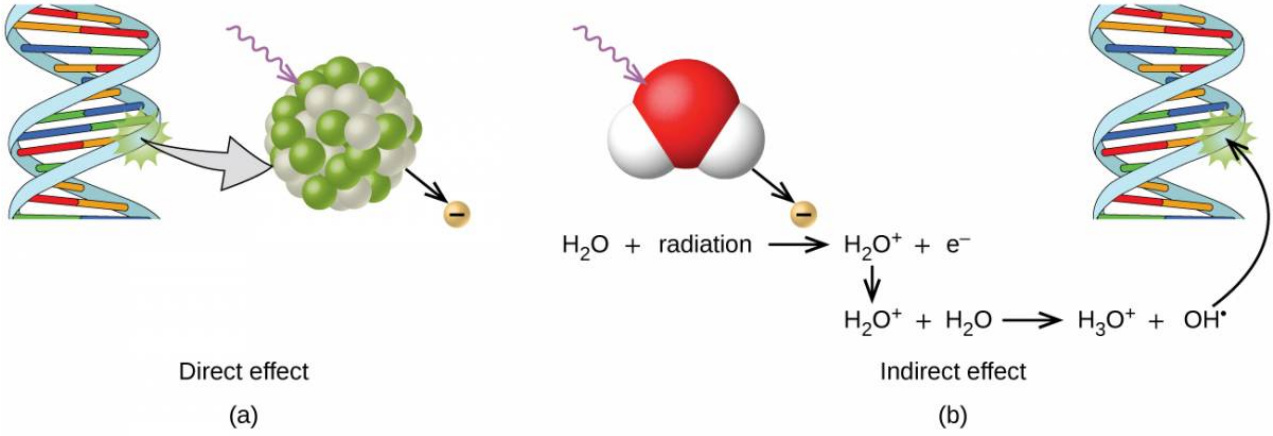
are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:



Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in Figure 14.3.

Figure 14.3

Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.



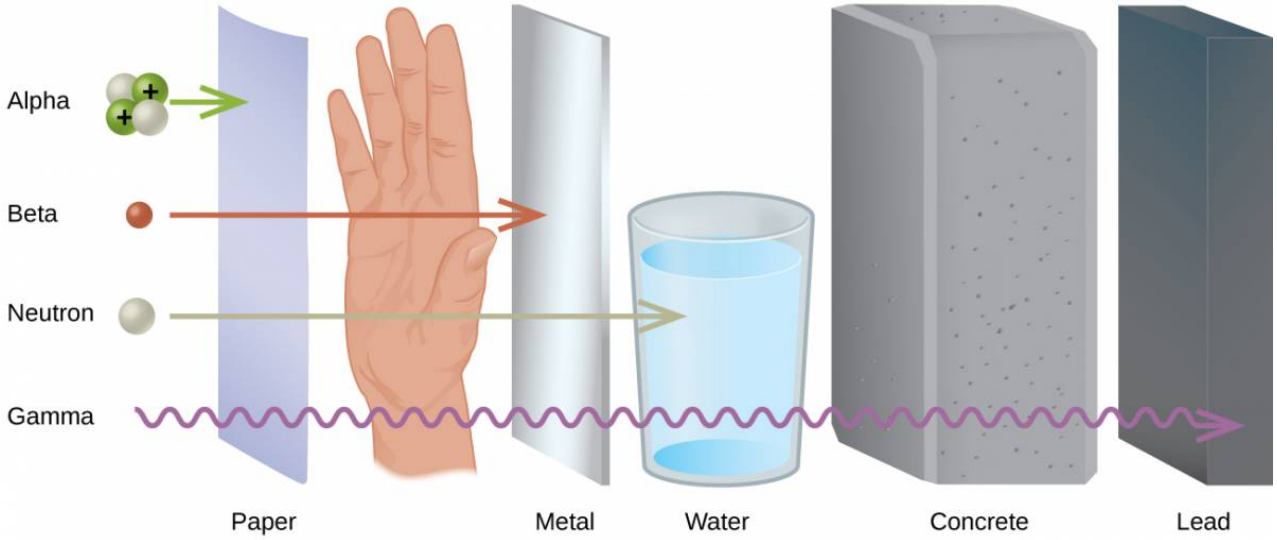
14.1.1.1 Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 14.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

Figure 14.4

The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.



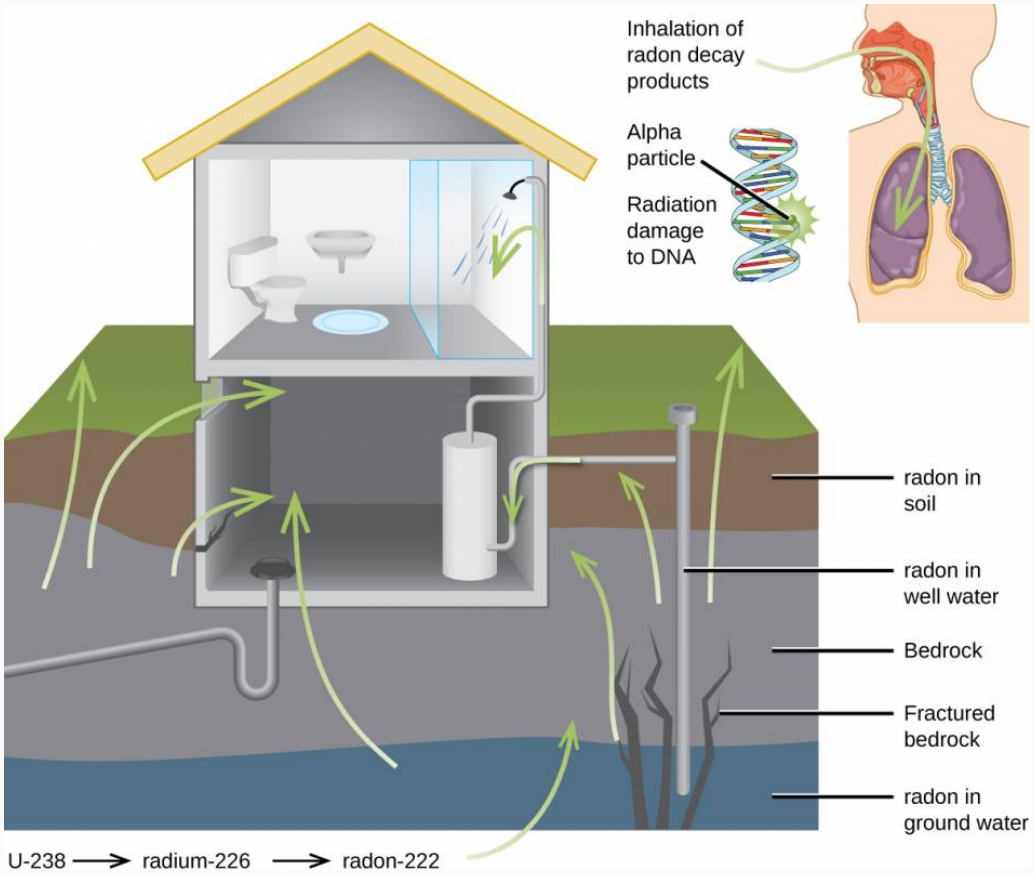
14.1.2 IN EVERYDAY LIFE

Radon Exposure

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 14.5).

Figure 14.5

Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.



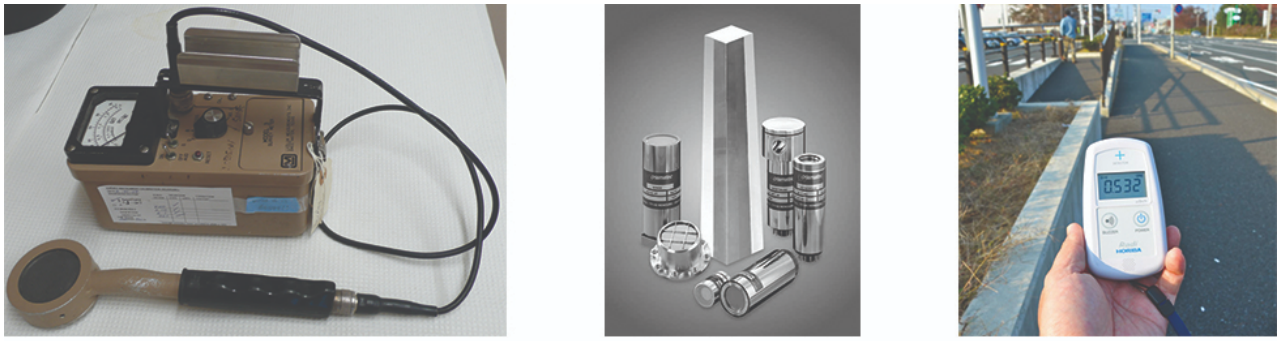
Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

14.1.3 Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 14.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

Figure 14.6

Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons)



A variety of units are used to measure various aspects of radiation (Figure 14.7). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7

×

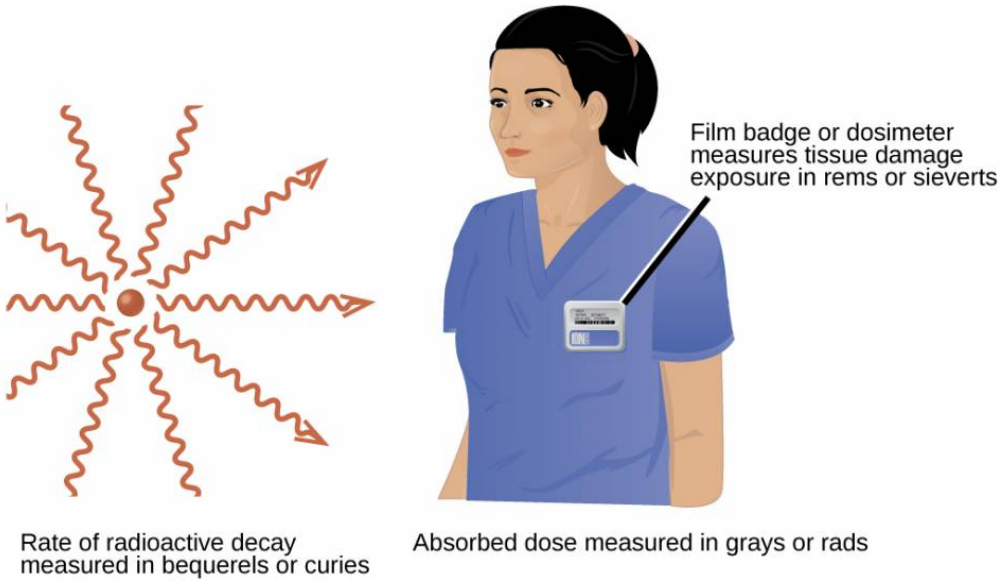
10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (100 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

Figure 14.7

Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.



14.1.3.1 Units of Radiation Measurement

Table 14.1 summarizes the units used for measuring radiation.

Table 14.8

Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

EXAMPLE 14.1.4

Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.
(a) What is its activity in Bq?

(b) What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right)N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of Co–60 that decay}$$

And to convert this to decays per second:

$$0.659\ \tfrac{\text{g}}{\text{y}} \times \tfrac{1\ \text{y}}{365\ \text{d}} \times \tfrac{1\ \text{d}}{24\ \text{h}} \times \tfrac{1\ \text{h}}{3600\ \text{s}} \times \tfrac{1\ \text{mol}}{59.9\ \text{g}} \times \tfrac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \tfrac{1\ \text{decay}}{1\ \text{atom}}$$
$$= 2.10 \times 10^{14}\ \tfrac{\text{decay}}{\text{s}}$$

(a) Since 1 Bq =

$\frac{1\ \text{decay}}{\text{s}}$,

the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since 1 Ci =

$\frac{3.7 \times 10^{11}\ \text{decay}}{\text{s}}$,

the activity in curie (Ci) is:

$$2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{\frac{3.7 \times 10^{11}\ \text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

Check Your Learning

Tritium is a radioactive isotope of hydrogen ($t_{1/2}$ = 12.32 y) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

(a) 14.1.5 ×× 1011 Bq; (b) 0.962 C

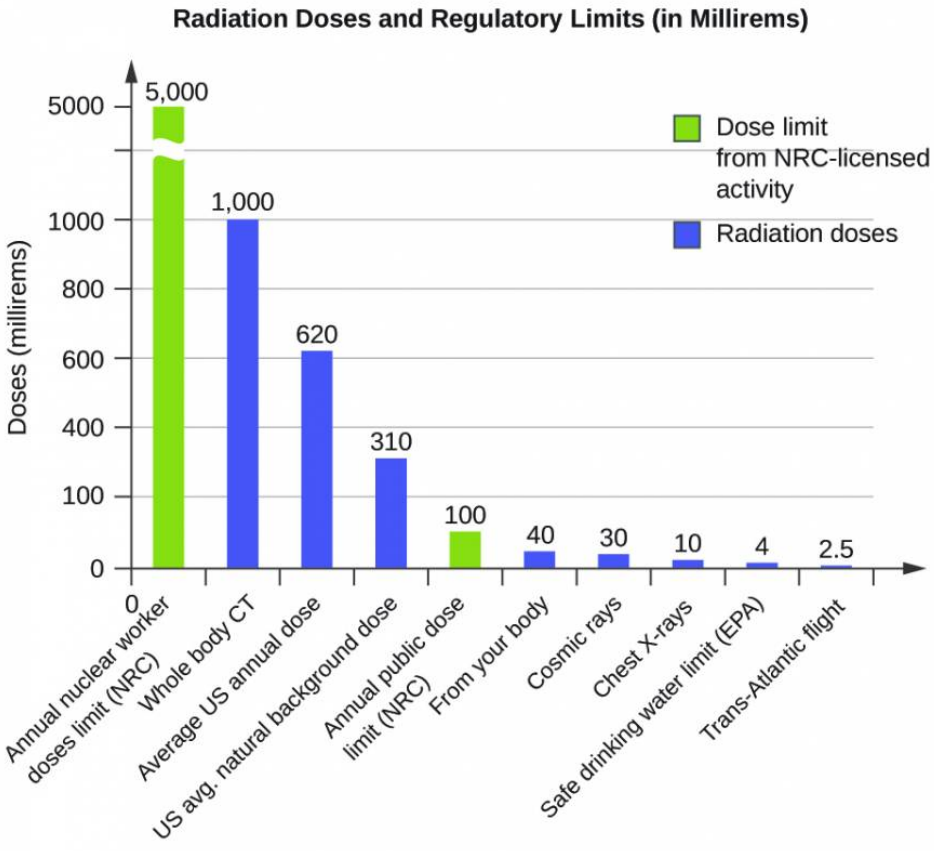
14.1.6 Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 14.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other

human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

Figure 14.9

The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)



A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 14.2.

Table 14.10

Health Effects of Radiation[2]

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—

Exposure (rem)	Health Effect	Time to Onset (without treatment)
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

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Unit 4

Equilibrium and Thermodynamics

Equilibrium Constants
Reaction Quotients and Le Chatelier
Equilibrium Calculations
Review of Thermodynamics Calculations
ΔG and Q, ΔG° and K
Temperature Dependence of K

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15

Equilibrium Constants

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species. The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient, Q. For a reaction at equilibrium, the composition is constant, and Q is called the equilibrium constant, K. 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.

15.1 Chemical Equilibria

Learning Objectives

By the end of this section, you will be able to:

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

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of "reactant" and "product," a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

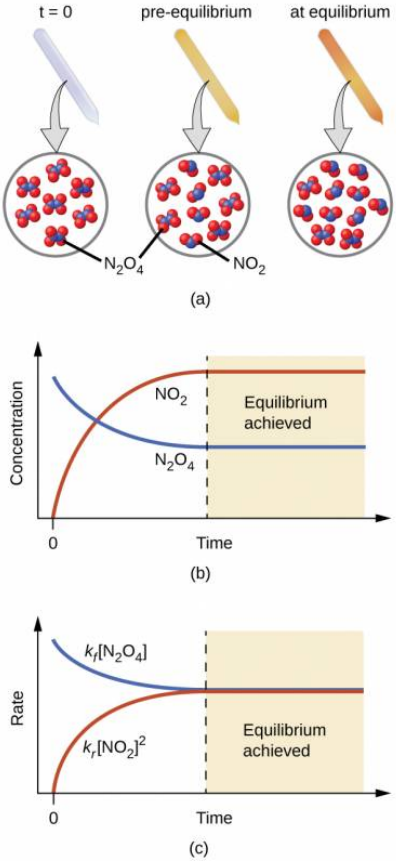
Figure 15.1 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

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

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

Figure 15.1

(a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.



For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

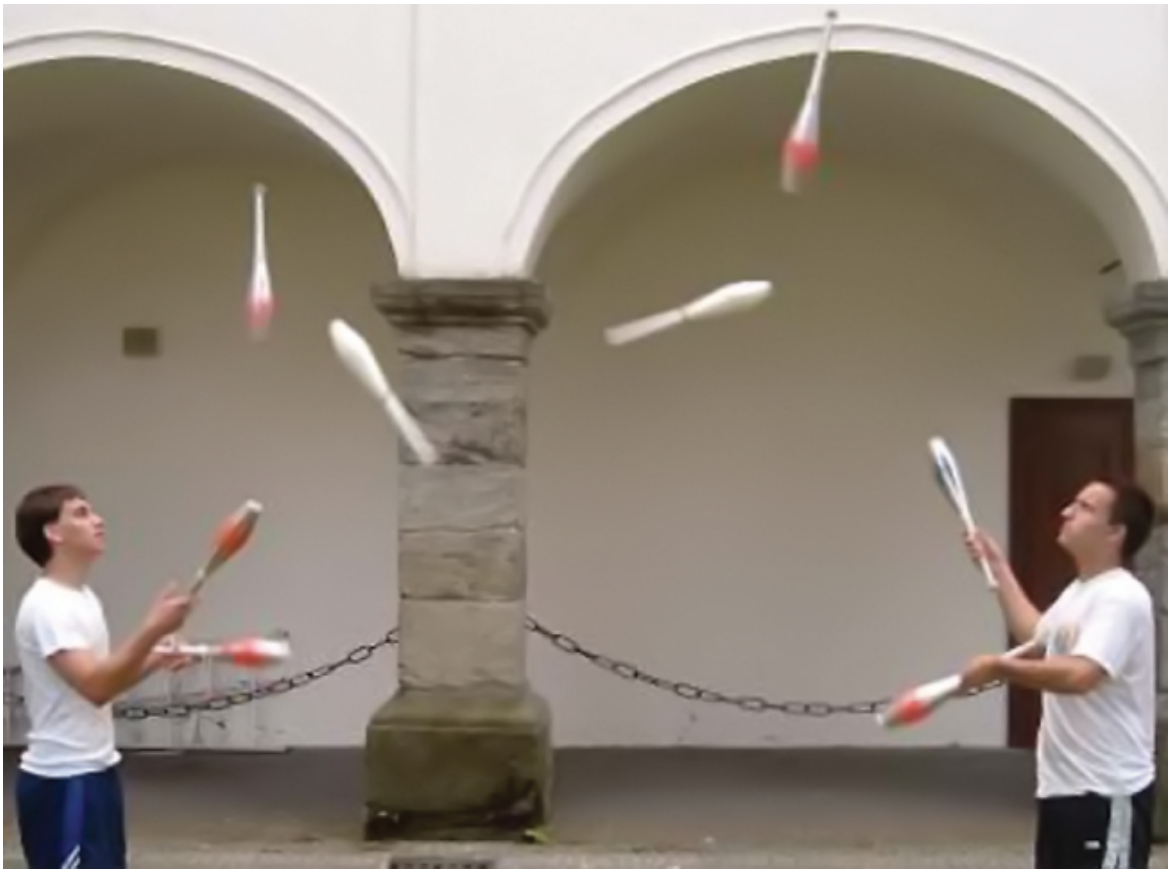
$$\text{rate}_f = k_f [\text{N}_2\text{O}_4]$$

$$\text{rate}_r = k_r [\text{NO}_2]^2$$

As the reaction begins ($t = 0$), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure 15.1**b**). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 15.1**c**). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure 15.1**b** and Figure 15.1**c**). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not "stopped," but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.

Figure 15.2

A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.



Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\mathrm{Br_2}\,(l) \rightleftharpoons \mathrm{Br_2}\,(g)$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in Figure 15.3.

Figure 15.3

A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

15.2 Equilibrium Constants

Learning Objectives

By the end of this section, you will be able to:

- 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

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient** (Q). For a reversible reaction described by

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D},$$

the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[\mathrm{C}]^x\,[\mathrm{D}]^y}{[\mathrm{A}]^m\,[\mathrm{B}]^n},$$

where the subscript *c* denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{{P_\mathrm{C}}^x\,{P_\mathrm{D}}^y}{{P_\mathrm{A}}^m\,{P_\mathrm{B}}^n}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing *Q*. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

EXAMPLE 15.2.1

Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:
(a)

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

(b)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(c)

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$$

Solution

(a)

$$Q_c = \frac{[O_3]^2}{[O_2]^3}$$

(b)

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(c)

$$Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

Check Your Learning

Write the concentration-based reaction quotient expression for each of the following reactions:
(a)

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(b)

$$C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$$

(c)

$$2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$$

Answer

(a)

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]};$$

(b)

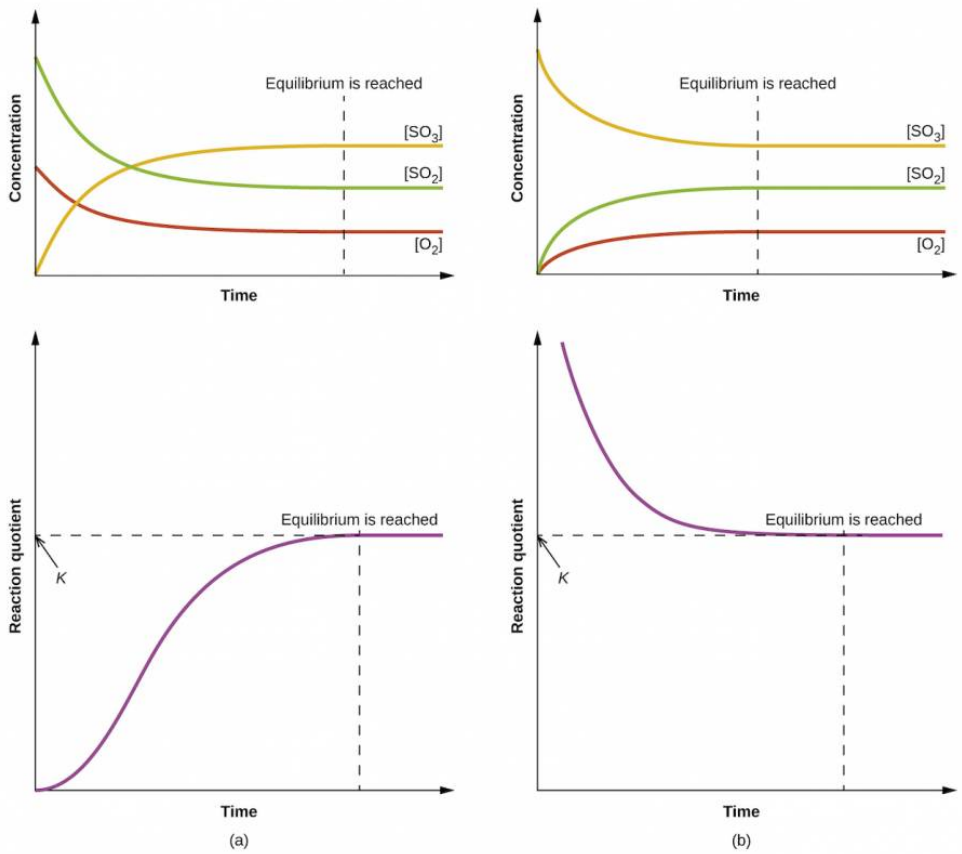
$$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]};$$

(c)

$$Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

Figure 15.4

Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.



The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

Two different experimental scenarios are depicted in Figure 15.4, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{0^2}{[SO_2]^2\,[O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the **equilibrium constant, *K***:

$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in Figure 15.4 shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**: At a given temperature, the reaction quotient for a system at equilibrium is constant.

EXAMPLE 15.2.2

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

As for all equilibrium calculations in this text, use the simplified equations for *Q* and *K* and disregard any concentration or pressure units, as noted previously in this section.
(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,

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium,

$$K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2\ .$$

The equilibrium constant is 1.6×10^2.

Check Your Learning

For the reaction

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g),$$

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

$K_c = 4.3$

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large K will reach equilibrium when most of the reactant has been converted to product, whereas a small K indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of K does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

15.3 Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$\begin{aligned}
\mathrm{C_2H_2}(aq) + 2\mathrm{Br_2}(aq) &\rightleftharpoons \mathrm{C_2H_2Br_4}(aq) & K_c &= \frac{[\mathrm{C_2H_2Br_4}]}{[\mathrm{C_2H_2}]\,[\mathrm{Br_2}]^2} \\
\mathrm{I_2}(aq) + \mathrm{I^-}(aq) &\rightleftharpoons \mathrm{I_3^-}(aq) & K_c &= \frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}][\mathrm{I^-}]} \\
\mathrm{HF}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) & K_c &= \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]} \\
\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) & K_c &= \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]}
\end{aligned}$$

These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the Q (or K) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

The equilibria below all involve gas-phase solutions:

$$\begin{aligned}
\mathrm{C_2H_6}(g) &\rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) & K_c &= \frac{[\mathrm{C_2H_4}]\,[\mathrm{H_2}]}{[\mathrm{C_2H_6}]} \\
3\mathrm{O_2}(g) &\rightleftharpoons 2\mathrm{O_3}(g) & K_c &= \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3} \\
\mathrm{N_2}(g) + 3\mathrm{H_2}(g) &\rightleftharpoons 2\mathrm{NH_3}(g) & K_c &= \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}]\,[\mathrm{H_2}]^3} \\
\mathrm{C_3H_8}(g) + 5\mathrm{O_2}(g) &\rightleftharpoons 3\mathrm{CO_2}(g) + 4\mathrm{H_2O}(g) & K_c &= \frac{[\mathrm{CO_2}]^3\,[\mathrm{H_2O}]^4}{[\mathrm{C_3H_8}][\mathrm{O_2}]^5}
\end{aligned}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

$$PV = nRT$$

$$P = (\frac{n}{V})RT$$

$$= MRT$$

where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}:$$

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

$$= K_c (RT)^{(x+y)-(m+n)}$$

$$= K_c (RT)^{\Delta n}$$

And so, the relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n}$$

where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (x+y) - (m+n)$$

EXAMPLE 15.3.1

Calculation of K_P

Write the equations relating K_c to K_P for each of the following reactions:
(a)

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

(b)

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(c)

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(d) K_c is equal to 0.28 for the following reaction at 900 °C:

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

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}

Check Your Learning

Write the equations relating K_c to K_P for each of the following reactions:

(a)

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(b)

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(c)

$$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$$

(d) At 227 °C, the following reaction has $K_c = 0.0952$:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

What would be the value of K_P at this temperature?

Answer

(a) $K_P = K_c(RT)^{-1}$; (b) $K_P = K_c(RT)$; (c) $K_P = K_c(RT)$; (d) 160 or 1.6

×

10^2

15.4 Heterogeneous Equilibria

A **heterogeneous equilibrium** involves reactants and products in two or more different phases, as illustrated by the following examples:

$$\begin{array}{rcll} PbCl_2(s) & \rightleftharpoons & Pb^{2+}(aq) + 2Cl^-(aq) & K_c = [Pb^{2+}][Cl^-]^2 \\ CaO(s) + CO_2(g) & \rightleftharpoons & CaCO_3(s) & K_c = \frac{1}{[CO_2]} \\ C(s) + 2S(g) & \rightleftharpoons & CS_2(g) & K_c = \frac{[CS_2]}{[S]^2} \\ Br_2(l) & \rightleftharpoons & Br_2(g) & K_c = [Br_2(g)] \end{array}$$

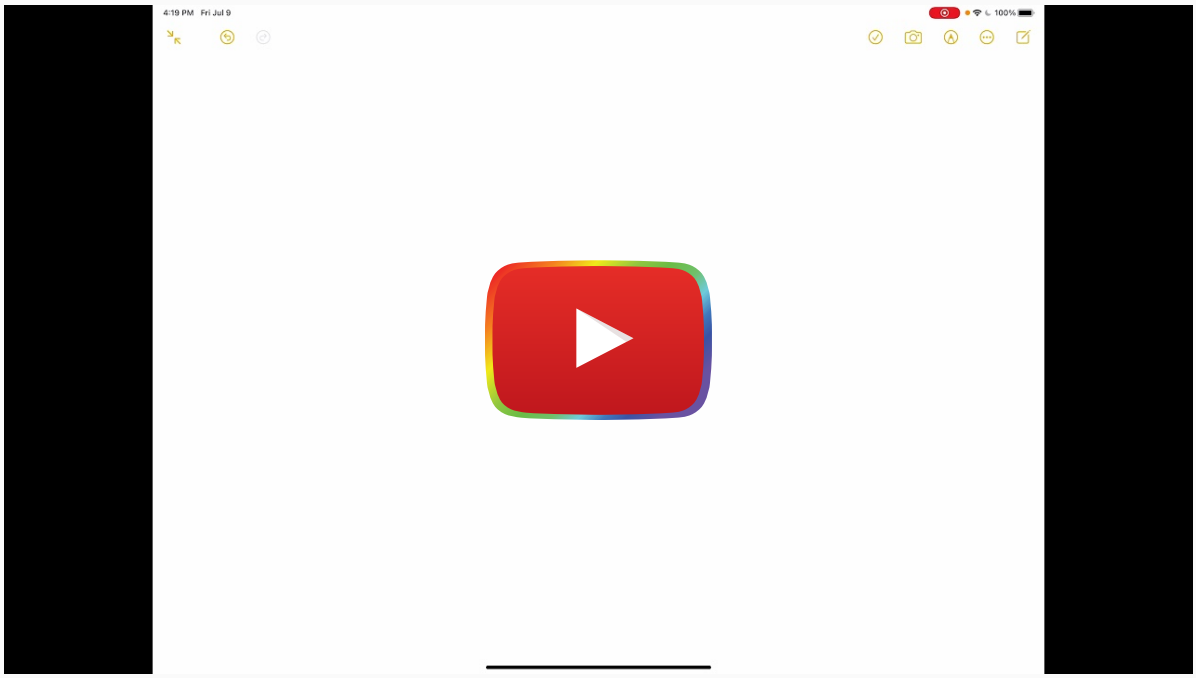
Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_p expressions may also be written:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \qquad K_P = \frac{1}{P_{\mathrm{CO_2}}}$$

$$\mathrm{C}(s) + 2\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \qquad K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2}$$

Keq Practice



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16

Reaction Quotients and Le Chatelier

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Châtelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible process, increasing the rate at which equilibrium is reached but not altering the equilibrium mixture's composition (K does not change).

16.1 Predicting the Direction of a Reaction

Learning Objectives

- Relate the magnitude of an equilibrium constant to properties of the chemical system

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing *Q* to *K* for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

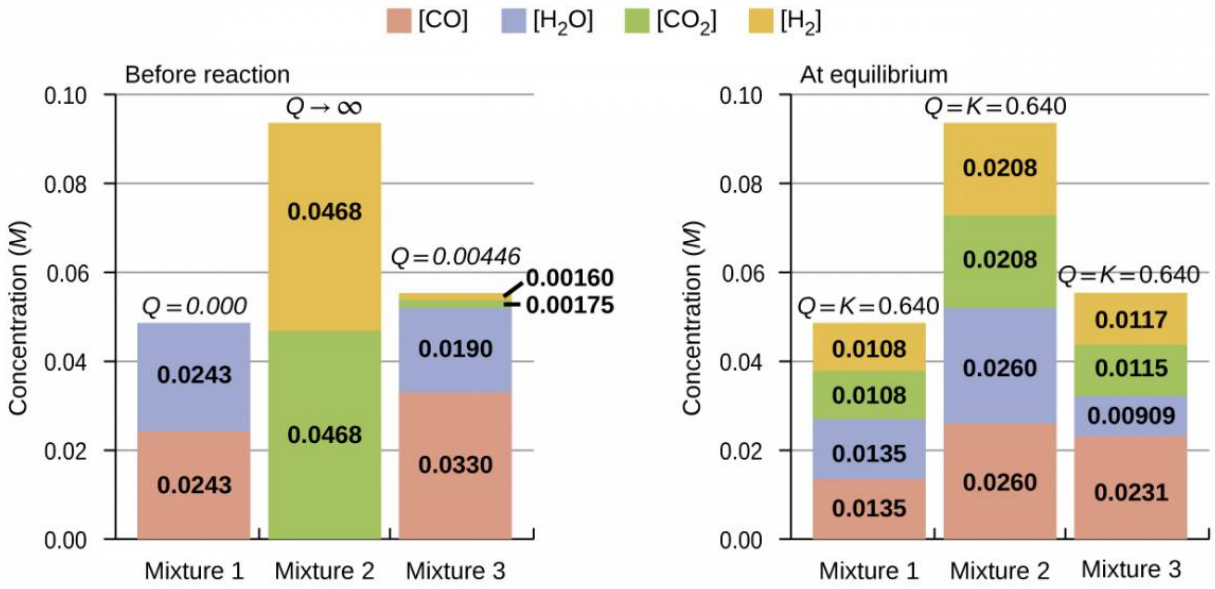
To further illustrate this important point, consider the reversible reaction shown below:

$$\mathrm{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)} \qquad K_c = 0.640 \qquad \mathrm{T = 800\ °C}$$

The bar charts in Figure 17.1 represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

Figure 16.1

Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction $\mathrm{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$.


[CO]
[H2O]
[CO2]
[H2]
Before reaction
At equilibrium
Concentration (M)
0.10
0.08
0.06
0.04
0.02
0.00
Q → ∞
Q = 0.000
Q = 0.00446
Q = K = 0.640
Q = K = 0.640
Q = K = 0.640
0.0243
0.0243
0.0468
0.0468
0.0190
0.0330
0.00160
0.00175
0.0108
0.0108
0.0135
0.0135
0.0208
0.0208
0.0260
0.0260
0.0117
0.0115
0.00909
0.0231
Mixture 1
Mixture 2
Mixture 3

EXAMPLE 16.1.1

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$$

$$K_c = 0.64$$

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
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *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:

$$Q_c = \frac{[\mathrm{CO_2}]\,[\mathrm{H_2}]}{[\mathrm{CO}]\,[\mathrm{H_2O}]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040\,.$$

$Q_c < K_c$ (0.040 < 0.64)

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[\mathrm{CO_2}]\,[\mathrm{H_2}]}{[\mathrm{CO}]\,[\mathrm{H_2O}]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[\mathrm{CO_2}]\,[\mathrm{H_2}]}{[\mathrm{CO}]\,[\mathrm{H_2O}]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

Check Your Learning

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:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$$

Answer

(a) $Q_c = 6.45\times10^3$, forward. (b) $Q_c = 0.23$, reverse. (c) $Q_c = 0$, forward.

16.2 Shifting Equilibria: Le Châtelier's principle

Learning Objectives

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by Le Châtelier's principle: *if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium*.

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

16.3 Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI(g)} \qquad\qquad K_c = 50.0 \text{ at } 400\ ^\circ\mathrm{C}$$

The rate laws for the forward and reverse reactions are

$$\begin{array}{ll} forward & \mathrm{H_2\,(g) + I_2\,(g) \rightarrow 2HI(g)} \qquad \mathrm{rate}_f = k_f[\mathrm{H_2}]^m[\mathrm{I_2}]^n \\ reverse & \mathrm{2HI(g) \rightarrow H_2\,(g) + I_2\,(g)} \qquad \mathrm{rate}_r = k_r[\mathrm{HI}]^x \end{array}$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\mathrm{rate}_f = \mathrm{rate}_r$$

If the system is stressed by adding reactant, either H_2 or I_2, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\mathrm{rate}_f > \mathrm{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (*the equilibrium will shift right*). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\mathrm{rate}_f < \mathrm{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will

consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2 and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the new equilibrium mixture will have greater concentrations of H_2 and I_2 and a lesser concentration of HI. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.

For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure P of an ideal gas is proportional to its molar concentration M,

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI(g)}$$

is described by the reaction quotient

$$Q_p = \frac{P_{\mathrm{HI}^2}}{P_{\mathrm{H}^2}\ P_{\mathrm{I}^2}} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q_p{}' = \frac{(3P_{\mathrm{HI}^2})^2}{3P_{\mathrm{H}^2}\ 3P_{\mathrm{I}^2}} = \frac{9P_{\mathrm{HI}^2}}{9P_{\mathrm{H}^2}\ P_{\mathrm{I}^2}} = \frac{P_{\mathrm{HI}^2}}{P_{\mathrm{H}^2}\ P_{\mathrm{I}^2}} = Q_p = K_p$$

$$Q_p{}' = Q_p = K_p$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system,

$$\mathrm{2NO_2\,(g) \rightleftharpoons 2\,NO(g) + O_2\,(g),}$$

however, yields a different result:

$$Q_p = \frac{P_{NO^2}\ P_{O^2}}{P_{(NO^2)^2}} = K_p$$

$$Q_p{}' = \frac{(3P_{NO})^2\ 3P_{O^2}}{(3P_{NO^2})^2} = \frac{9P_{NO^2}\ 3P_{O^2}}{9P_{(NO^2)^2}} = \frac{27P_{NO^2}\ P_{O^2}}{P_{(NO^2)^2}} = 3Q_p > K_p$$

$$Q_p{}' = 3Q_p > K_p$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better "accommodates" the volume change. In the second example, two moles of reactant (NO_2) yield three moles of product ($2NO + O_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

LINK TO LEARNING

Check out this link to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

16.3.1 CHEMISTRY IN EVERYDAY LIFE

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestly's approach involved production of carbon dioxidey reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

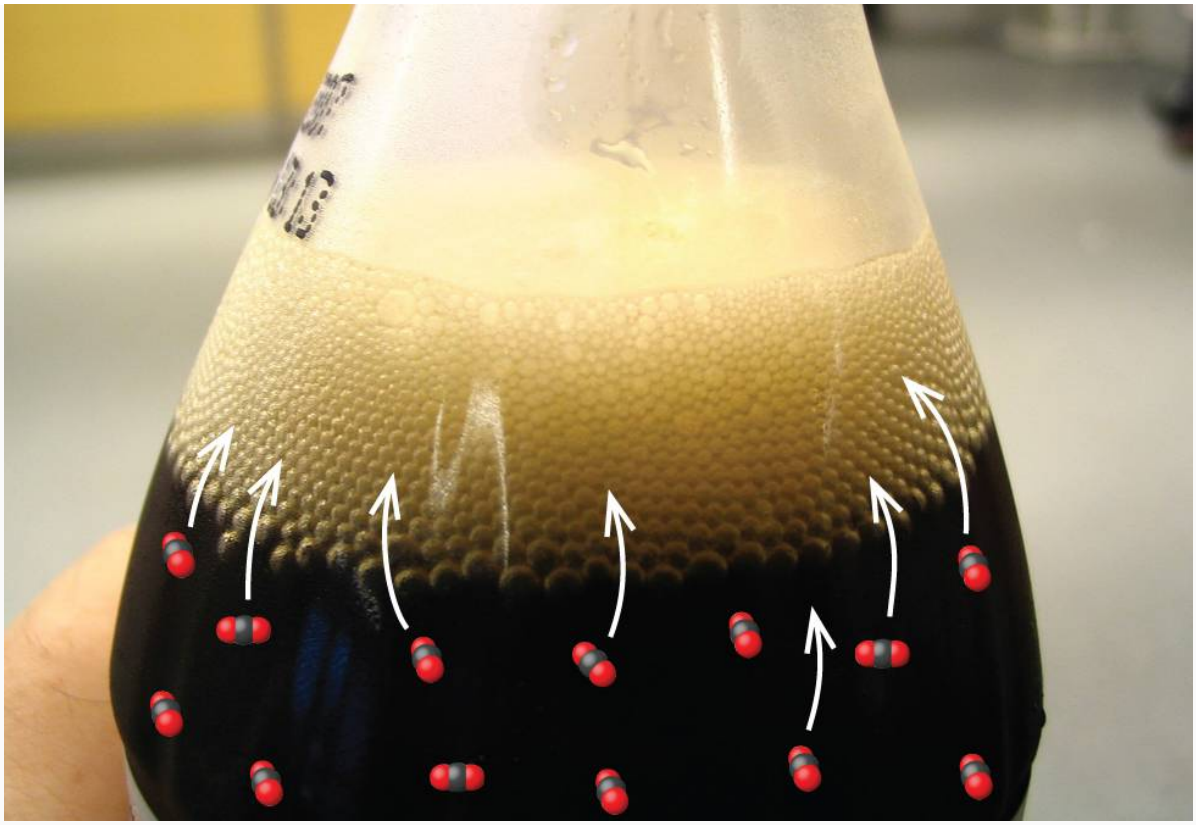
The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\begin{array}{ll} \text{dissolution} & \mathrm{CO_2}\,(g) = \mathrm{CO_2}\,(aq) \\ \text{hydrolysis} & \mathrm{CO_2}\,(aq) + \mathrm{H_2O}(l) = \mathrm{H_2CO_3}\,(aq) \\ \text{ionization} & \mathrm{H_2CO_3}\,(aq) = \mathrm{HCO_3^-}\,(aq) + \mathrm{H^+}\,(aq) \end{array}$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."

Figure 16.2
Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by "D Coetzee"/Flickr)



16.4 Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, *K*. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\begin{aligned} \text{rate}_f &= k_f [\mathrm{A}] \\ \text{rate}_r &= k_r [\mathrm{B}] \end{aligned}$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$\begin{aligned} k_f[\mathrm{A}] &= k_r[\mathrm{B}] \\ \frac{[\mathrm{B}]}{[\mathrm{A}]} &= \frac{k_f}{k_r} = K_c \end{aligned}$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\mathrm{N_2O_4(g) \rightleftharpoons 2NO_2(g)} \qquad\qquad \Delta H = 57.20\ \mathrm{kJ}$$

For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

$$\mathrm{heat + N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Files

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17

Equilibrium Calculations

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for performing equilibrium calculations.

17.1 Equilibrium Calculations

Learning Objectives

By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches
- Explain how temperature affects the spontaneity of some proceses
- Relate standard free energy changes to equilibrium constants

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

$$2\mathrm{NH_3}\,(g) \rightleftharpoons \mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g)$$

As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either NH_3 only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial

composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount *x*:

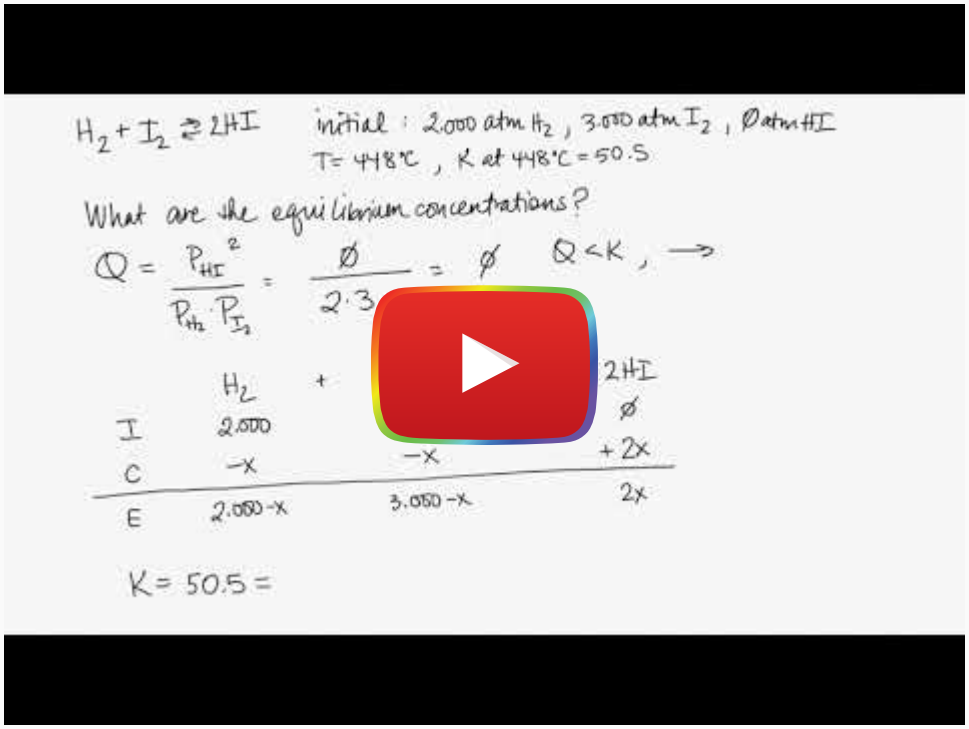
$$\Delta[\mathrm{N_2}] = +x,$$

the corresponding changes in the other species concentrations are

$$\Delta[\mathrm{H_2}] = \Delta[\mathrm{N_2}]\left(\frac{3\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ N_2}}\right) = +3x$$
$$\Delta[\mathrm{NH_3}] = -\Delta[\mathrm{N_2}]\left(\frac{2\ \mathrm{mol\ NH_3}}{1\ \mathrm{mol\ N_2}}\right) = -2x,$$

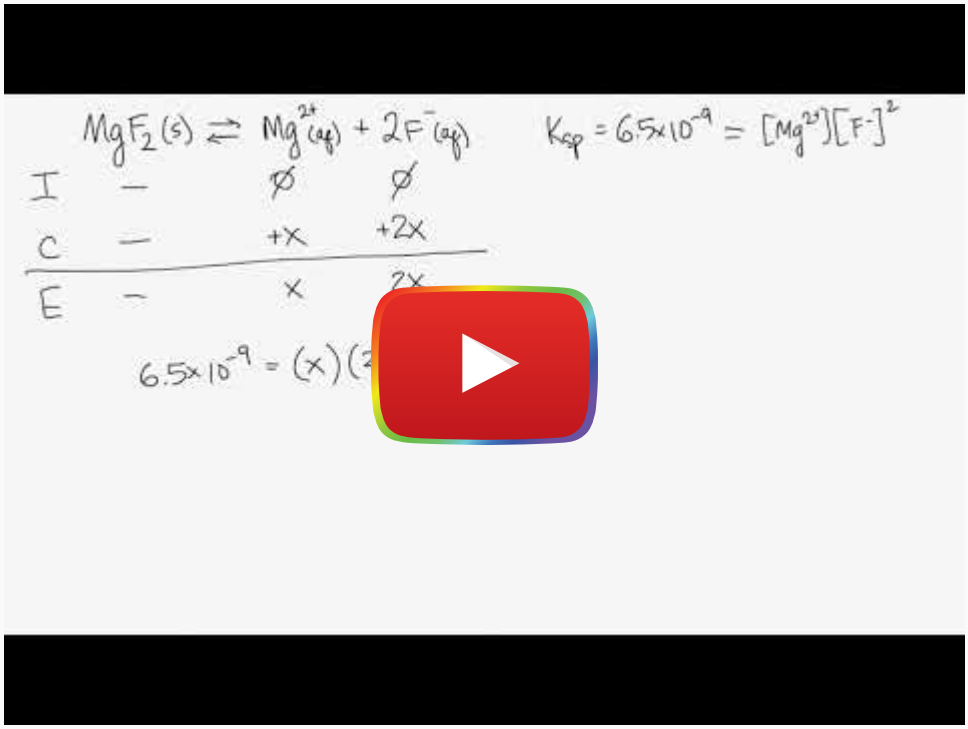
where the negative sign indicates a decrease in concentration.

Video: Equilibrium Practice Problem 17.1.1



Watch on YouTube

Video: Equilibrium Practice Problem 17.1.2



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EXAMPLE 17.1.3

Determining Relative Changes in Concentration

Derive the missing terms representing concentration changes for each of the following reactions.

(a)

$$\underset{x}{C_2H_2(g)} + \underset{_____}{2Br_2(g)} \rightleftharpoons \underset{_____}{C_2H_2Br_4(g)}$$

(b)

$$\underset{_____}{I_2(aq)} + \underset{_____}{I^-(aq)} \rightleftharpoons \underset{x}{I_3^-(aq)}$$

(c)

$$\underset{x}{C_3H_8(g)} + \underset{_____}{5O_2(g)} \rightleftharpoons \underset{_____}{3CO_2(g)} + \underset{_____}{4H_2O(g)}$$

Solution

(a)

$$\underset{x}{C_2H_2(g)} + \underset{2x}{2Br_2(g)} \rightleftharpoons \underset{-x}{C_2H_2Br_4(g)}$$

(b)

$$\underset{-x}{I_2(aq)} + \underset{-x}{I^-(aq)} \rightleftharpoons \underset{x}{I_3^-(aq)}$$

(c)

$$\underset{x}{C_3H_8(g)} + \underset{5x}{5O_2(g)} \rightleftharpoons \underset{-3x}{3CO_2(g)} + \underset{-4x}{4H_2O(g)}$$

Check Your Learning

Complete the changes in concentrations for each of the following reactions:

(a)

$$\underset{_____}{2SO_2(g)} + \underset{x}{O_2(g)} \rightleftharpoons \underset{_____}{2SO_3(g)}$$

(b)

$$\underset{_____}{C_4H_8(g)} \rightleftharpoons \underset{-2x}{2C_2H_4(g)}$$

(c)

$$\underset{_____}{4NH_3(g)} + \underset{_____}{7O_2(g)} \rightleftharpoons \underset{_____}{4NO_2(g)} + \underset{_____}{6H_2O(g)}$$

Answer

(a) $2x$, x, $-2x$; (b) x, $-2x$; (c) $4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

17.2 Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the *K* expression. A slightly more challenging example is provided next, in which the reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they are when the system reaches *equilibrium*. The acronym ICE is commonly used to refer to this mathematical approach, and the concentrations terms are usually gathered in a tabular format called an ICE table.

EXAMPLE 17.2.1

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

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

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_C = \frac{[I_3^-]}{[I_2][I^-]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	I_2 + I^- ⇌ 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

At equilibrium the concentration of I_2 is 6.61

×

10^{-4} *M* so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$= 3.39 \times 10^{-4}\ M$$

The ICE table may now be updated with numerical values for all its concentrations:

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the *K* expression and solve:

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

Check Your Learning

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 a solute in this reaction.)

Answer

$K_c = 4$

17.3 Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

EXAMPLE 17.3.1

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 K_c for the reaction,

$$\mathrm{N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO(g),}$$

is 4.1×10^{-4}. Calculate the equilibrium concentration of NO(*g*) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

Substitute the provided quantities into the equilibrium constant expression and solve for [NO]:

$$K_c = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}]\,[\mathrm{O_2}]}$$

$$[\mathrm{NO}]^2 = K_c\,[\mathrm{N_2}]\,[\mathrm{O_2}]$$

$$[\mathrm{NO}] = \sqrt{K_c\,[\mathrm{N_2}]\,[\mathrm{O_2}]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for *K*:

$$\begin{aligned} K_c &= \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}]\,[\mathrm{O_2}]} \\ &= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)} \\ &= 4.0 \times 10^{-4} \end{aligned}$$

This result is consistent with the provided value for K within nominal uncertainty, differing by just 1 in the least significant digit's place.

Check Your Learning

The equilibrium constant K_c 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

17.4 Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Develop an ICE table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

EXAMPLE 17.4.1

Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c 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 in a mixture that initially contained only PCl_5 at a concentration of 1.00 *M*?

Solution

Use the stepwise process described earlier.

1. Step 1.
   Determine the direction the reaction proceeds.

   The balanced equation for the decomposition of PCl_5 is

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

   Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right.

2. Step 2.
   Develop an ICE table.

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x	x

3. Step 3.
   Solve for the change and the equilibrium concentrations.

   Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3\,][Cl_2\,]}{[PCl_5\,]} = 0.0211$$

$$= \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211(1.00 - x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

   Appendix B shows 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:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

For this scenario, only the positive root is physically meaningful (concentrations are either zero or positive), and so x = 0.135 M.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87\,M$$

$$[PCl_3] = x = 0.135\,M$$

$$[Cl_2] = x = 0.135\,M$$

4. Step 4.
Confirm the calculated equilibrium concentrations.

Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

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).

Check Your Learning

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 for a mixture that is initially 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?

Answer

$[CH_3CO_2H] = 0.18$ *M*, $[C_2H_5OH] = 0.18$ *M*, $[CH_3CO_2C_2H_5] = 0.37$ *M*, $[H_2O] = 0.37$ *M*

Check Your Learning

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?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Answer

$[H_2] = 0.06$ *M*, $[I_2] = 1.06$ *M*, $[HI] = 1.88$ *M*

EXAMPLE 17.4.2

Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{CN}^-(aq) \qquad K_c = 4.9 \times 10^{-10}$$

Solution

Using "*x*" to represent the concentration of each product at equilibrium gives this ICE table.

	HCN(*aq*) ⇌	H^+(*aq*)	+ CN^-(*aq*)
Initial concentration (*M*)	0.15	0	0
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium concentration (*M*)	0.15 − *x*	*x*	*x*

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

Rearrange to the quadratic form and solve for *x*

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

$$x = 8.56 \times 10^{-6}\ M\,(3\text{ sig. figs.}) = 8.6 \times 10^{-6}\ M\,(2\text{ sig. figs.})$$

Thus $[H^+] = [CN^-] = x = 8.6\times10^{-6}$ *M* and [HCN] = 0.15 − *x* = 0.15 *M*.

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small *K*), and so the initial concentration experiences a negligible change:

$$\text{if } x \ll 0.15\text{ M, then } (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

The value of *x* calculated is, indeed, much less than the initial concentration

$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for *x* that did *not* justify the approximation, the calculation would need to be repeated without making the approximation.

Check Your Learning

What are the equilibrium concentrations in a 0.25 *M* NH_3 solution?

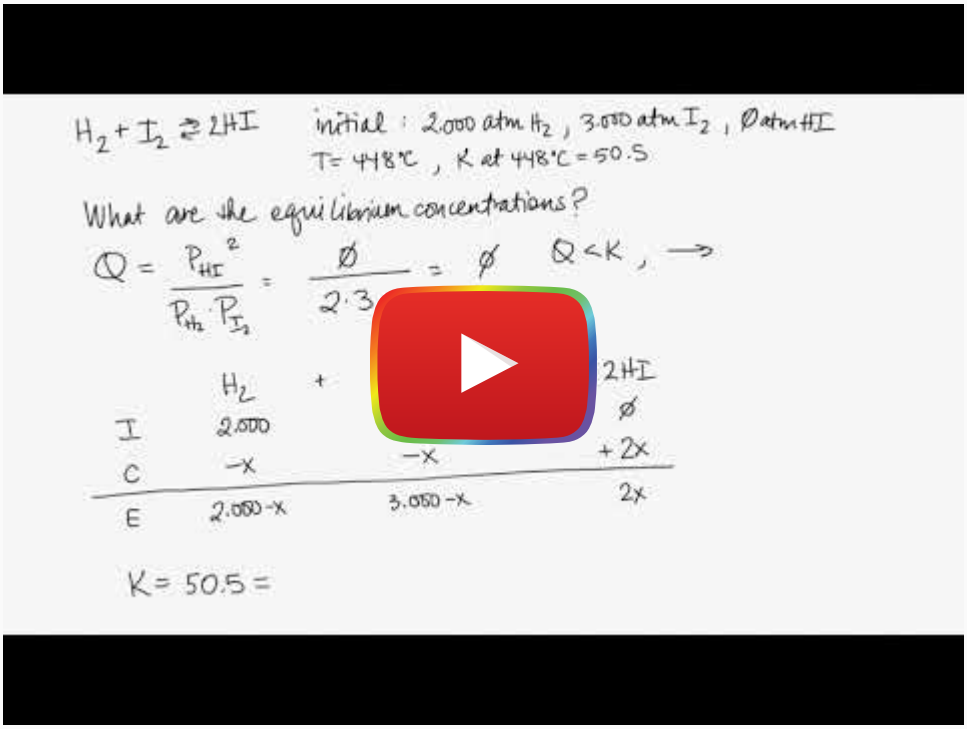
$$NH_3\,(aq) + H_2O(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \qquad K_c = 1.8 \times 10^{-5}$$

Answer

$[OH^-] = [NH_4^+] = 0.0021\ M;$

$[NH_3] = 0.25\ M$

17.4.3 Practice Problem



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18

Review of Thermodynamics Calculations

The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. The standard enthalpy of formation, $\Delta Hf°$, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar and 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A number of approaches to the computation of free energy changes are possible.

18.1 Standard Enthalpy of Formation

Learning Objectives

By the end of this section, you will be able to:

- Define standard enthalpy of formation
- Explain Hess's law and use it to compute reaction enthalpies

A standard enthalpy of formation

$\Delta H_{\mathrm{f}}^{\circ}$

is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

$$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta H_{\mathrm{f}}^{\circ} = \Delta H° = -393.5\ \mathrm{kJ}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide,

$NO_2(g)$,

ΔH_f°

is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H_f^\circ = \Delta H^\circ = +33.2 \text{ kJ}$$

A reaction equation with

$\frac{1}{2}$

mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Appendix G. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

EXAMPLE 18.1.1

Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation,

$$\Delta H_f^\circ$$

of ozone from the following information:

$$3O_2(g) \longrightarrow 2O_3(g) \qquad \Delta H° = +286 \text{ kJ}$$

Solution

$$\Delta H_f^\circ$$

is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus,

$$\Delta H_f^\circ$$

for $O_3(g)$ is the enthalpy change for the reaction:

$$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$$

For the formation of 2 mol of $O_3(g)$,

$$\Delta H° = +286 \text{ kJ}.$$

This ratio,

$$\left(\frac{286 \text{ kJ}}{2 \text{ mol } O_3}\right),$$

can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

$$\Delta H° \text{ for 1 mole of } O_3(g) = 1 \text{ mol } O_3 \times \frac{286 \text{ kJ}}{2 \text{ mol } O_3} = 143 \text{ kJ}$$

Therefore,

$$\Delta H_f^\circ [O_3(g)] = +143 \text{ kJ/mol}.$$

Check Your Learning

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, HCl(*g*). What is the enthalpy change for the reaction of 1 mole of H_2(*g*) with 1 mole of Cl_2(*g*) if both the reactants and products are at standard state conditions? The standard enthalpy of formation of HCl(*g*) is −92.3 kJ/mol.

Answer

For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H° = -184.6\ \text{kJ}$$

EXAMPLE 18.1.2

Writing Reaction Equations for

ΔH_f°

Write the heat of formation reaction equations for:
(a) $C_2H_5OH(l)$

(b) $Ca_3(PO_4)_2(s)$

Solution

Remembering that

ΔH_f°

reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:
(a)

$$2C(s,\ \text{graphite}) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$$

(b)

$$3Ca(s) + \tfrac{1}{2}P_4(s) + 4O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Check Your Learning

Write the heat of formation reaction equations for:
(a) $C_2H_5OC_2H_5(l)$

(b) $Na_2CO_3(s)$

Answer

(a)

$$4C(s,\ \text{graphite}) + 5H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l);$$

(b)

$$2\text{Na}(s) + \text{C}(s,\ \text{graphite}) + \tfrac{3}{2}\text{O}_2\,(g) \longrightarrow \text{Na}_2\,\text{CO}_3\,(s)$$

18.2 Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$\text{C}(s) + \text{O}_2\,(g) \longrightarrow \text{CO}_2\,(g) \qquad \Delta H° = -394\ \text{kJ}$$

In the two-step process, first carbon monoxide is formed:

$$\text{C}(s) + \frac{1}{2}\text{O}_2\,(g) \longrightarrow \text{CO}(g) \qquad \Delta H° = -111\ \text{kJ}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\text{CO}(g) + \frac{1}{2}\text{O}_2\,(g) \longrightarrow \text{CO}_2\,(g) \qquad \Delta H° = -283\ \text{kJ}$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{gathered}\text{Step 1: C}(s) + \tfrac{1}{2}\text{O}_2\,(g) \longrightarrow \text{CO}(g)\\ \text{Step 2: CO}(g) + \tfrac{1}{2}\text{O}_2\,(g) \longrightarrow \text{CO}_2\,(g)\\ \text{Sum: C}(s) + \tfrac{1}{2}\text{O}_2\,(g) + \text{CO}(g) + \tfrac{1}{2}\text{O}_2\,(g) \longrightarrow \text{CO}(g) + \text{CO}_2\,(g)\end{gathered}$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$\text{C}(s) + \text{O}_2\,(g) \longrightarrow \text{CO}_2\,(g)$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.

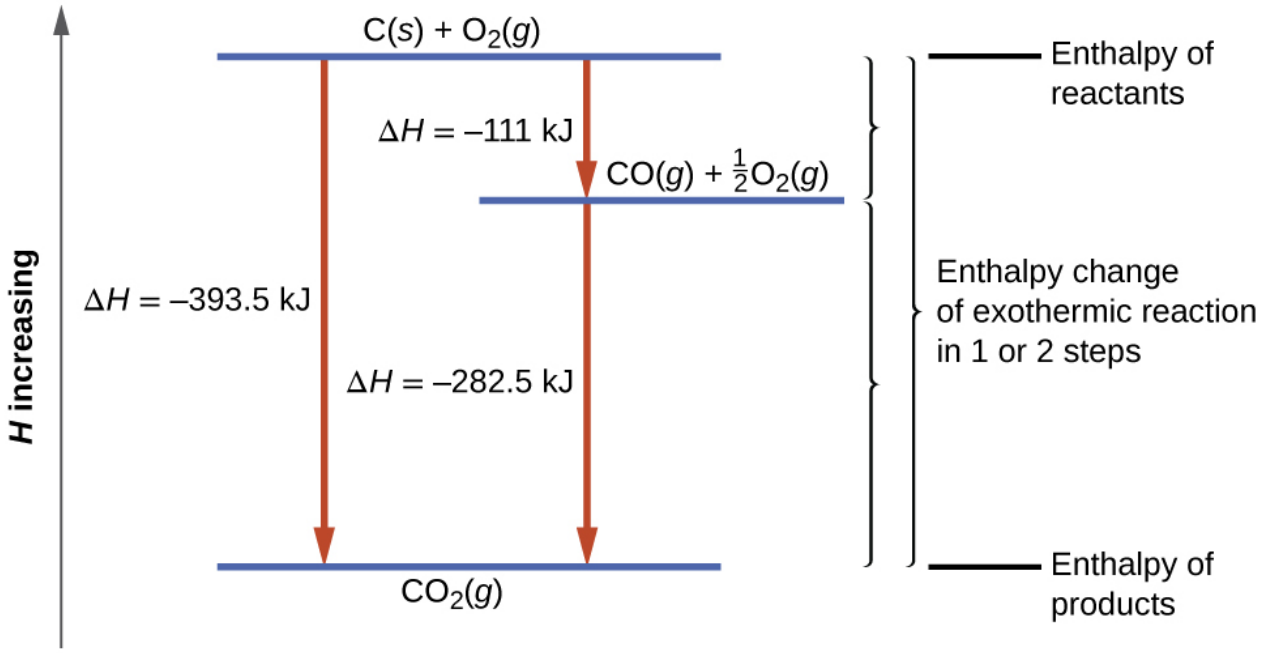
$$\mathrm{C}(s) + \tfrac{1}{2}\mathrm{O}_2\,(g) \longrightarrow \mathrm{CO}(g) \quad \Delta H° = -111\ \mathrm{kJ}$$

$$\frac{\mathrm{CO}(g) + \tfrac{1}{2}\mathrm{O}_2\,(g) \longrightarrow \mathrm{CO}_2\,(g)}{\mathrm{C}(s) + \mathrm{O}_2\,(g) \longrightarrow \mathrm{CO}_2\,(g)} \qquad \begin{matrix} \Delta H° = -283\ \mathrm{kJ} \\ \Delta H° = -394\ \mathrm{kJ} \end{matrix}$$

The result is shown in Figure 18.1. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of ΔH values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

Figure 18.1

The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.



Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = +33.2 \text{ kJ}$$

When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = +66.4 \text{ kJ}$$

In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -184.6 \text{ kJ}$$

Then, for the “reverse” reaction, the enthalpy change is also “reversed”:

$$2HCl(g) \longrightarrow H_2(g) + Cl_2(g) \qquad \Delta H = +184.6 \text{ kJ}$$

EXAMPLE 18.2.1

Stepwise Calculation of

ΔH_f°

Using Hess's Law

Determine the enthalpy of formation,

ΔH_f°,

of $FeCl_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s) \qquad \Delta H° = -341.8\ kJ$$

$$FeCl_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s) \qquad \Delta H° = -57.7\ kJ$$

Solution

We are trying to find the standard enthalpy of formation of $FeCl_3(s)$, which is equal to $\Delta H°$ for the reaction:

$$Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s) \qquad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find $\Delta H°$ is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:

$$\begin{array}{ll} Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s) & \Delta H° = -341.8\ kJ \\ \underline{FeCl_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow FeCl_3(s)} & \underline{\Delta H° = -57.7\ kJ} \\ Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s) & \Delta H° = -399.5\ kJ \end{array}$$

The enthalpy of formation,

ΔH_f°,

of $FeCl_3(s)$ is −399.5 kJ/mol.

Check Your Learning

Calculate ΔH for the process:

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$$

from the following information:

$$N_2(g) + O_2(g) \longrightarrow 2NO(g) \qquad \Delta H = 180.5\ \text{kJ}$$

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g) \qquad \Delta H = -57.06\ \text{kJ}$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

EXAMPLE 18.2.2

A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

(i)

$$\mathrm{ClF(g) + F_2\,(g) \longrightarrow ClF_3\,(g)} \qquad \Delta H° = \ ?$$

Use the reactions here to determine the $\Delta H°$ for reaction *(i)*:

(ii)

$$\mathrm{2OF_2\,(g) \longrightarrow O_2\,(g) + 2F_2\,(g)} \qquad \Delta H^{\circ}_{(ii)} = -49.4\ \mathrm{kJ}$$

(iii)

$$\mathrm{2ClF(g) + O_2\,(g) \longrightarrow Cl_2\,O(g) + OF_2\,(g)} \qquad \Delta H^{\circ}_{(iii)} = +214.0\ \mathrm{kJ}$$

(iv)

$$\mathrm{ClF_3\,(g) + O_2\,(g) \longrightarrow \tfrac{1}{2}Cl_2\,O(g) + \tfrac{3}{2}OF_2\,(g)} \qquad \Delta H^{\circ}_{(iv)} = +236.2\ \mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions *(ii)*, *(iii)*, and *(iv)* such that they add up to reaction *(i)*. Going from left to right in *(i)*, we first see that ClF(*g*) is needed as a reactant. This can be obtained by multiplying reaction *(iii)* by

$\frac{1}{2}$,

which means that the $\Delta H°$ change is also multiplied by

$\frac{1}{2}$:

$$\mathrm{ClF(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow \tfrac{1}{2}Cl_2\,O(g) + \tfrac{1}{2}OF_2\,(g)} \qquad \Delta H° = \tfrac{1}{2}(214.0) = +107.0\ \mathrm{kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the $\Delta H°$ changes sign and is halved:

$$\mathrm{\tfrac{1}{2}O_2\,(g) + F_2\,(g) \longrightarrow OF_2\,(g)} \qquad \Delta H° = +24.7\ \mathrm{kJ}$$

To get ClF_3 as a product, reverse *(iv)*, changing the sign of $\Delta H°$:

$$\frac{1}{2}Cl_2O(g) + \frac{3}{2}OF_2(g) \longrightarrow ClF_3(g) + O_2(g) \qquad \Delta H° = -236.2\ \text{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{array}{ll} ClF(g) + \frac{1}{2}O_2(g) \longrightarrow \frac{1}{2}Cl_2O(g) + \frac{1}{2}OF_2(g) & \Delta H° = +107.0\ \text{kJ} \\ \frac{1}{2}O_2(g) + F_2(g) \longrightarrow OF_2(g) & \Delta H° = +24.7\ \text{kJ} \\ \hline \frac{\frac{1}{2}Cl_2O(g) + \frac{3}{2}OF_2(g) \longrightarrow ClF_3(g) + O_2(g)}{ClF(g) + F_2 \longrightarrow ClF_3(g)} & \begin{array}{l} \Delta H° = -236.2\ \text{kJ} \\ \hline \Delta H° = -104.5\ \text{kJ} \end{array} \end{array}$$

Reactants

$\frac{1}{2}O_2$

and

$\frac{1}{2}O_2$

cancel out product O_2; product

$\frac{1}{2}Cl_2O$

cancels reactant

$\frac{1}{2}Cl_2O;$

and reactant

$\frac{3}{2}OF_2$

is cancelled by products

$\frac{1}{2}OF_2$

and OF_2. This leaves only reactants $ClF(g)$ and $F_2(g)$ and product $ClF_3(g)$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified $\Delta H°$ values will give the desired $\Delta H°$:

$$\Delta H° = (+107.0\ \text{kJ}) + (24.7\ \text{kJ}) + (-236.2\ \text{kJ}) = -104.5\ \text{kJ}$$

Check Your Learning

Aluminum chloride can be formed from its elements:
(i)

$$2\text{Al}(s) + 3\text{Cl}_2(g) \longrightarrow 2\text{AlCl}_3(s) \qquad \Delta H° = \ ?$$

Use the reactions here to determine the $\Delta H°$ for reaction *(i)*:

(ii)

$$\text{HCl}(g) \longrightarrow \text{HCl}(aq) \qquad \Delta H^\circ_{(ii)} = -74.8 \text{ kJ}$$

(iii)

$$\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g) \qquad \Delta H^\circ_{(iii)} = -185 \text{ kJ}$$

(iv)

$$\text{AlCl}_3(aq) \longrightarrow \text{AlCl}_3(s) \qquad \Delta H^\circ_{(iv)} = +323 \text{ kJ/mol}$$

(v)

$$2\text{Al}(s) + 6\text{HCl}(aq) \longrightarrow 2\text{AlCl}_3(aq) + 3\text{H}_2(g) \qquad \Delta H^\circ_{(v)} = -1049 \text{ kJ}$$

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with ∑ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_{\text{f}}(\text{products}) - \sum n \times \Delta H^\circ_{\text{f}}(\text{reactants})$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

EXAMPLE 18.2.3

Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3NO_2\,(g) + H_2O(l) \longrightarrow 2HNO_3\,(aq) + NO(g) \qquad \Delta H° = \ ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously, and values from Appendix G:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f\,(\text{products}) - \sum n \times \Delta H^\circ_f\,(\text{reactants})$$

$$= [2\ \text{mol}\ HNO_3\,(aq) \times \tfrac{-207.4\ \text{kJ}}{\text{mol}\ HNO_3\,(aq)} + 1\ \text{mol}\ NO(g) \times \tfrac{+90.2\ \text{kJ}}{\text{mol}\ NO(g)}]$$
$$-[3\ \text{mol}\ NO_2\,(g) \times \tfrac{+33.2\ \text{kJ}}{\text{mol}\ NO_2\,(g)} + 1\ \text{mol}\ H_2O(l) \times \tfrac{-285.8\ \text{kJ}}{\text{mol}\ H_2O(l)}]$$
$$= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)]$$
$$= -323.03 + 186.23$$
$$= -136.80\ \text{kJ}$$

Solution: Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3NO_2(g)$ and $1H_2O(l)$ into their constituent elements, and the formation of $2HNO_3(aq)$ and $1NO(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the

ΔH°_f

values for these compounds (from Appendix G), we have:

$$3NO_2\,(g) \longrightarrow 3/2N_2\,(g) + 3O_2\,(g) \qquad \Delta H^\circ_1 = -99.6\ \text{kJ}$$

$$H_2O(l) \longrightarrow H_2\,(g) + \tfrac{1}{2}O_2\,(g) \qquad \Delta H^\circ_2 = +285.8\ \text{kJ}\ [-1 \times \Delta H^\circ_f\,(H_2O)]$$

$$H_2\,(g) + N_2\,(g) + 3O_2\,(g) \longrightarrow 2HNO_3\,(aq) \qquad \Delta H^\circ_3 = -414.8\ \text{kJ}\ [2 \times \Delta H^\circ_f\,(HNO_3)]$$

$$\tfrac{1}{2}N_2\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow NO(g) \qquad \Delta H^\circ_4 = +90.2\ \text{kJ}\ [1 \times (NO)]$$

Summing these reaction equations gives the reaction we are interested in:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\Delta H^\circ_{rxn} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 = (-99.6\ \text{kJ}) + (+285.8\ \text{kJ}) + (-414.8\ \text{kJ}) + (+90.2\ \text{kJ}) = -138.4\ \text{kJ}$$

So the standard enthalpy change for this reaction is $\Delta H^\circ = -138.4$ kJ.

Note that this result was obtained by (1) multiplying the

$$\Delta H^\circ_f$$

of each product by its stoichiometric coefficient and summing those values, (2) multiplying the

$$\Delta H^\circ_f$$

of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

Check Your Learning

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

18.3 Temperature Dependence of Spontaneity

Learning Objectives

By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Explain how temperature affects the spontaneity of some proceses

As was previously demonstrated in the section on entropy in an earlier chapter, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction

or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH. If the $T\Delta S$ term is less than ΔH, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*
2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH. If the $T\Delta S$ term's magnitude is greater than ΔH, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*
3. **ΔH is positive and ΔS is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*
4. **ΔH is negative and ΔS is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in Figure 18.2.

Figure 18.2

There are four possibilities regarding the signs of enthalpy and entropy changes.

Summary of the Four Scenarios for Enthalpy and Entropy Changes

	$\Delta H > 0$ (endothermic)	**$\Delta H < 0$ (exothermic)**
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

EXAMPLE 18.3.1

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\mathrm{C}(s) + \mathrm{O}_2\,(g) \longrightarrow 2\mathrm{CO}(g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\mathrm{Fe}(s) + 3\mathrm{O}_2\,(g) \longrightarrow 2\mathrm{Fe}_2\,\mathrm{O}_3\,(s)$$

How does the spontaneity of this process depend upon temperature?

Answer

ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in “spontaneity” (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

$$\Delta G = \Delta H - T\Delta S$$

$$y = b + mx$$

Such a plot is shown in Figure 18.3. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero:

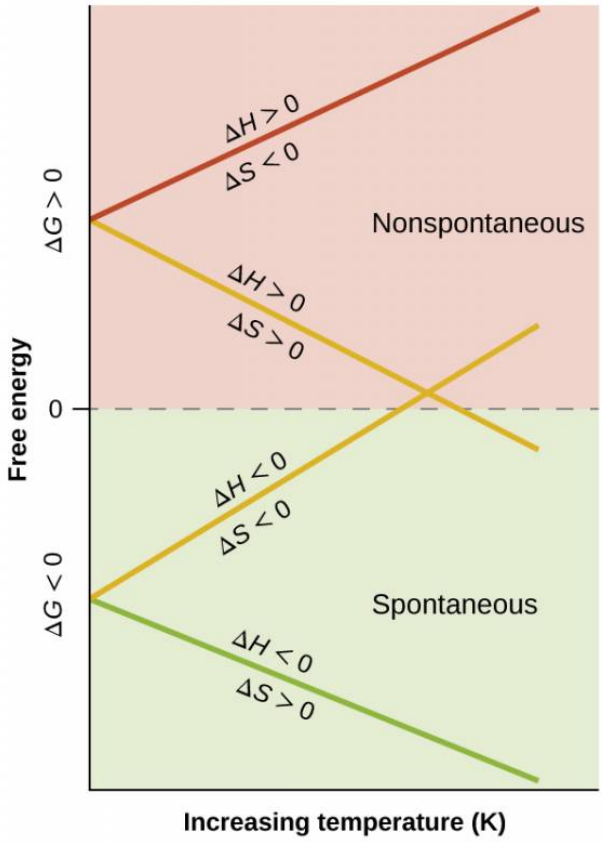
$$\Delta G = 0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, the condition of ΔG = 0 describes a system at equilibrium.

Figure 18.3

These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS.



EXAMPLE 18.3.2

Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Appendix G to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H° - T\Delta S° \qquad \text{or} \qquad T = \frac{\Delta H°}{\Delta S°}$$

Using the standard thermodynamic data from Appendix G,

$$\begin{aligned}
\Delta H° &= 1\ \text{mol} \times \Delta H_f^\circ(\mathrm{H_2O}(g)) - 1\ \text{mol} \times \Delta H_f^\circ(\mathrm{H_2O}(l)) \\
&= (1\ \text{mol}) - 241.82\ \text{kJ/mol} - (1\ \text{mol})(-241.82\ \text{kJ/mol}) = 44.01\ \text{kJ} \\
\Delta S° &= 1\ \text{mol} \times \Delta S^\circ(\mathrm{H_2O}(g)) - 1\ \text{mol} \times \Delta S^\circ(\mathrm{H_2O}(l)) \\
&= (1\ \text{mol})188.8\ \text{J/K·mol} - (1\ \text{mol})70.0\ \text{J/K·mol} = 118.8\ \text{J/K} \\
T &= \frac{\Delta H°}{\Delta S°} = \frac{44.01 \times 10^3\ \text{J}}{118.8\ \text{J/K}} = 370.5\ \text{K} = 97.3\ °\text{C}
\end{aligned}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Appendix G). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Check Your Learning

Use the information in Appendix G to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K)

Files

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Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (12.1-12.4, 13.4)

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19

ΔG and Q, ΔG° and K

In this chapter, we learn to relate the reaction quotient (Q) to Gibb's free energy mathematically through the expression ΔG = ΔG° + RT ln Q. We also learn about the relationship between the equilibrium constant (K) and ΔG°, which can be expressed through the equation ΔG° = −RTlnKeq. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium.

19.1 Free Energy and Equilibrium

Learning Objectives

By the end of this section, you will be able to:

- Relate standard free energy changes to equilibrium constants

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium).

In the section on equilibrium, the *reaction quotient*, *Q*, was introduced as a convenient measure of the status of an equilibrium system. Recall that *Q* is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When *Q* is lesser than the equilibrium constant, *K*, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change, according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in Example 19.1.

EXAMPLE 19.1.1

Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?
T = 25 °C,

$$P_{N_2} = 0.870 \text{ atm},$$

$$P_{H_2} = 0.250 \text{ atm},$$

and

$$P_{NH_3} = 12.9 \text{ atm}$$

$$2NH_3\,(g) \longrightarrow 3H_2\,(g) + N_2\,(g) \qquad \Delta G° = 33.0 \text{ kJ/mol}$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\Delta G = \Delta G° + RT \ln Q = 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2}\right) = 9680$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

Check Your Learning

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

ΔG = −47 kJ/mol; yes

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

$$0 = \Delta G° + RT \ln K \qquad \text{(at equilibrium)}$$

$$\Delta G° = -RT \ln K \qquad \text{or} \qquad K = e^{-\frac{\Delta G°}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 19.1.

Table 19.1

Relations between Standard Free Energy Changes and Equilibrium Constants

K	$\Delta G°$	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

EXAMPLE 19.1.2

Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \qquad K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G° &= [\Delta G_f^\circ(\mathrm{Ag}^+(aq)) + \Delta G_f^\circ(\mathrm{Cl}^-(aq))] - [\Delta G_f^\circ(\mathrm{AgCl}(s))] \\ &= [\,77.1\ \mathrm{kJ/mol} - 131.2\ \mathrm{kJ/mol}\,] - [-109.8\ \mathrm{kJ/mol}] = 55.7\ \mathrm{kJ/mol}\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{sp} = e^{-\frac{\Delta G°}{RT}} = \exp\left(-\frac{\Delta G°}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol\cdot K} \times 298.15\ \mathrm{K}}\right) = \exp(-22.470) = e^{-22.470} =$$

This result is in reasonable agreement with the value provided in Appendix J.

Check Your Learning

Use the thermodynamic data provided in Appendix G to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

Answer

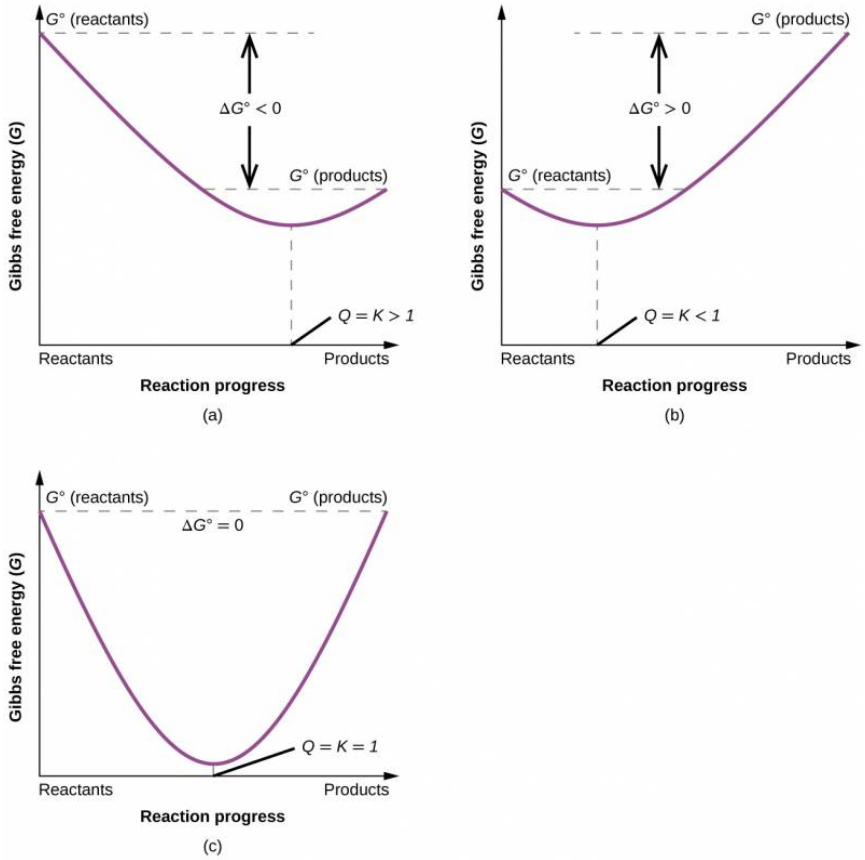
K = 0.32

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 19.1). If a system consists of reactants and products in

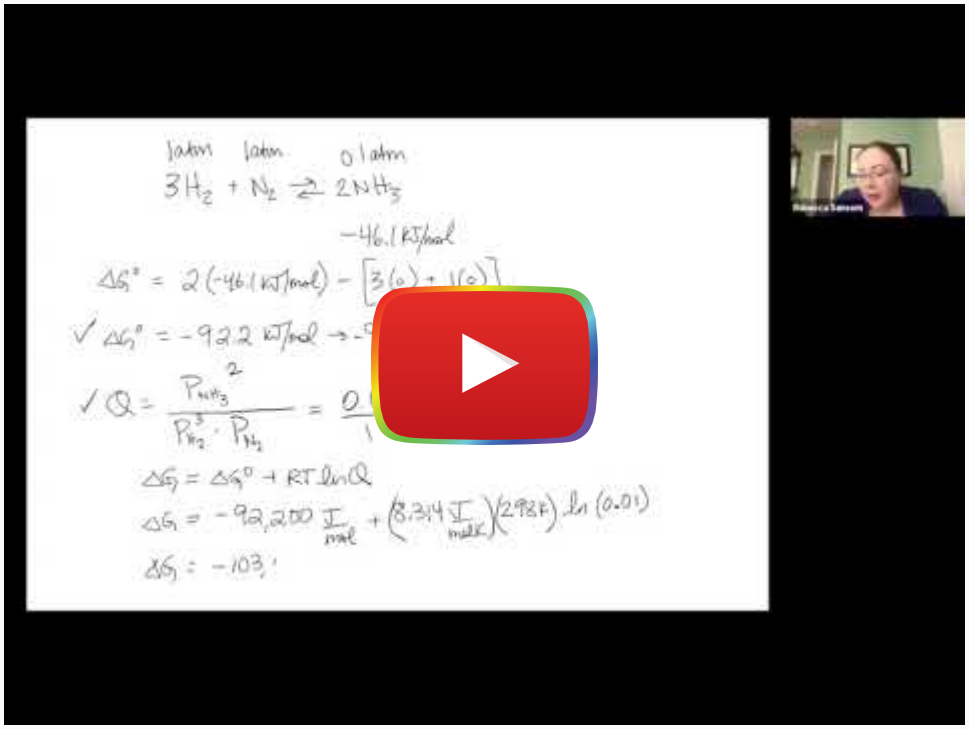
nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

Figure 19.2

These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.



19.1.3 Non-Standard Delta G



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20

Temperature Dependence of K

20.1 Effect of a Change in Temperature

Learning Objectives

- Predict the response of a stressed equilibrium using Le Châtelier's principle

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, *K*. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\begin{aligned} \text{rate}_f &= k_f\,[\mathrm{A}] \\ \text{rate}_r &= k_r\,[\mathrm{B}] \end{aligned}$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$\begin{aligned} k_f\,[\mathrm{A}] &= k_r\,[\mathrm{B}] \\ \frac{[\mathrm{B}]}{[\mathrm{A}]} &= \frac{k_f}{k_r} = K_c \end{aligned}$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\mathrm{N_2O_4(g) \rightleftharpoons 2NO_2(g)} \qquad\qquad \Delta H = 57.20\ \mathrm{kJ}$$

For purposes of applying Le Chatelier's principle, heat (*q*) may be viewed as a reactant:

$$\mathrm{heat + N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

20.2 Temperature Dependence of Equilibrium Constants - the van't Hoff Equation

The value of K_p is independent of pressure, although the composition of a system at equilibrium may be very much dependent on pressure. Temperature dependence is another matter. Because the value of K_p is dependent on temperature, the value of K is as well. The form of the temperature dependence can be taken from the definition of the Gibbs function. At constant temperature and pressure

$$\frac{\Delta G^o_{T_2}}{T_2} - \frac{\Delta G^o_{T_1}}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting

$$\Delta G^o = -RT\ln K$$

For the two values of $\ln(K)$ and using the appropriate temperatures, yields

$$\frac{-RT_2 \ln K_2}{T_2} - \frac{-RT_1 \ln K_1}{T_1} = \Delta H^o \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

And simplifying the expression so that only terms involving $-\Delta H^o / R$ are on the left and all other terms are on the right results in the **van 't Hoff equation**, which describes the temperature dependence of the equilibrium constant.

$$\ln(\frac{K_2}{K_1}) = \frac{\Delta H^o}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \quad (9.6.1)$$

Because of the assumptions made in the derivation of the Gibbs-Helmholtz equation, this relationship only holds if $\Delta H^o_{rxm} = 32.4kJ/mol$ is independent of temperature over the range being considered. This expression also suggests that a plot of $\Delta H^o_{rxm} = 32.4kJ/mol$ as a function of $\ln(\frac{K_2}{0.0260}) = -\frac{32400J/mol}{8.314K/(molK)}(\frac{1}{310K} - \frac{1}{298K}) = 0.0431$ should produce a straight line with a slope equal to K_2 $\mathrm{P-Cl}$. Such a plot is known as a **van 't Hoff plot**, and can be used to determine the reaction enthalpy.

Example 20.2.1

A certain reaction has a value of $\mathrm{PCl_5 \rightleftharpoons PCl_3 + Cl_2}$ at 25 °C and $\Delta H^o_{rxm} = 32.4kJ/mol$. Calculate the value of $\Delta H^o_{rxm} = 32.4kJ/mol$ at 37 °C.

Answer

This is a job for the van 't Hoff equation!

- T_1 = 298 K
- T_2 = 310 K
- $\ln(\frac{K_2}{0.0260}) = -\frac{32400J/mol}{8.314K/(molK)}(\frac{1}{310K} - \frac{1}{298K}) = 0.0431$
- K_1 = 0.0260
- K_2 = ?

So Equation $\mathrm{P-Cl}$ becomes

$$\mathrm{PCl_5 \rightleftharpoons PCl_3 + Cl_2}$$

Note: the value of K_2 **increased** with **increasing** temperature, which is what is expected for an **endothermic** reaction. An increase in temperature should result in an increase of product formation in the equilibrium mixture. But unlike a change in pressure, a change in temperature actually leads to a change in the value of the equilibrium constant!

Example 20.2.2

Given the following average bond enthalpies for $\mathrm{PCl_5 \rightleftharpoons PCl_3 + Cl_2}$ and $\mathrm{Cl-Cl}$ bonds, predict whether or not an increase in temperature will lead to a larger or smaller degree of dissociation for the reaction

$$\mathrm{PCl_5 \rightleftharpoons PCl_3 + Cl_2}$$

X-Y	D(X-Y) (kJ/mol)
P-Cl	326
Cl-Cl	240

Answer

The estimated reaction enthalpy is given by the total energy expended breaking bonds minus the energy recovered by the formation of bonds. Since this reaction involves breaking two P-Cl bonds (costing 652 kJ/mol) and the formation of one Cl-Cl bond (recovering 240 kJ/mol), it is clear that the reaction is endothermic (by approximately 412 kJ/mol). As such, an increase in temperature should increase the value of the equilibrium constant, causing the degree of dissociation to be increased at the higher temperature.

20.2.3 Van 't Hoff plot

For a reversible reaction, the equilibrium constant can be measured at a variety of temperatures. This data can be plotted on a graph with ln K_{eq} on the *y*-axis and $1/T$ on the *x-axis*. The data should have a linear relationship, the equation for which can be found by fitting the data using the linear form of the Van 't Hoff equation

$$\ln K_{\mathrm{eq}} = -\frac{\Delta_r H^{\ominus}}{RT} + \frac{\Delta_r S^{\ominus}}{R}.$$

This graph is called the "Van 't Hoff plot" and is widely used to estimate the enthalpy and entropy of a chemical reaction. From this plot, $-\Delta_r H/R$ is the slope, and $\Delta_r S/R$ is the intercept of the linear fit.

By measuring the equilibrium constant, K_{eq}, at different temperatures, the Van 't Hoff plot can be used to assess a reaction when the temperature changes.
Knowing the slope and intercept from the Van 't Hoff plot, the enthalpy, and entropy of a reaction can be easily obtained using

$$\Delta_r H = -R \times \text{slope},$$
$$\Delta_r S = R \times \text{intercept}.$$

The Van 't Hoff plot can be used to quickly determine the enthalpy of a chemical reaction both qualitatively and quantitatively. This change in enthalpy can be positive or negative, leading to two major forms of the Van 't Hoff plot.

20.2.4 Endothermic reactions

For an endothermic reaction, heat is absorbed, making the net enthalpy change positive. Thus, according to the definition of the slope:

$$\mathbf{slope} = -\frac{\Delta_r H}{R},$$

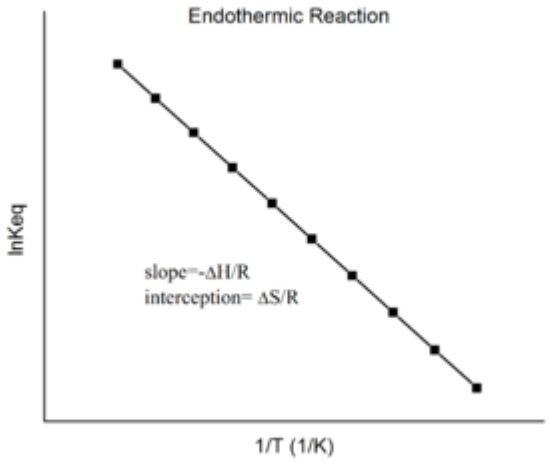
When the reaction is endothermic, $\Delta_r H > 0$ (and the gas constant $R > 0$), so

$$\mathbf{slope} = -\frac{\Delta_r H}{R} < 0.$$

Thus, for an endothermic reaction, the Van 't Hoff plot should always have a negative slope.

Figure 21.1

Van 't Hoff plot for an endothermic reaction



20.2.5 Exothermic reactions

For an exothermic reaction, heat is released, making the net enthalpy change negative. Thus, according to the definition of the slope:

$$\mathbf{slope} = -\frac{\Delta_r H}{R},$$

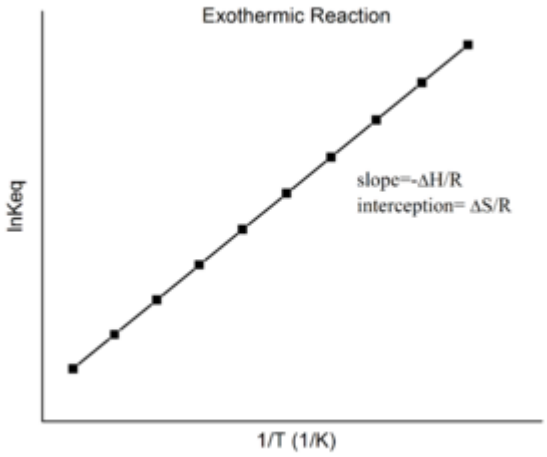
For an exothermic reaction $\Delta_r H < 0$, so

$$\mathbf{slope} = -\frac{\Delta_r H}{R} > 0.$$

Thus, for an exothermic reaction, the Van 't Hoff plot should always have a positive slope.

figure 20.2

Van 't Hoff plot for an exothermic reaction



20.2.6 Error propagation

At first glance, using the fact that $\Delta_r G^\ominus = -RT \ln K = \Delta_r H^\ominus - T\Delta_r S^\ominus$ it would appear that two measurements of K would suffice to be able to obtain an accurate value of $\Delta_r H^\ominus$:

$$\Delta_r H^\ominus = R\frac{\ln K_1 - \ln K_2}{\frac{1}{T_2} - \frac{1}{T_1}},$$

where K_1 and K_2 are the equilibrium constant values obtained at temperatures T_1 and T_2 respectively. However, the precision of $\Delta_r H^\ominus$ values obtained in this way is highly dependent on the precision of the measured equilibrium constant values.

The use of error propagation shows that the error in $\Delta_r H^\ominus$ will be about 76 kJ/mol times the experimental uncertainty in ($\ln K_1 - \ln K_2$), or about 110 kJ/mol times the uncertainty in the $\ln K$ values. Similar considerations apply to the entropy of reaction obtained from $\Delta_r S^\ominus = 1/T(\Delta H^\ominus + RT \ln K)$.

Notably, when equilibrium constants are measured at three or more temperatures, values of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are often obtained by straight-line fitting.
The expectation is that the error will be reduced by this procedure, although the assumption that the enthalpy and entropy of reaction are constant may or may not prove to be correct. If there is significant temperature dependence in either or both quantities, it should manifest itself in nonlinear behavior in the Van t'Hoff plot; however, more than three data points would presumably be needed in order to observe this.

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“Effect of a change in temperature” from https://edtechbooks.org/-xiKi https://edtechbooks.org/-CLJF Van’t hoff plot (includes thermic and exothermic reactions but not error propagation) from: https://edtechbooks.org/-FYdRT Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (13.4)

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Unit 5

Acids, Bases, and Buffers

Acids and Bases
Autoionization and pH Calculations
Weak Acids and Bases
Polyprotic Acids
pH of Salt Solutions
Buffers
DBL Acid Base
Titrations I
Titrations II

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21

Acids and Bases

Acid-base reactions involve the transfer of hydrogen ions between reactants. A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base.

21.1 Acid-Base Reactions

An acid-base reaction is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion, and a full chapter is devoted to this topic later in the text.

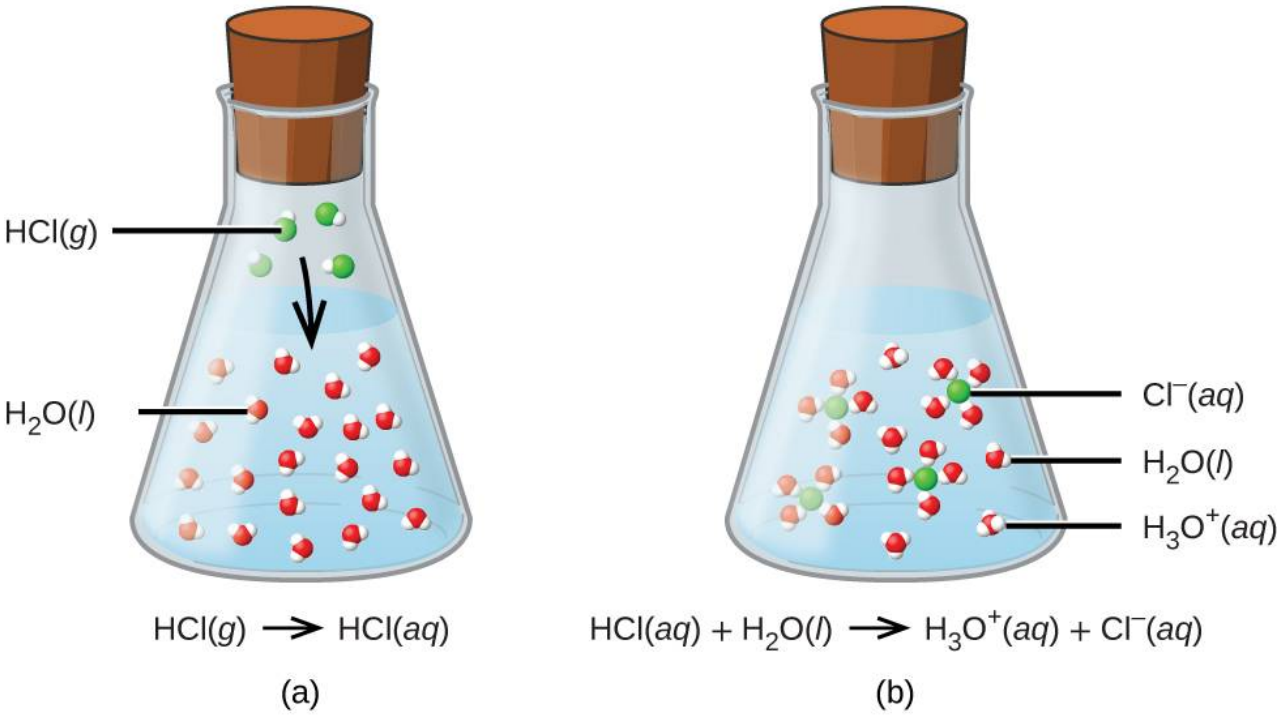
For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an acid is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(aq) \longrightarrow \mathrm{Cl^-}(aq) + \mathrm{H_3O^+}(aq)$$

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (Figure 22.1).

Figure 21.1

When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).



The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called strong acids, and HCl is one among just a handful of common acid compounds that are classified as strong (Table 21.1). A far greater number of compounds behave as weak acids and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2^-}(aq) + \mathrm{H_3O^+}(aq)$$

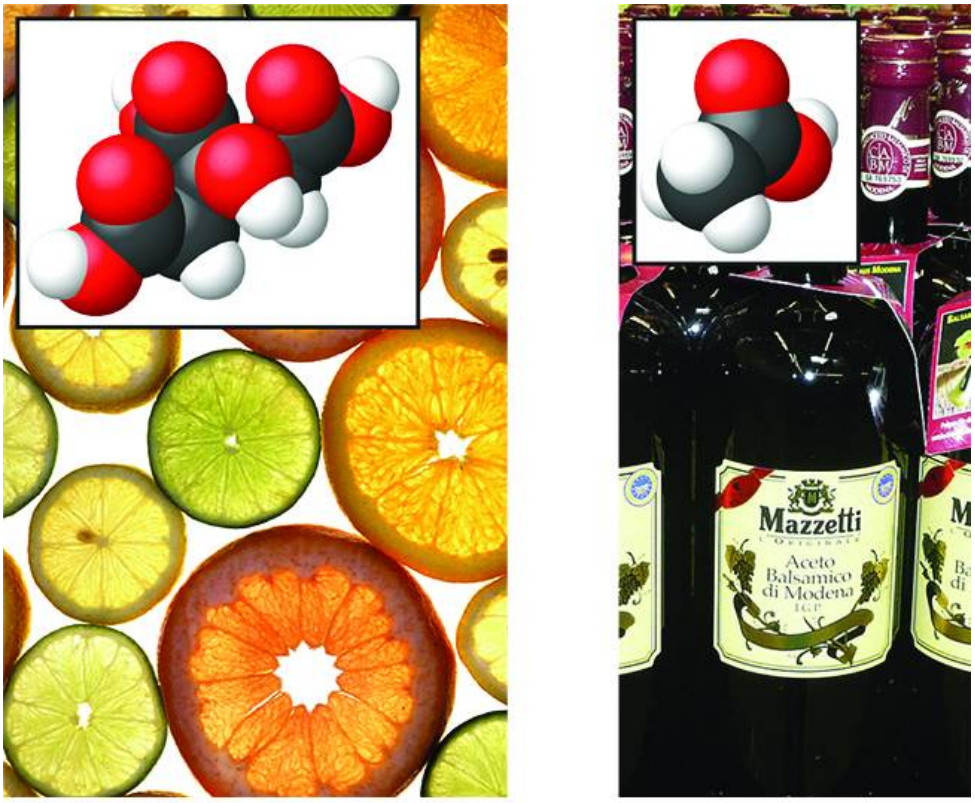
When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form,

$$\mathrm{CH_3CO_2^-}$$

(Figure 21.2). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)

Figure 21.2

(a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)



(a) (b)

Table 21.3

Common Strong Acids

Compound Formula	Name in Aqueous Solution
HBr	hydrobromic acid
HCl	hydrochloric acid
HI	hydroiodic acid
HNO_3	nitric acid
$HClO_4$	perchloric acid
H_2SO_4	sulfuric acid

A base is a substance that will dissolve in water to yield hydroxide ions, OH^-. The most common bases are ionic compounds composed of alkali or alkaline earth metal cations (groups 1 and 2) combined with the hydroxide ion—for example, NaOH and $Ca(OH)_2$. Unlike the acid compounds discussed previously, these compounds do not react chemically with water; instead they dissolve and dissociate, releasing hydroxide ions directly into the solution. For example, KOH and $Ba(OH)_2$ dissolve in water and dissociate completely to produce cations (K^+ and Ba^{2+}, respectively) and hydroxide ions, OH^-. These bases, along with other hydroxides that completely dissociate in water, are considered strong bases.

Consider as an example the dissolution of lye (sodium hydroxide) in water:

$$\mathrm{NaOH}(s) \longrightarrow \mathrm{Na}^+(aq) + \mathrm{OH}^-(aq)$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as weak bases. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure 21.3). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$\mathrm{NH_3}\,(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4}^+\,(aq) + \mathrm{OH}^-\,(aq)$$

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as

$$\mathrm{NH_4}^+$$

ions.

Figure 21.4

Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

(a) (b)

A neutralization reaction is a specific type of acid-base reaction in which the reactants are an acid and a base (but not water), and the products are often a salt and water

$$\text{acid} + \text{base} \longrightarrow \text{salt} + \text{water}$$

To illustrate a neutralization reaction, consider what happens when a typical antacid such as milk of magnesia (an aqueous suspension of solid $Mg(OH)_2$) is ingested to ease symptoms associated with excess stomach acid (HCl):

$$\mathrm{Mg(OH)_2}\,(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}\,(aq) + 2\mathrm{H_2O}(l).$$

Note that in addition to water, this reaction produces a salt, magnesium chloride.

EXAMPLE 21.1.1

Writing Equations for Acid-Base Reactions

Write balanced chemical equations for the acid-base reactions described here:
(a) the weak acid hydrogen hypochlorite reacts with water

(b) a solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

(a) The two reactants are provided, HOCl and H_2O. Since the substance is reported to be an acid, its reaction with water will involve the transfer of H^+ from HOCl to H_2O to generate hydronium ions, H_3O^+ and hypochlorite ions, OCl^-.

$$\mathrm{HOCl}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OCl^-}(aq) + \mathrm{H_3O^+}(aq)$$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion

(NO_3^-).

$$\mathrm{Ba(OH)_2}(aq) + 2\mathrm{HNO_3}(aq) \longrightarrow \mathrm{Ba(NO_3)_2}(aq) + 2\mathrm{H_2O}(l)$$

Check Your Learning

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. (Hint: Consider the ions produced when a strong acid is dissolved in water.)

Answer

$$\mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow 2\mathrm{H_2O}(l)$$

21.1.2 CHEMISTRY IN EVERYDAY LIFE

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$\mathrm{CaCO_3}\,(s) + 2\mathrm{HCl}(aq) \rightleftharpoons \mathrm{CaCl_2}\,(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}\,(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$\mathrm{Mg(OH)_2}\,(s) \rightleftharpoons \mathrm{Mg^{2+}}\,(aq) + 2\mathrm{OH^-}\,(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

$$\mathrm{H_3O^+} + \mathrm{OH^-} \rightleftharpoons 2\mathrm{H_2O}(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

21.1.3 CHEMISTRY IN EVERYDAY LIFE

Culinary Aspects of Chemistry

Examples of acid-base chemistry are abundant in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 21.4). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.

Figure 21.5

A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

$$CH_3COOH + NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow CH_3COO^- + NH_3^+CH_2CH_2CH_2CH_2NH_2$$

Acetic acid + Putrescine → Acetate ion + Putrescinium ion

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

LINK TO LEARNING

Explore the microscopic view of strong and weak acids and bases.

21.2 Brønsted-Lowry Acids and Bases

Learning Objectives

By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

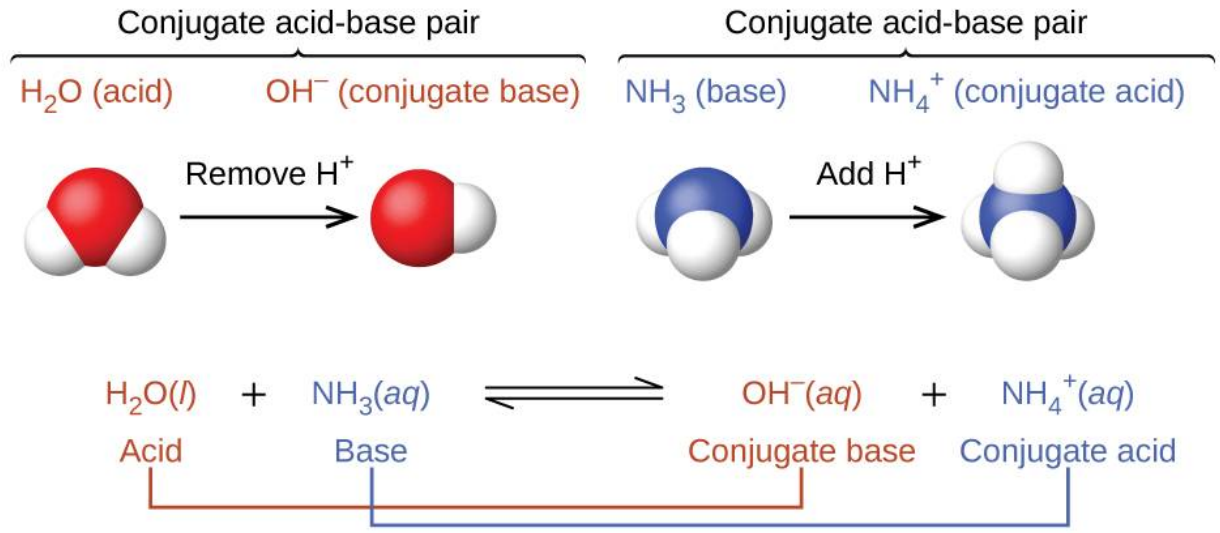
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.) A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

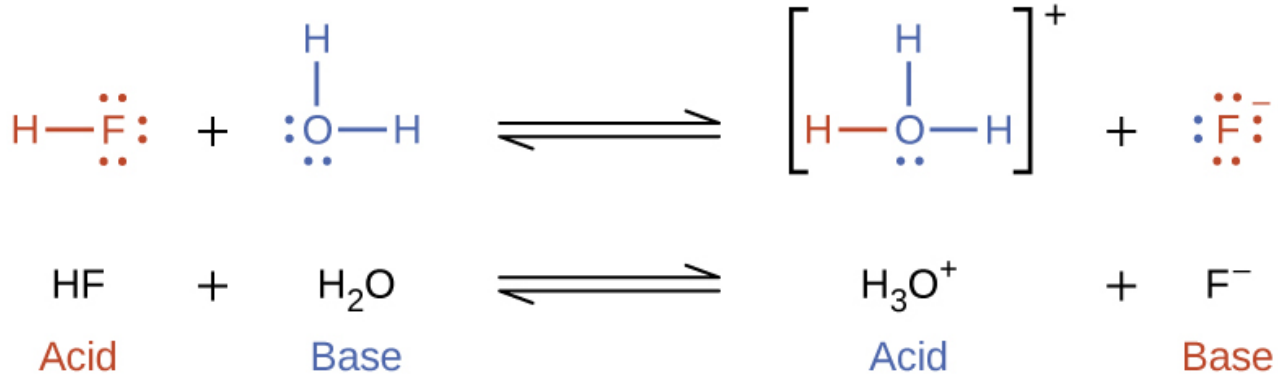
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion,

$$NH_4^+,$$

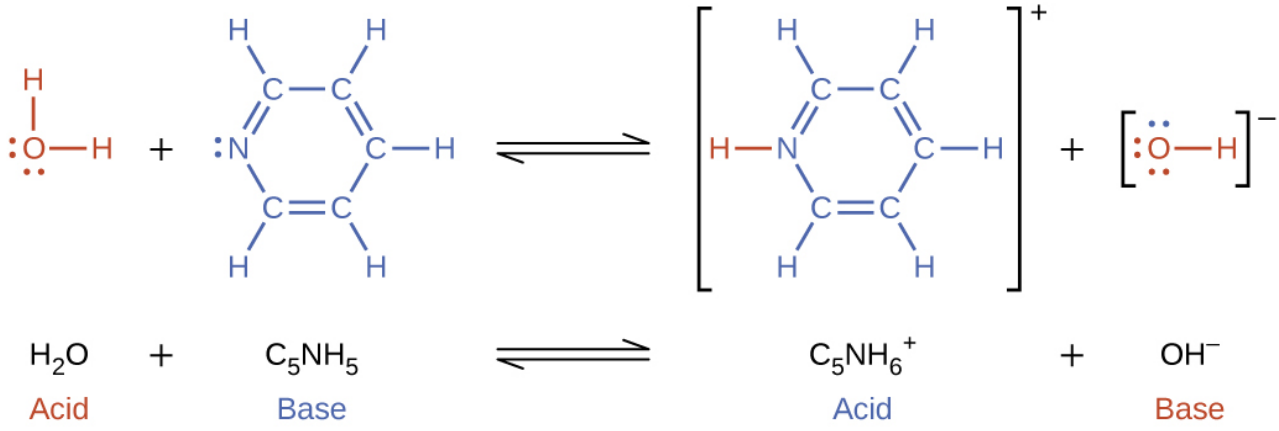
the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be used for acids and bases per definitions other

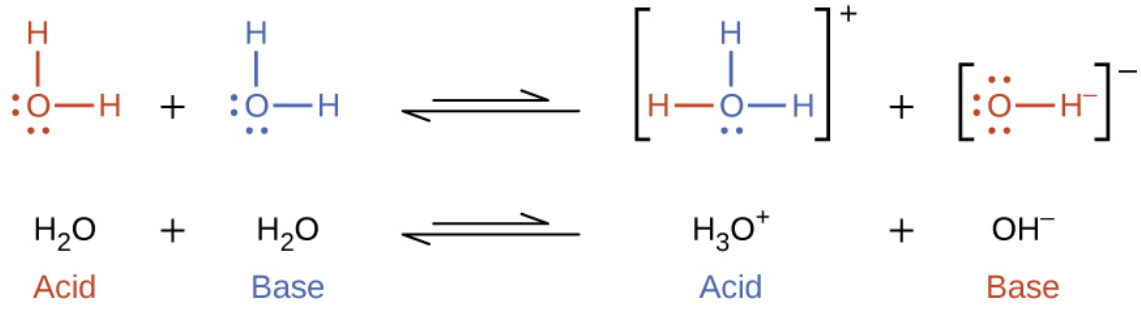
than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$HCO_3^-(aq) + H_2O(l) \qquad CO_3^{2-}(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \qquad H_2CO_3(aq) + OH^-(aq)$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:



EXAMPLE 21.2.1

Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-] = x$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

$$x = [H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, 1.0

×

10^{-7} *M*.

Check Your Learning

The ion product of water at 80 °C is 2.4

×

10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9$

×

10^{-7} *M*

EXAMPLE 21.2.2

Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of

HSO_3^-

(a) as an acid with OH^-

(b) as a base with HI

Solution

(a)

$$HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$$

(b)

$$HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$$

Check Your Learning

Write separate equations representing the reaction of

$H_2PO_4^-$

(a) as a base with HBr

(b) as an acid with OH^-

Answer

(a)

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq);$$

(b)

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$$

21.3 Effect of Molecular Structure on Acid-Base Strength

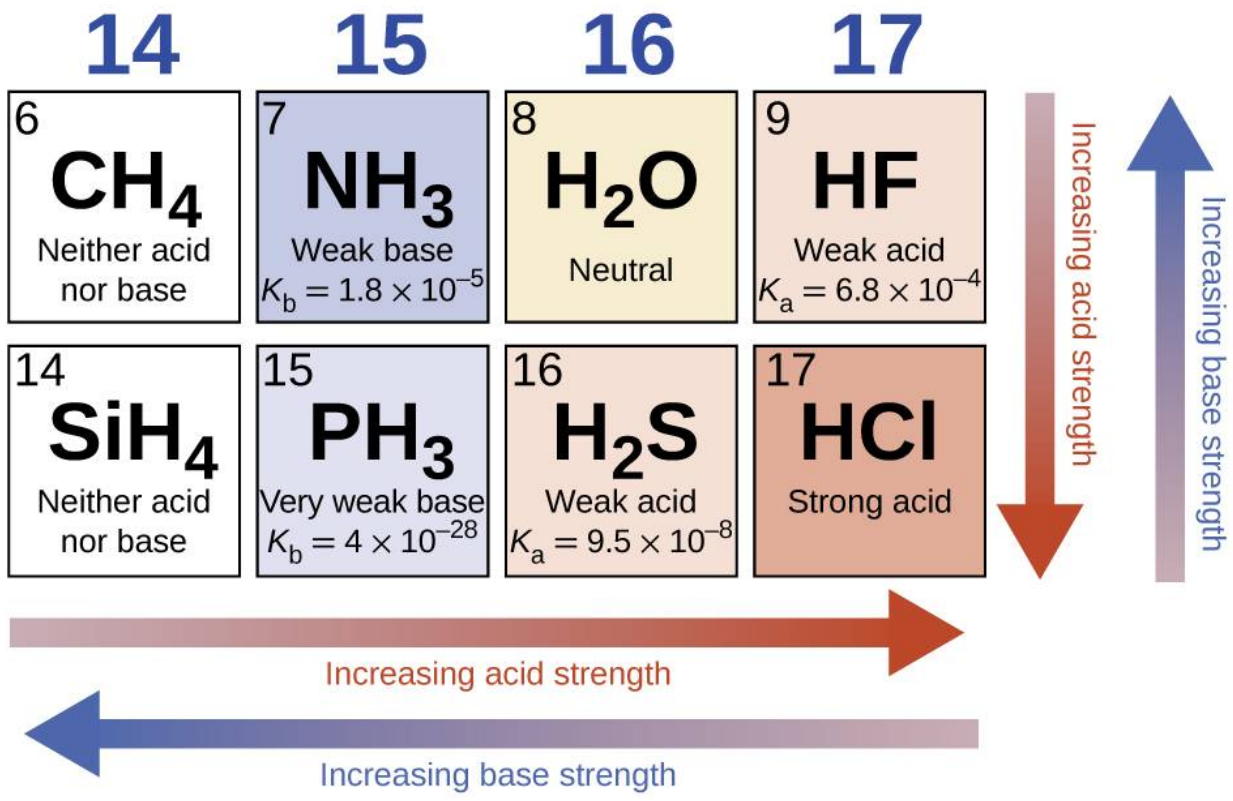
Binary Acids and Bases

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is HF < HCl < HBr < HI. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S <$ HCl (see Figure 21.5).

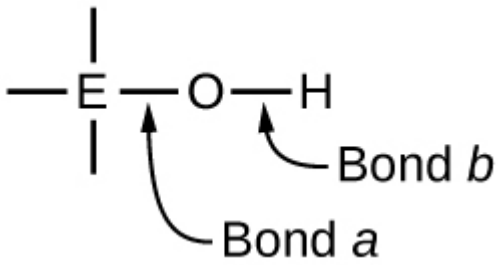
Figure 21.6

The figure shows trends in the strengths of binary acids and bases.



21.4 Ternary Acids and Bases

Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $O_mE(OH)_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



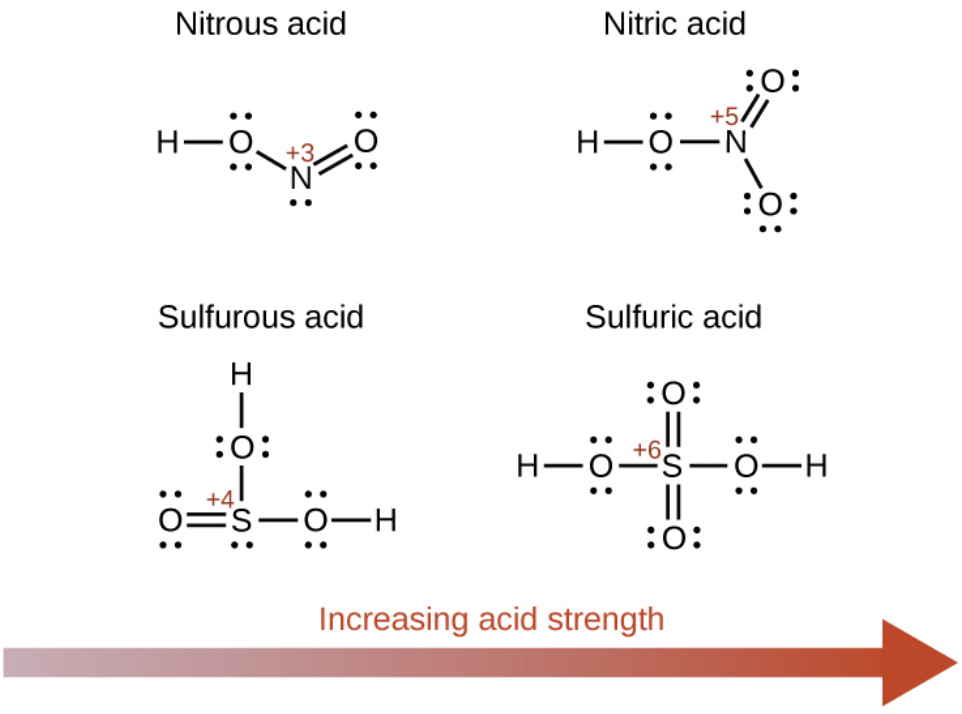
If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic –OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 21.6).

Figure 21.7

As the oxidation number of the central atom E increases, the acidity also increases.



Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion,

$$[\mathrm{Al(H_2O)_2(OH)_4}]^-,$$

by reaction with hydroxide ion:

$$\mathrm{Al(H_2O)_3(OH)_3}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{H_2O}(l) + [\mathrm{Al(H_2O)_2(OH)_4}]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion

$$[\mathrm{Al(H_2O)_6}]^{3+}$$

by reaction with hydronium ion:

$$3\mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_3(OH)_3}(aq) \rightleftharpoons \mathrm{Al(H_2O)_6}^{3+}(aq) + 3\mathrm{H_2O}(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

Files

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22

Autoionization and pH Calculations

Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization: $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$. The ion product of water, K_W is the equilibrium constant for the autoionization reaction: $K_W=[H_3O^+][OH^-] = 1.0\times10^{-14}$ at 25°C. Concentrations of hydronium and hydroxide ions in aqueous media are often represented as logarithmic pH and pOH values, respectively. At 25°C, the autoprotolysis equilibrium for water requires the sum of pH and pOH to equal 14 for any aqueous solution. The relative concentrations of hydronium and hydroxide ion in a solution define its status as acidic ($[H_3O^+] > [OH^-]$), basic ($[H_3O^+] < [OH^-]$), or neutral ($[H_3O^+] = [OH^-]$) At 25°C, a pH < 7 indicates an acidic solution, a pH > 7 a basic solution, and a pH = 7 a neutral solution.

22.1 pH and pOH

Learning Objectives

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w:

$$\mathrm{H_2O}(l) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) \qquad K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium

ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

EXAMPLE 22.1.1

The Inverse Relation between $[H_3O^+]$ and $[OH^-]$

A solution of an acid in water has a hydronium ion concentration of 2.0×10^{-6} *M*. What is the concentration of hydroxide ion at 25 °C?

Solution

Use the value of the ion-product constant for water at 25 °C

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

to calculate the missing equilibrium concentration.

Rearrangement of the K_w expression shows that $[OH^-]$ is inversely proportional to $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Châtelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Answer

$[H_3O^+]$ = 1

×

10^{-11} *M*

Hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}]$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}]$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH}$$

The hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} *M* at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} *M* and hydroxide ion molarities less than 1.0×10^{-7} *M* (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than 1.0×10^{-7} *M* and hydroxide ion molarities greater than 1.0×10^{-7} *M* (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.9 \times 10^{-7}) = 6.31$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C (Table 22.1).

Table 22.1

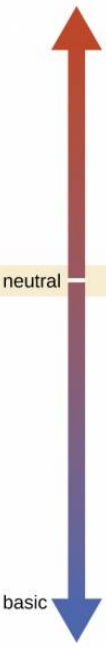
Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 22.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

Figure 22.2
The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^{1}	10^{-15}	–1	15	
10^{0} or 1	10^{-14}	0	14	1 M HCl
10^{-1}	10^{-13}	1	13	
10^{-2}	10^{-12}	2	12	gastric juice, lime juice, 1 M CH_3CO_2H (vinegar)
10^{-3}	10^{-11}	3	11	stomach acid
10^{-4}	10^{-10}	4	10	wine, orange juice
10^{-5}	10^{-9}	5	9	coffee
10^{-6}	10^{-8}	6	8	rain water
10^{-7}	10^{-7}	7	7	pure water
10^{-8}	10^{-6}	8	6	blood, ocean water
10^{-9}	10^{-5}	9	5	baking soda
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	Milk of Magnesia
10^{-12}	10^{-2}	12	2	household ammonia, NH_3
10^{-13}	10^{-1}	13	1	bleach
10^{-14}	10^{0} or 1	14	0	1 M NaOH
10^{-15}	10^{1}	15	–1	



EXAMPLE 22.1.2

Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} *M*?

Solution

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$= -\log(1.2 \times 10^{-3})$$

$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in Appendix B. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Check Your Learning

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\text{CO}_2\,(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3\,(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of 2.0×10^{-6} *M*, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

EXAMPLE 22.1.3

Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.3$$

$$\log[\text{H}_3\text{O}^+] = -7.3$$

$$[\text{H}_3\text{O}^+] = 10^{-7.3} \text{ or } [\text{H}_3\text{O}^+] = \text{antilog of } -7.3$$

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 *M*

22.1.4 HOW SCIENCES INTERCONNECT

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)$$

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

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq)$$

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 22.2). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this website hosted by the US Environmental Protection Agency.

Figure 22.3
(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

(a)

(b)

EXAMPLE 22.1.5

Calculation of pOH

What are the pOH and the pH of a 0.0125-*M* solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125$ *M*:

$$\text{pOH} = -\log[\text{OH}^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

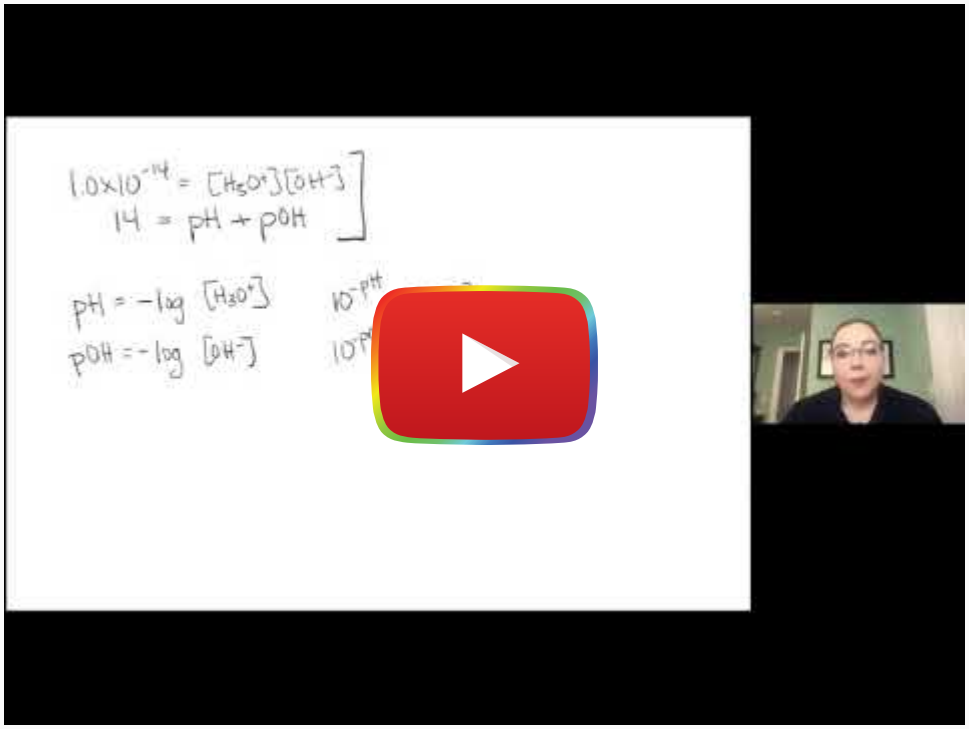
Check Your Learning

The hydronium ion concentration of vinegar is approximately 4×10^{-3} *M*. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6, pH = 2.4

22.1.6 Introduction to pH Calculations



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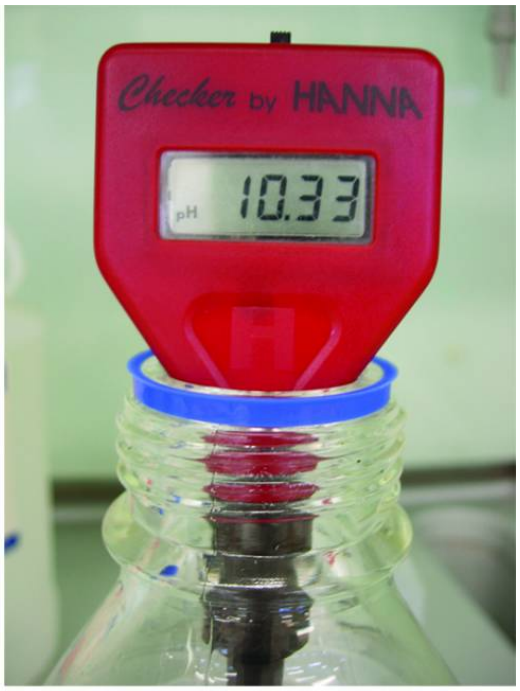
The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 23.3).

Figure 22.4

(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

(a)

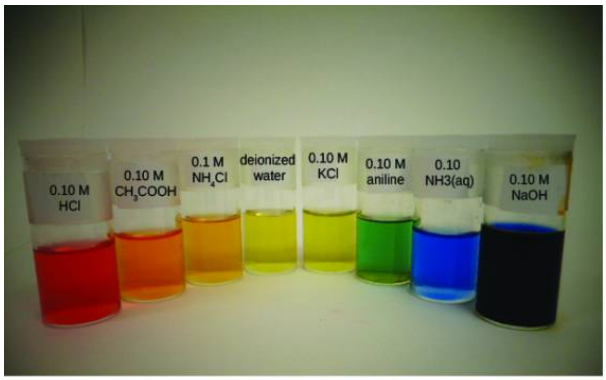


(b)

The pH of a solution may also be visually estimated using colored indicators (Figure 22.4). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.

Figure 22.5

(a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)



(a)

(b)

Files

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23

Weak Acids and Bases

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. Water exerts a leveling effect on dissolved acids or bases, reacting completely to generate its characteristic hydronium and hydroxide ions (the strongest acid and base that may exist in water).

23.1 Relative Strengths of Acids and Bases

Learning Objectives

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

23.2 Acid and Base Ionization Constants

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Figure 23.1.

Figure 23.1

Some of the common strong acids and bases are listed here.

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq),$$

the acid ionization constant is written

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the K_a of an acid, the larger the concentration of

$\mathrm{H_3O^+}$

and A^- relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called “weak,” and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in Appendix H.

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order $CH_3CO_2H < HNO_2 <$

$\mathrm{HSO_4^-}$:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(aq) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_\mathrm{a} = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\%\ \text{ionization} = \frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$). Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

EXAMPLE 23.2.1

Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H_3O^+]_{eq}}{[HNO_2]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[H_3O^+] = 10^{-2.09} = 0.0081\ M$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

Check Your Learning

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

LINK TO LEARNING

View the simulation of strong and weak acids and bases at the molecular level.

Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

the ionization constant is written as

$$K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order

$\mathrm{NO_2^-} < \mathrm{CH_2CO_2^-} < \mathrm{NH_3}$.

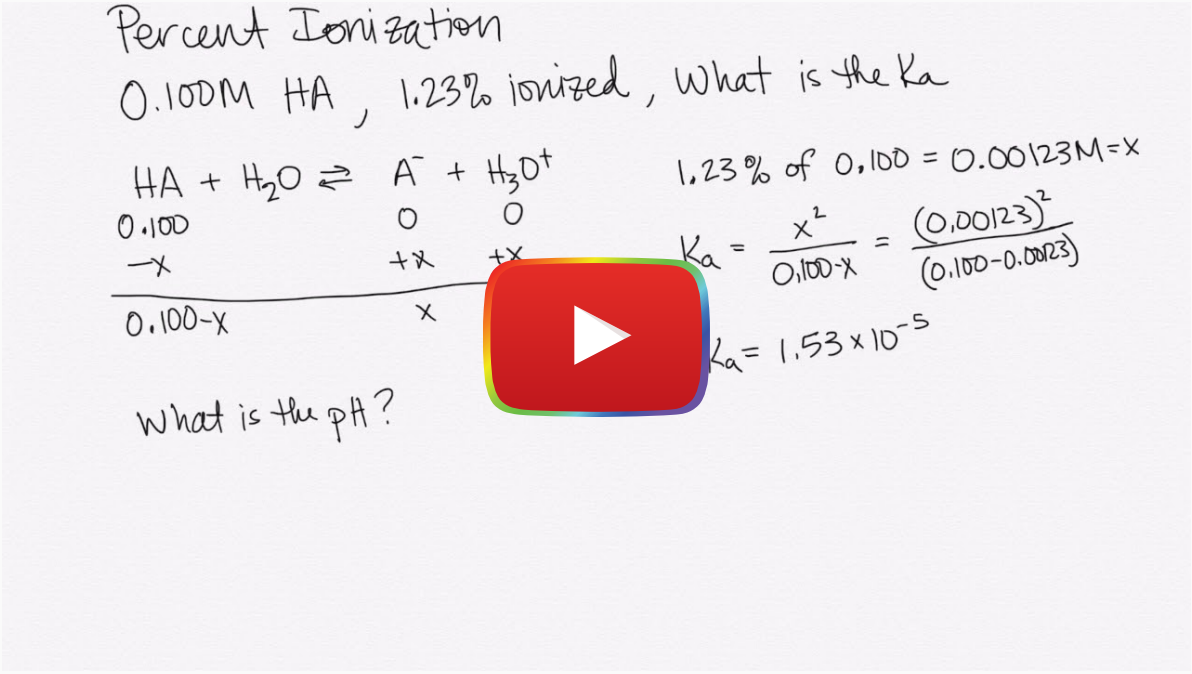
$$\begin{aligned}
\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 2.17 \times 10^{-11} \\
\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 5.6 \times 10^{-10} \\
\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 1.8 \times 10^{-5}
\end{aligned}$$

A table of ionization constants for weak bases appears in Appendix I. As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\%\ \text{ionization} = [\mathrm{OH^-}]_{eq}/[\mathrm{B}]_0 \times 100\%$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

23.2.2 Calculating Percent Ionization



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23.3 Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair HA / A^-, ionization equilibrium equations and ionization constant expressions are

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \qquad K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq) \qquad K_b = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) + \mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) + \mathrm{OH^-}(aq) + \mathrm{HA}(aq)$$

$$2\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = K_w / K_b \text{ or } K_b = K_w / K_a$$

The inverse proportional relation between K_a and K_b means *the stronger the acid or base, the weaker its conjugate partner*. Figure 34.2 illustrates this relation for several conjugate acid-base pairs.

Figure 23.2

Relative strengths of several conjugate acid-base pairs are shown.

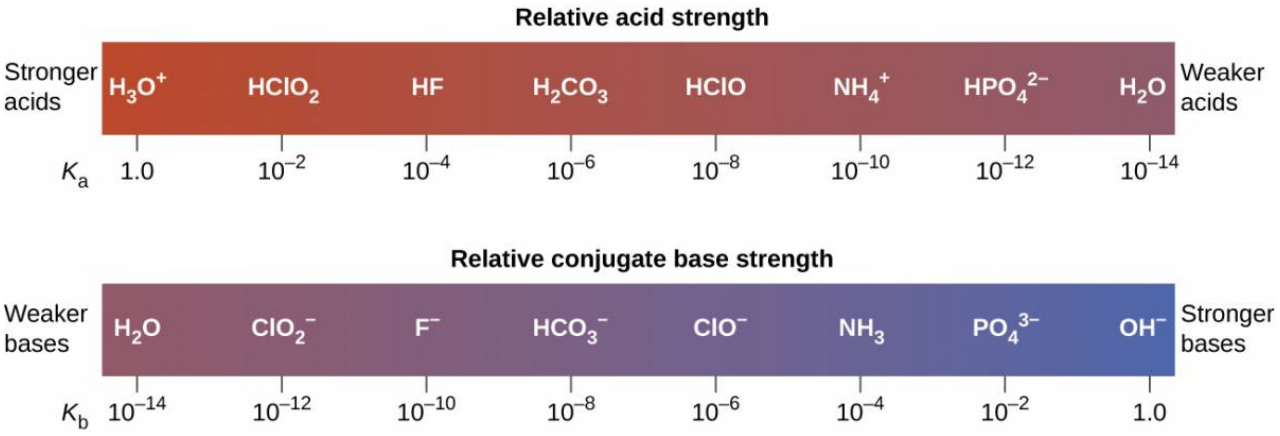
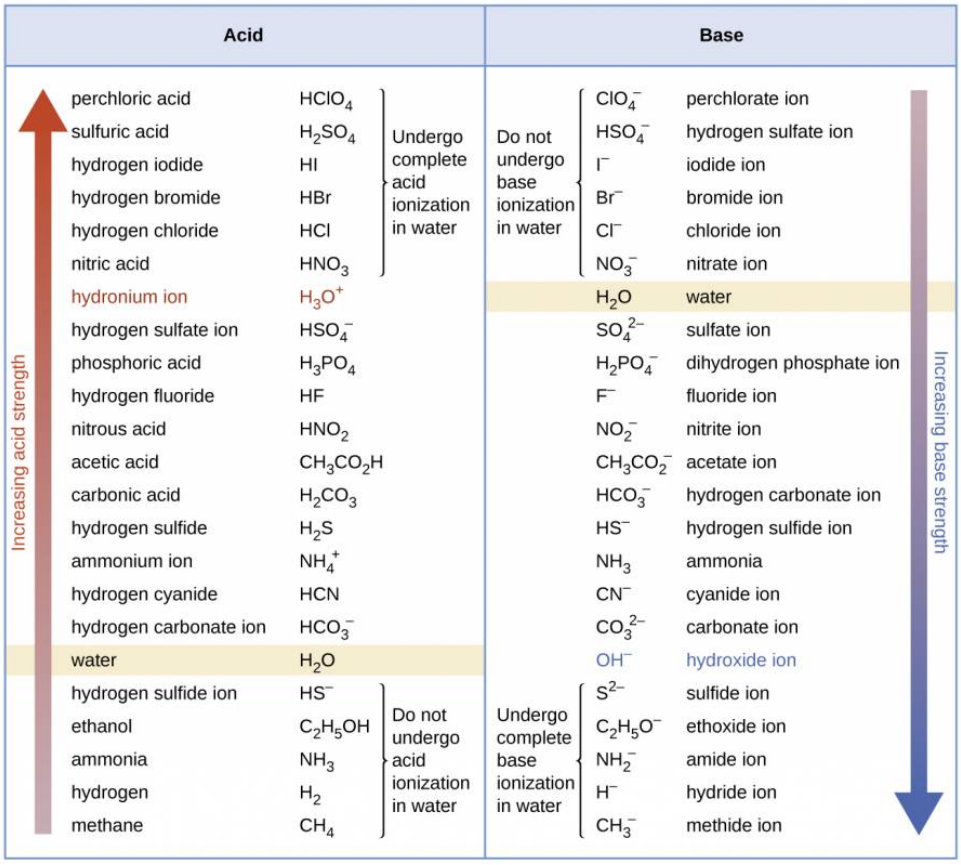


Figure 23.3

This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.



The listing of conjugate acid–base pairs shown in Figure 23.3 is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, wheres those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $H_3O^+(aq)$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for "strong" acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be "weak," and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing HCl < HBr < HI).

The right column of Figure 23.3 lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a, and so its conjugate base will exhibit a K_b that is essentially zero:

$$\text{strong acid:} \quad K_a \approx \infty$$
$$\text{conjugate base:} \quad K_b = K_w / K_a = K_w / \infty \approx 0$$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

EXAMPLE 23.3.1

Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the K_b for the nitrite ion,

NO_2^-,

to calculate the K_a for its conjugate acid.

Solution

K_b for

NO_2^-

is given in this section as 2.17

×

10^{-11}. The conjugate acid of

NO_2^-

is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a yields

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Appendix H.

Check Your Learning

Determine the relative acid strengths of

NH_4^+

and HCN by comparing their ionization constants. The ionization constant of HCN is given in Appendix H as 4.9×10^{-10}. The ionization constant of

NH_4^+

is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}.

Answer

NH_4^+

is the slightly stronger acid (K_a for

NH_4^+

= 5.6

×

10^{-10}).

23.4 Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.

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EXAMPLE 23.4.1

Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 23.4) that provides its sour taste. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and

$$[H_3O^+] = [CH_3CO_2^-] = 0.00118\,M.$$

What is the value of K_a for acetic acid?

Figure 23.4

Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_a for acetic acid.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Check Your Learning

The

HSO_4^-

ion, weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition:

$[H_3O^+]$

= 0.027 *M*;

$[HSO_4^-] = 0.29\ M$;

and

$[SO_4^{2-}] = 0.13\ M$?

Answer

K_a for

HSO_4^-

= 1.2

×

10^{-2}

EXAMPLE 23.4.2

Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*,

$$[\mathrm{C_8\,H_{10}\,N_4\,O_2\,H^+}]$$

= 5.0

×

10^{-3} *M*, and $[OH^-]$ = 2.5

×

10^{-3} *M*?

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_b for caffeine.

$$\mathrm{C_8\,H_{10}\,N_4\,O_2}\,(aq) + \mathrm{H_2\,O}(l) \rightleftharpoons \mathrm{C_8\,H_{10}\,N_4\,O_2\,H^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

$$K_\mathrm{b} = \frac{[\mathrm{C_8\,H_{10}\,N_4\,O_2\,H^+}][\mathrm{OH^-}]}{[\mathrm{C_8\,H_{10}\,N_4\,O_2}]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Check Your Learning

What is the equilibrium constant for the ionization of the

$$\mathrm{HPO_4}^{2-}$$

ion, a weak base

$$\mathrm{HPO_4}^{2-}\,(aq) + \mathrm{H_2\,O}(l) \rightleftharpoons \mathrm{H_2\,PO_4}^{-}\,(aq) + \mathrm{OH^-}\,(aq)$$

if the composition of an equilibrium mixture is as follows: $[OH^-]$ = 1.3

×

10^{-6} *M*;

$$[\mathrm{H_2\,PO_4}^{-}] = 0.042\ M;$$

and

$[HPO_4^{2-}] = 0.341\ M$?

Answer

K_b for

$HPO_4^{2-} = 1.6 \times 10^{-7}$

EXAMPLE 23.4.3

Determination of K_a or K_b from pH

The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2\,(aq) + H_2O(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq)$$

Solution

The nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as "initial" values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of H_3O^+ is present (1×10^{-7} *M*) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an "equilibrium" value for the ICE table:

$$[H_3O^+] = 10^{-2.34} = 0.0046\,M$$

The ICE table for this system is then

	HNO_2 + H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516	~0	0
Change (*M*)	–0.0046	+0.0046	+0.0046
Equilibrium concentration (*M*)	0.0470	0.0046	0.0046

Finally, calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

Check Your Learning.

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

K_b = 1.8

×

10^{-5}

EXAMPLE 23.4.4

Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, HCO_2H, is one irritant that causes the body's reaction to some ant bites and stings (Figure 23.5).

Figure 23.5

The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH of a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \qquad K_a = 1.8 \times 10^{-4}$$

Solution

The ICE table for this system is

	HCO_2H	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HCO_2^-
Initial concentration (*M*)	0.534				~0		0
Change (*M*)					$+x$		$+x$
Equilibrium concentration (*M*)	$0.534 - x$				x		x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying assumption that *x* will be much lesser than 0.534, and so the equation becomes

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for *x* yields

$$x^2 = 0.534 \times (1.8 \times 10^{-4}) = 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}\ M$$

To check the assumption that *x* is small compared to 0.534, its relative magnitude can be estimated:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2}\ (1.8\%\ \text{of}\ 0.534)$$

Because *x* is less than 5% of the initial concentration, the assumption is valid.

As defined in the ICE table, *x* is equal to the equilibrium concentration of hydronium ion:

$$x = [\mathrm{H_3O^+}] = 0.0098\ M$$

Finally, the pH is calculated to be

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(0.0098) = 2.01$$

Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_a = 1.8 \times 10^{-5}$$

Answer

percent ionization = 1.3%

EXAMPLE 23.4.5

Calculating Equilibrium Concentrations in a Weak Base Solution

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \qquad K_b = 6.3 \times 10^{-5}$$

Solution

The ICE table for this system is

	$(CH_3)_3N$ + H_2O ⇌	$(CH_3)_3NH^+$	+ OH^-
Initial concentration (*M*)	0.25	0	~0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.25 + (-x)$	$0 + x$	$\sim 0 + x$

Substituting the equilibrium concentration terms into the K_b expression gives

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming $x << 0.25$ and solving for x yields

$$x = 4.0 \times 10^{-3}\ M$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified.
As defined in the ICE table, x is equal to the equilibrium concentration of hydroxide ion:

$$[OH^-] = \sim 0 + x = x = 4.0 \times 10^{-3}\ M$$

$$= 4.0 \times 10^{-3}\ M$$

The pOH is calculated to be

$$\text{pOH} = -\log(4.0 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_\text{w} = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

Check Your Learning

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Answer

7.56

×

10^{-4} *M*, 2.33%

In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that *x* is negligible cannot be made. Calculations of this sort are demonstrated in Example 23.4.6 below.

EXAMPLE 23.4.6

Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers as a source of the

HSO_4^-

ion, a weak acid. What is the pH of a 0.50-*M* solution of

HSO_4^- ?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

Solution

The ICE table for this system is

	HSO_4^-	+ H_2O ⇌	H_3O^+	+ SO_4^{2-}
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.50 - x$		x	x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that $x << 0.5$ is made, simplifying and solving the above equation yields

$$x = 0.077\ M$$

This value of x is clearly not significantly less than 0.50 *M*; rather, it is approximately 15% of the initial concentration:
When we check the assumption, we calculate:

$$\frac{x}{[\mathrm{HSO_4}^-]_\mathrm{i}}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15\,(15\%)$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

$$K_\mathrm{a} = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}\,x = x^2$$

Writing the equation in quadratic form gives

$$x^2 + 1.2 \times 10^{-2}\,x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to *x*. As defined in the ICE table, *x* is equal to the hydronium concentration.

$$x = [\mathrm{H_3O^+}] = 0.072\,M$$
$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(0.072) = 1.14$$

Check Your Learning

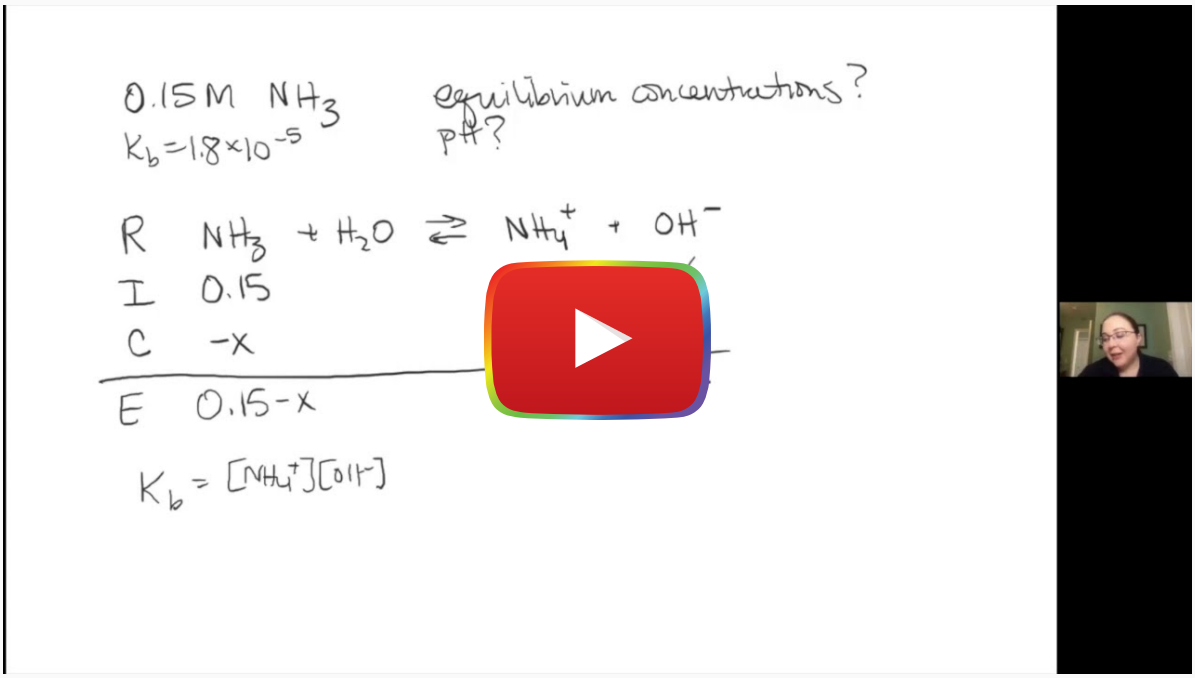
Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\mathrm{C_8H_{10}N_4O_2}\,(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}\,(aq) + \mathrm{OH^-}\,(aq) \qquad K_\mathrm{b} = 2.5 \times 10^{-}$$

Answer

pH 11.16

23.4.7 Calculating pH for a Solution of Weak Base



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24

Polyprotic Acids

An acid that contains more than one ionizable proton is a polyprotic acid. These acids undergo stepwise ionization reactions involving the transfer of single protons. The ionization constants for polyprotic acids decrease with each subsequent step; these decreases typically are large enough to permit simple equilibrium calculations that treat each step separately.

Learning Objectives

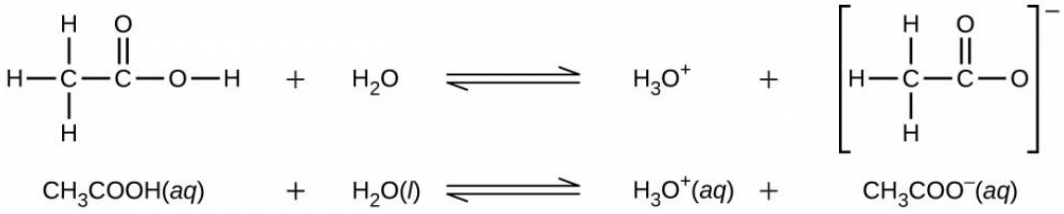
By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\begin{aligned} \mathrm{HCl}(aq) + \mathrm{H_2O}(l) &\longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq) \\ \mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) &\longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq) \\ \mathrm{HCN}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq) \end{aligned}$$

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxyl group (COOH) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong

acid, ionizes as follows:

$$\text{First ionization: } H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq) \qquad K_{a1} = \text{more than 1}$$

$$\text{Second ionization: } HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_{a2}$$

$$\text{Second ionization: } HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_{a2} = 1.2 \times 10^{-}$$

This stepwise ionization process occurs for all polyprotic acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

First ionization:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

Second ionization:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.7 \times 1$$

$K_{H_2CO_3}$

is larger than

$K_{HCO_3^-}$

by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the

HCO_3^-

formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and

HCO_3^-

are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This approach is demonstrated in the following example exercise.

EXAMPLE 25.0.1

Ionization of a Diprotic Acid

"Carbonated water" contains a palatable amount of dissolved carbon dioxide. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are

$[H_3O^+]$,

$[HCO_3^-]$,

and

$[CO_3^{2-}]$

in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than

HCO_3^-,

so the stepwise ionization reactions may be treated separately.
The first ionization reaction is

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

Using provided information, an ICE table for this first step is prepared:

	H_2CO_3	+
Initial concentration (*M*)	0.033	
Change (*M*)	$-x$	
Equilibrium concentration (*M*)	$0.033 - x$	

Substituting the equilibrium concentrations into the equilibrium equation gives

$$K_{\mathrm{H_2CO_3}} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming x << 0.033 and solving the simplified equation yields

$$x = 1.2 \times 10^{-4}$$

The ICE table defined x as equal to the bicarbonate ion molarity and the hydronium ion molarity:

$$[\mathrm{H_2CO_3}] = 0.033\ M$$
$$[\mathrm{H_3O^+}] = [\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq)$$
$$K_{\mathrm{HCO_3^-}} = \frac{[\mathrm{H_3O^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = \frac{(1.2 \times 10^{-4})[\mathrm{CO_3^{2-}}]}{1.2 \times 10^{-4}}$$
$$[\mathrm{CO_3^{2-}}] = \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11}\ M$$

To summarize: at equilibrium [H_2CO_3] = 0.033 *M*;

$[\mathrm{H_3O^+}]$

= 1.2×10^{-4};

$[\mathrm{HCO_3^-}] = 1.2 \times 10^{-4}\ M$;

$[\mathrm{CO_3^{2-}}] = 4.7 \times 10^{-11}\ M$.

Check Your Learning

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 *M*. Calculate

$[\mathrm{H_3O^+}]$,

[HS^-], and [S^{2-}] in the solution:

$$\mathrm{H_2S}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HS^-}(aq) \qquad K_{a1} = 8.9 \times 10^{-8}$$
$$\mathrm{HS^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{S^{2-}}(aq) \qquad K_{a2} = 1.0 \times 10^{-19}$$

Answer

[H_2S] = 0.1 *M*;

$[\mathrm{H_3O^+}]$

= [HS^-] = 0.000094 *M*; [S^{2-}] = 1

×

10^{-19} *M*

A triprotic acid is an acid that has three ionizable H atoms. Phosphoric acid is one example:

$$\text{First ionization: } H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = 7.5 \times 10$$

$$\text{Second ionization: } H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times$$

$$\text{Third ionization: } HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 4.2 \times 10$$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6.

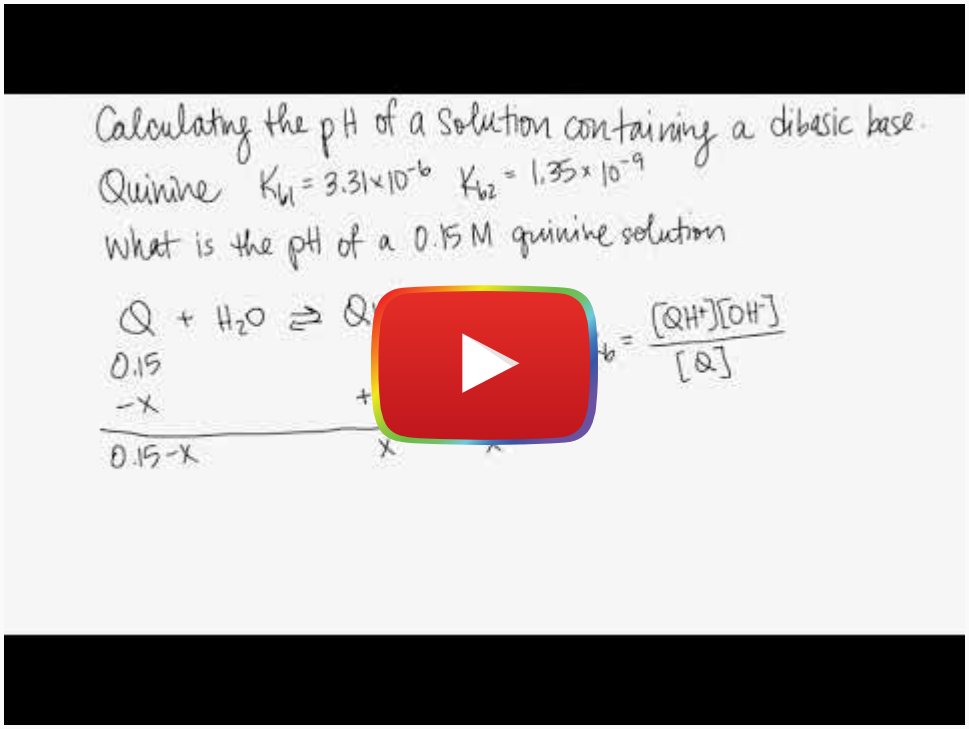
This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a diprotic base, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \qquad K_{b1} = 2.1 \times 10^{-4}$$

$$H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \qquad K_{b2} = 2.3 \times 10^{-8}$$

25.0.2 pH of Dibasic Base



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25

pH of Salt Solutions

The ions composing salts may possess acidic or basic character, ionizing when dissolved in water to yield acidic or basic solutions. Acidic cations are typically the conjugate partners of weak bases, and basic anions are the conjugate partners of weak acids. Many metal ions bond to water molecules when dissolved to yield complex ions that may function as acids.

Learning Objectives

By the end of this section, you will be able to:

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

25.1 Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{Cl^-}(aq)$$

The ammonium ion is the conjugate acid of the base ammonia, NH_3; its acid ionization (or acid hydrolysis) reaction is represented by

$$\mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \qquad K_a = K_w/K_b$$

Since ammonia is a weak base, K_b is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\mathrm{Cl}^{-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HCl}(aq) + \mathrm{OH}^{-}(aq) \qquad K_\mathrm{b} = K_\mathrm{w}/K_\mathrm{a}$$

Since HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$ (chloride ions don't undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations ($\mathrm{NH_4}^{+}$) and inert anions (Cl^-), resulting in an acidic solution.

EXAMPLE 25.1.1

Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride,

$$[C_6H_5NH_3]Cl,$$

a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of anilinium chloride

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$$

Solution

The K_a for anilinium ion is derived from the K_b for its conjugate base, aniline (see Appendix H):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Using the provided information, an ICE table for this system is prepared:

	$C_6H_5NH_3^+$	+ H_2O ⇌	$C_6H_5NH_2$	+ H_3O^+
Initial concentration (*M*)	0.233		0	~0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.233 - x$		x	x

Substituting these equilibrium concentration terms into the K_a expression gives

$$K_a = [C_6H_5NH_2][H_3O^+]/[C_6H_5NH_3^+]$$
$$2.3 \times 10^{-5} = (x)(x)/0.233 - x)$$

Assuming x << 0.233, the equation is simplified and solved for x:

$$2.3 \times 10^{-5} = x^2/0.233$$
$$x = 0.0023\ M$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$pH = -\log[H_3O^+] = -\log(0.0023) = 2.64$$

Check Your Learning

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions

NH_4^+

and

NO_3^- .

Which is the stronger acid

$C_6H_5NH_3^+$

or

NH_4^+ ?

Answer

$[H_3O^+]$ = 7.5

×

10^{-6} *M*,

$C_6H_5NH_3^+$

is the stronger acid.

25.2 Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$NaCH_3CO_2(s) \rightleftharpoons Na^+(aq) + CH_3CO_2^-(aq)$$

The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion,

$\mathrm{CH_3CO_2^-}$,

is the conjugate base of acetic acid, $\mathrm{CH_3CO_2H}$, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = K_\mathrm{w}/K_\mathrm{a}$$

Because acetic acid is a weak acid, its K_a is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and weak base anions

$(\mathrm{CH_3CO_2^-})$,

resulting in a basic solution.

EXAMPLE 25.2.1

Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with

$$[CH_3CO_2^-] = 0.050\ M$$

and $[OH^-] = 2.5\times10^{-6}$ *M* at equilibrium. The reaction is:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

Solution

The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$K_b\ (\text{for } CH_3CO_2^-) = \frac{K_w}{K_a\ (\text{for } CH_3CO_2H)} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

Substituting the available values into the K_b expression gives

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} = 5.6\times10^{-10}$$

$$= \frac{[CH_3CO_2H](2.5\times10^{-6})}{(0.050)} = 5.6\times10^{-10}$$

Solving the above equation for the acetic acid molarity yields $[CH_3CO_2H] = 1.1\times10^{-5}$ *M*.

Check Your Learning

What is the pH of a 0.083-*M* solution of NaCN?

Answer

11.11

25.3 Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion's acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the K_a and K_b values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

EXAMPLE 25.3.1

Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:
(a) KBr

(b) $NaHCO_3$

(c) Na_2HPO_4

(d) NH_4F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:
(a) The K^+ cation is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The Na^+ cation is inert and will not affect the pH of the solution; while the

$$HCO_3^-$$

anion is amphiprotic. The K_a of

$$HCO_3^-$$

is 4.7×10^{-11},and its K_b is

$$\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8} .$$

Since $K_b >> K_a$, the solution is basic.

(c) The Na^+ cation is inert and will not affect the pH of the solution, while the

$$HPO_4^{2-}$$

anion is amphiprotic. The K_a of

$$HPO_4^{2-}$$

is 4.2×10^{-13},

and its K_b is

$$\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} .$$

Because $K_b >> K_a$, the solution is basic.

(d) The

NH_4^+

ion is acidic (see above discussion) and the F^- ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of

NH_4^+

is 5.6×10^{-10} and the K_b of F^- is 1.6×10^{-11}, so the solution is acidic, since $K_a > K_b$.

Check Your Learning

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:
(a) K_2CO_3

(b) $CaCl_2$

(c) KH_2PO_4

(d) $(NH_4)_2CO_3$

Answer

(a) basic; (b) neutral; (c) acidic; (d) basic

25.4 The Ionization of Hydrated Metal Ions

Unlike the group 1 and 2 metal ions of the preceding examples (Na^+, Ca^{2+}, etc.), some metal ions function as acids in aqueous solutions. These ions are not just loosely solvated by water molecules when dissolved, instead they are covalently bonded to a fixed number of water molecules to yield a complex ion (see chapter on coordination chemistry). As an example, the dissolution of aluminum nitrate in water is typically represented as

$$\mathrm{Al(NO_3)}(s) \rightleftharpoons \mathrm{Al}^{3+}(aq) + 3\mathrm{NO_3}^-(aq)$$

However, the aluminum(III) ion actually reacts with six water molecules to form a stable complex ion, and so the more explicit representation of the dissolution process is

$$\mathrm{Al(NO_3)_3}(s) + 6\mathrm{H_2O}(l) \rightleftharpoons \mathrm{Al(H_2O)_6}^{3+}(aq) + 3\mathrm{NO_3}^-(aq)$$

As shown in Figure 25.1, the

$Al(H_2O)_6^{3+}$

ions involve bonds between a central Al atom and the O atoms of the six water molecules. Consequently, the bonded water molecules' O–H bonds are more polar than in nonbonded water molecules, making the bonded molecules more

prone to donation of a hydrogen ion:

$$\mathrm{Al(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_5(OH)^{2+}}(aq) \qquad K_a = 1.4 \times 10^{-5}$$

The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in few equations below:

$$\mathrm{Al(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_5(OH)^{2+}}(aq)$$

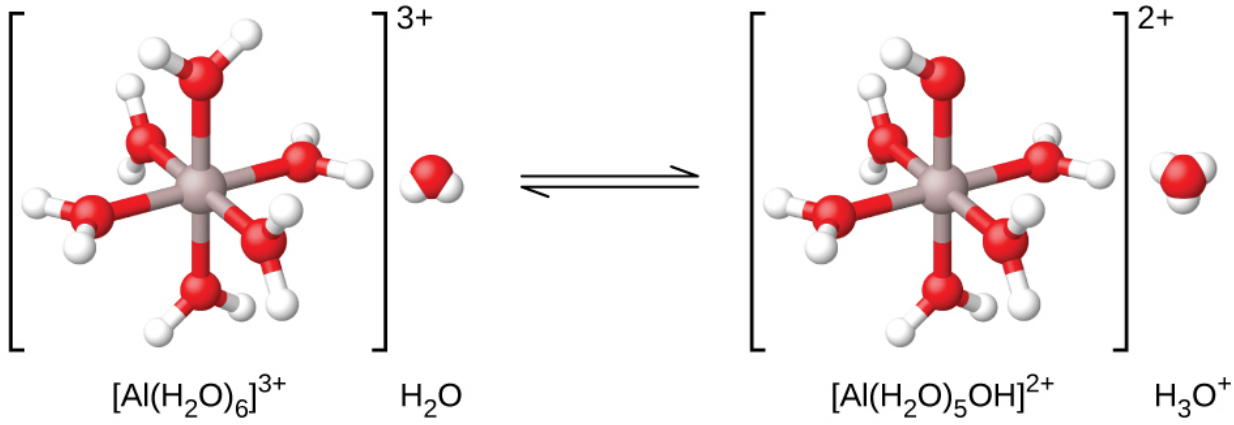
$$\mathrm{Al(H_2O)_5(OH)^{2+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_4(OH)_2^{+}}(aq)$$

$$\mathrm{Al(H_2O)_4(OH)_2^{+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_3(OH)_3}(aq)$$

This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.

Figure 25.1

When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.



Aside from the alkali metals (group 1) and some alkaline earth metals (group 2), most other metal ions will undergo acid ionization to some extent when dissolved in water. The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions. The first-step acid ionization equations for a few other acidic metal ions are shown below:

$$\mathrm{Fe(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Fe(H_2O)_5(OH)^{2+}}(aq) \qquad pK_a = 2.74$$

$$\mathrm{Cu(H_2O)_6^{2+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Cu(H_2O)_5(OH)^{+}}(aq) \qquad pK_a = \sim 6.3$$

$$\mathrm{Zn(H_2O)_4^{2+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Zn(H_2O)_3(OH)^{+}}(aq) \qquad pK_a = 9.6$$

EXAMPLE 25.4.1

Hydrolysis of $[Al(H_2O)_6]^{3+}$

Calculate the pH of a 0.10-*M* solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion

$$[Al(H_2O)_6]^{3+}$$

in solution.

Solution

The equation for the reaction and K_a are:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq) \qquad K_a = 1.4 \times 10^{-}$$

An ICE table with the provided information is

	$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}$		
Initial concentration (*M*)	0.10	~0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$	x	x

Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[H_3O^+][Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6^{3+}]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Assuming x << 0.10 and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3}\ M$$

The ICE table defined x as equal to the hydronium ion concentration, and so the pH is calculated to be

$$[H_3O^+] = 0 + x = 1.2 \times 10^{-3}\ M$$

$$\text{pH} = -\log[H_3O^+] = 2.92 \text{ (an acidic solution)}$$

Check Your Learning

What is

$$[Al(H_2O)_5(OH)^{2+}]$$

in a 0.15-*M* solution of $Al(NO_3)_3$ that contains enough of the strong acid HNO_3 to bring $[H_3O^+]$ to 0.10 *M*?

Answer

2.1

×

10^{-5} *M*

Files

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26

Buffers

Solutions that contain appreciable amounts of a weak conjugate acid-base pair are called buffers. A buffered solution will experience only slight changes in pH when small amounts of acid or base are added. Addition of large amounts of acid or base can exceed the buffer capacity, consuming most of one conjugate partner and preventing further buffering action.

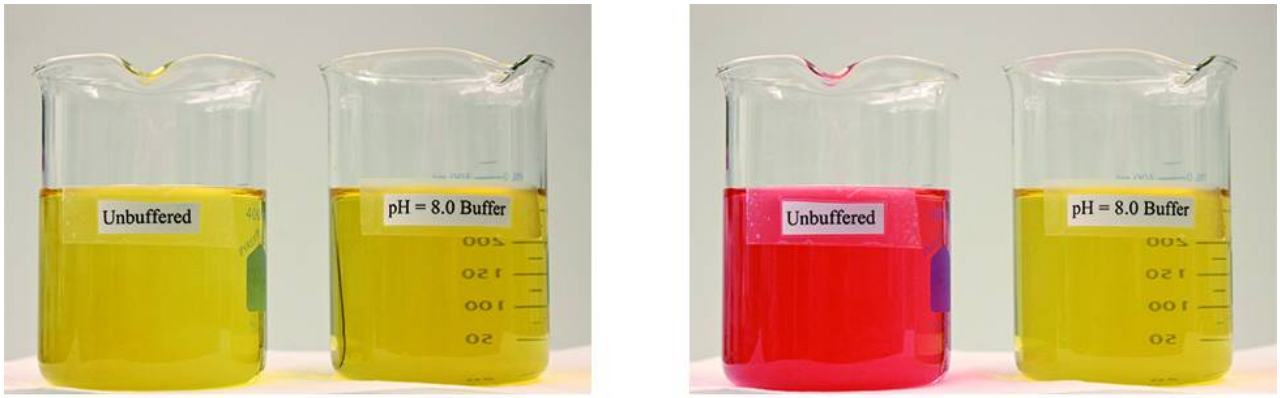
Learning Objectives

By the end of this section, you will be able to:

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 26.1). A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).

Figure 26.1
(a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)



(a) (b)

26.1 How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, strong base added to this solution will neutralize hydronium ion, causing the acetic acid ionization equilibrium to shift to the right and generate additional amounts of the weak conjugate base (acetate ion):

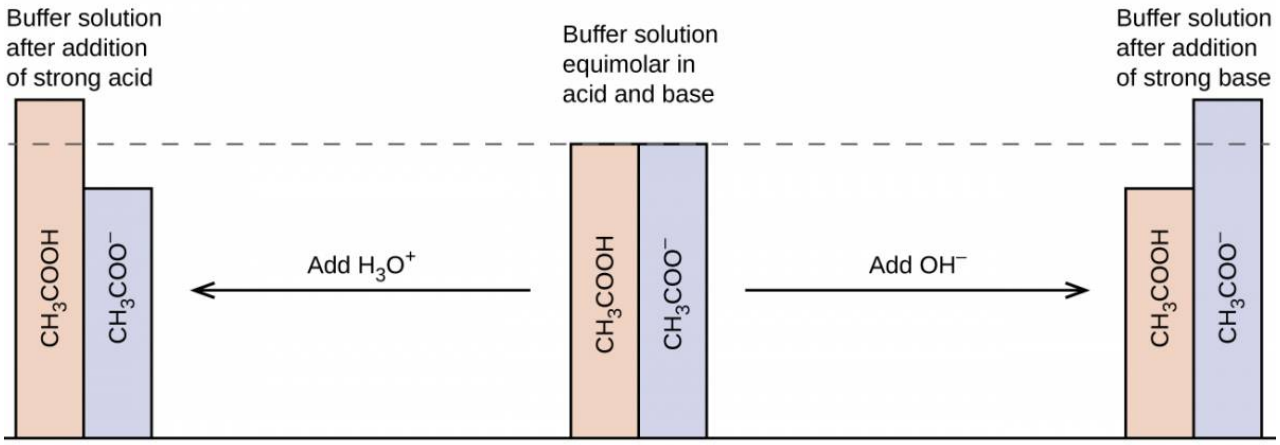
$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

Likewise, strong acid added to this buffer solution will shift the above ionization equilibrium left, producing additional amounts of the weak conjugate acid (acetic acid). Figure 26.2 provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

Figure 26.2

Buffering action in a mixture of acetic acid and acetate salt.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$



EXAMPLE 26.1.1

pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.
(a) Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

(b) Calculate the pH after 1.0 mL of 0.10 NaOH is added to 100 mL of this buffer.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

	CH_3CO_2H +	H_2O ⇌	H_3O^+ +	$CH_3CO_2^-$
Initial concentration (*M*)	0.10		~0	0.10
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$		x	$0.10 + x$

Substituting the equilibrium concentration terms into the K_a expression, assuming $x << 0.10$, and solving the simplified equation for x yields

$$x = 1.8 \times 10^{-5}\,M$$

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

$$\text{pH} = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer.

Adding strong base will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$0.0010\ \text{L} \times \left(\frac{0.10\ \text{mol NaOH}}{1\ \text{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100\ \text{L} \times \left(\frac{0.100\ \text{mol}\ \text{CH}_3\,\text{CO}_2\,\text{H}}{1\ \text{L}}\right) = 1.00 \times 10^{-2}\ \text{mol}\ \text{CH}_3\,\text{CO}_2\,\text{H}$$

The amount of acetic acid remaining after some is neutralized by the added base is

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2}\ \text{mol}\ \text{CH}_3\,\text{CO}_2\,\text{H}$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$(1.0 \times 10^{-2}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2}\ \text{mol}\ \text{NaCH}_3\,\text{CO}_2$$

Compute molar concentrations for the two buffer components:

$$[\text{CH}_3\,\text{CO}_2\,\text{H}] = \frac{9.9 \times 10^{-3}\ \text{mol}}{0.101\ \text{L}} = 0.098\ M$$

$$[\text{NaCH}_3\,\text{CO}_2] = \frac{1.01 \times 10^{-2}\ \text{mol}}{0.101\ \text{L}} = 0.100\ M$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydronium ion initially present in the solution is

$$[\text{H}_3\,\text{O}^+] = 10^{-4.74} = 1.8 \times 10^{-5}\ M$$

$$\text{mol}\ \text{H}_3\,\text{O}^+ = (0.100\ L)(1.8 \times 10^{-5}\ M) = 1.8 \times 10^{-6}\ \text{mol}\ \text{H}_3\,\text{O}^+$$

The amount of hydroxide ion added to the solution is

$$\text{mol}\ \text{OH}^- = (0.0010\ L)(0.10\ M) = 1.0 \times 10^{-4}\ \text{mol}\ \text{OH}^-$$

The added hydroxide will neutralize hydronium ion via the reaction

$$\text{H}_3\,\text{O}^+(aq) + \text{OH}^-(aq) \rightleftharpoons 2\text{H}_2\,\text{O}(l)$$

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

$$1.0 \times 10^{-4}\ \text{mol} - 1.8 \times 10^{-6}\ \text{mol} = 9.8 \times 10^{-5}\ \text{mol OH}^-$$

corresponding to a hydroxide molarity of

$$9.8 \times 10^{-5}\ \text{mol OH}^- / 0.101\ L = 9.7 \times 10^{-4}\ M$$

The pH of the solution is then calculated to be

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - -\log(9.7 \times 10^{-4}) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

Check Your Learning

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8

×

10^{-5} *M* HCl; pH = −log[H_3O^+] = −log[1.8

×

10^{-5}] = 4.74
Moles of H_3O^+ in 100 mL 1.8

×

10^{-5} *M* HCl; 1.8

×

10^{-5} moles/L

×

0.100 L = 1.8

×

10^{-6}

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L

×

0.0010 L = 1.0

×

10^{-4} moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mo}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right.$$

26.2 Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 27.3). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.

Figure 26.3

The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

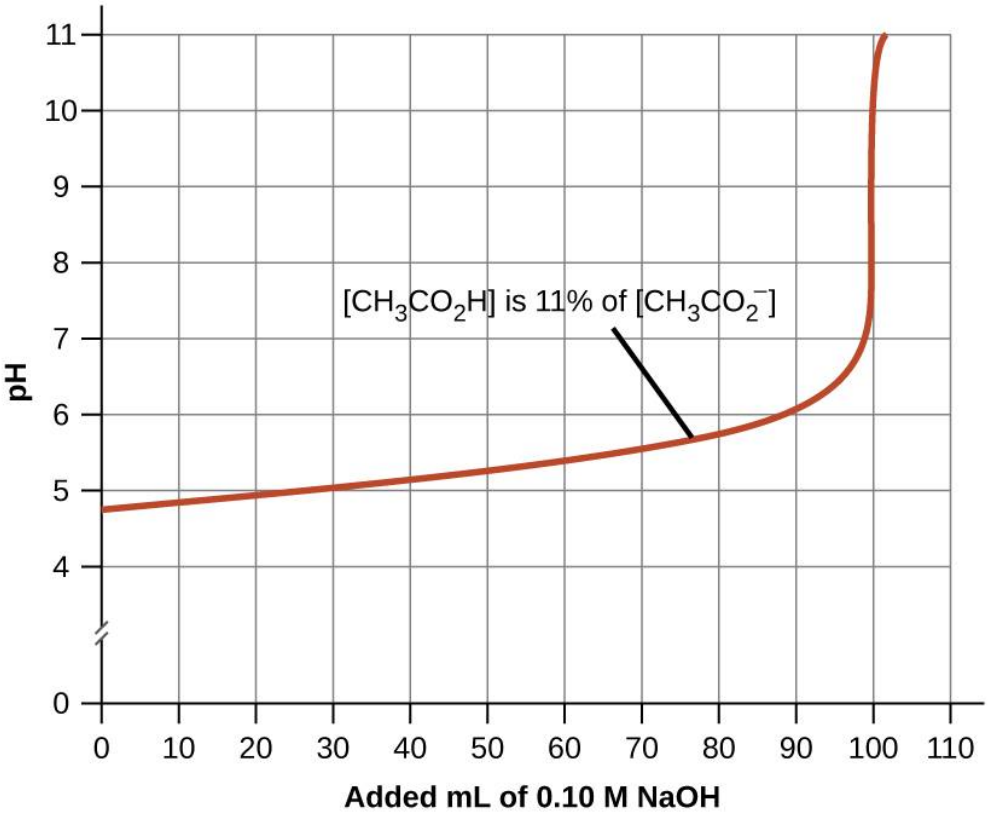
The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even

though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

26.3 Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 26.4 shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.
   Figure 26.4
   Change in pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, [CH_3CO_2H] = 0.10 M and $[\mathrm{CH_3CO_2^-}] = 0.10\,M$. *Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.*



2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion,

$$HCO_3^-.$$

When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$\mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \longrightarrow \mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l)$$

An added hydroxide ion is removed by the reaction:

$$\mathrm{OH^-}(aq) + \mathrm{H_2CO_3}(aq) \longrightarrow \mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l)$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to HCO_3^-). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

26.4 The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

Rearranging to solve for $[H_3O^+]$ yields:

$$[\mathrm{H_3O^+}] = K_a \times \frac{[\mathrm{HA}]}{[\mathrm{A^-}]}$$

Taking the negative logarithm of both sides of this equation gives

$$-\log[\mathrm{H_3O^+}] = -\log K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A^-}]},$$

which can be written as

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

where pK_a is the negative of the logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch equation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

26.4.1 PORTRAIT OF A CHEMIST

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

26.4.2 HOW SCIENCES INTERCONNECT

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2\,(g) + 2H_2\,O(\mathit{l})} \rightleftharpoons \mathrm{H_2\,CO_3\,(\mathit{aq})} \rightleftharpoons \mathrm{HCO_3^-\,(\mathit{aq}) + H_3\,O^+\,(\mathit{aq})}$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion,

$$\mathrm{HCO_3^-},$$

is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.4 + \log\frac{0.024}{0.0012} = 7.7$$

The fact that the H_2CO_3 concentration is significantly lower than that of the

$$\mathrm{HCO_3^-}$$

ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the

$$\mathrm{HCO_3^-}$$

ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

LINK TO LEARNING

View information on the buffer system encountered in natural waters.

Files

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Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (15.1, 15.3, 14.6)

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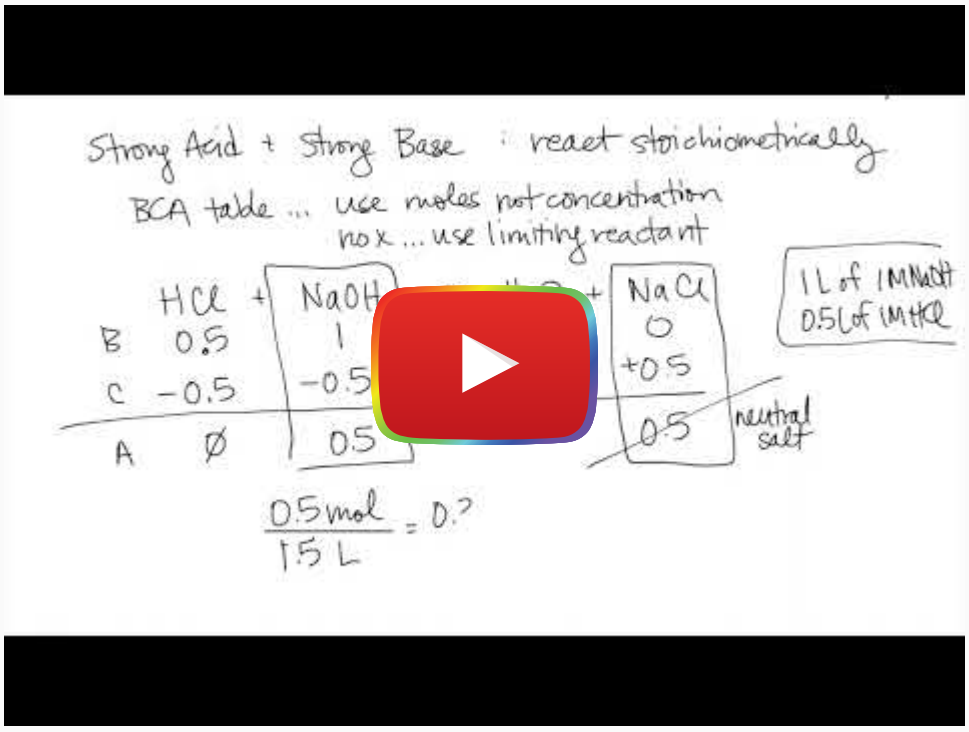
27

DBL Acid Base

The following video will help you use your critical thinking skills to determine the strategies you should employ for varied acid-base problems. As you watch the video, make note of patterns that you can apply to different problems.

27.0.1 Acid Base Decision Based Learning



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https://open.byu.edu/general_college_chemistry_2/dbl_acid_base.

28

Titrations I

Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction. The titration curve for an acid-base titration is typically a plot of pH versus volume of added titrant. These curves are useful in selecting appropriate acid-base indicators that will permit accurate determinations of titration end points.

Learning Objectives

By the end of this section, you will be able to:

- Describe the fundamental aspects of titrations.
- Perform stoichiometric calculations using typical titration data.

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3, which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid, CH_3CO_2H, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

$$2\mathrm{CH_3\,CO_2\,H}(aq) + \mathrm{K_2\,CO_3}\,(s) \longrightarrow 2\mathrm{CH_3\,CO_2\,K}(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2\,O}(l)$$

The bubbling was due to the production of CO_2.

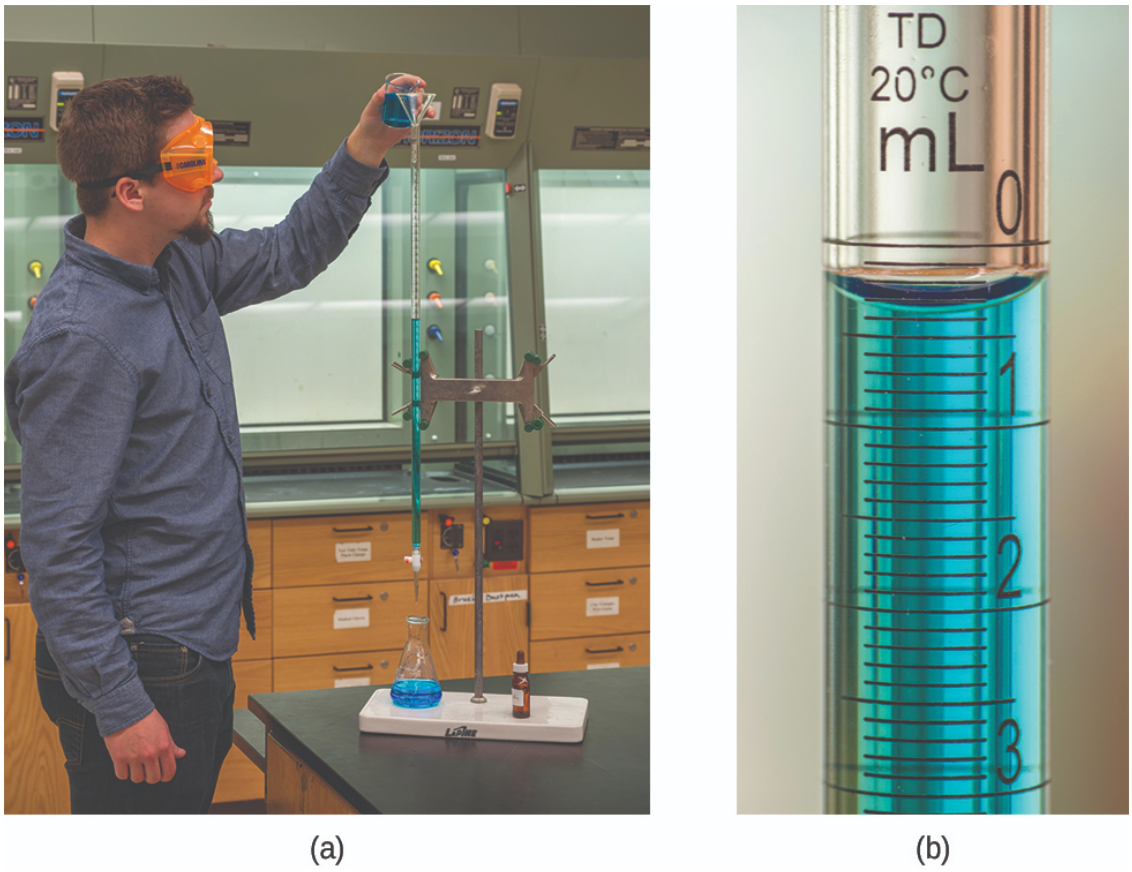
The test of vinegar with potassium carbonate is one type of quantitative analysis—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

28.1 Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as titration analysis. A typical titration analysis involves the use of a buret (Figure 7.16) to make incremental additions of a solution containing a known concentration of some substance (the titrant) to a sample solution containing the substance whose concentration is to be measured (the analyte). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the equivalence point of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called indicators are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the end point. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.

Figure 28.1

(a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.01 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)



EXAMPLE 28.1.1

Titration Analysis

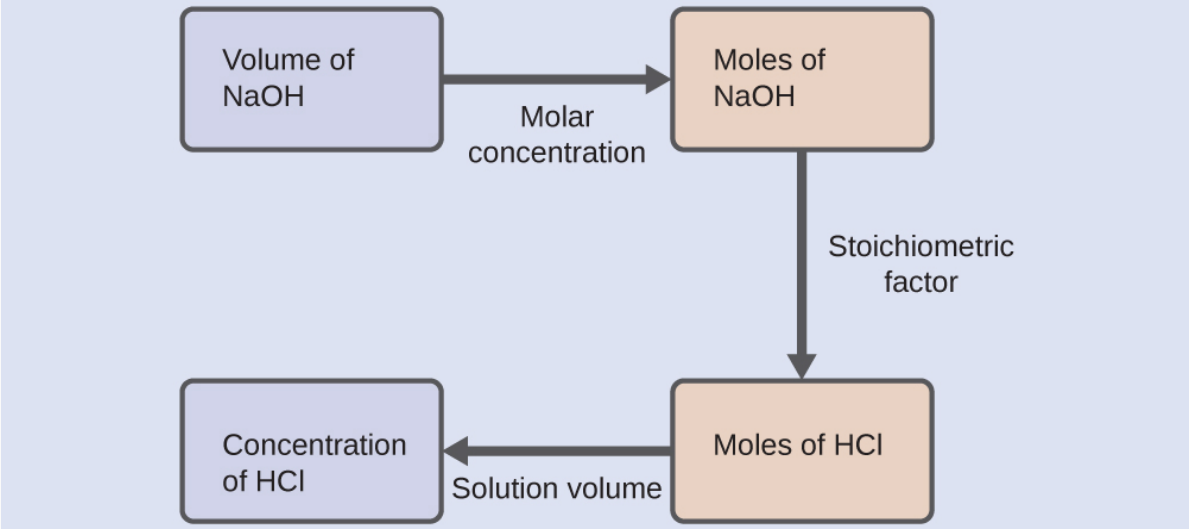
The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.
For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

$$35.23\ \text{mL NaOH} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{0.250\ \text{mol NaOH}}{1\ \text{L}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} = 8.81 \times 10^{-3}\ \text{mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3}\ \text{mol HCl}}{50.00\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}}$$

$$M = 0.176\ M$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *milli*moles of solute per *milli*liter of solution:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3 \text{ mmol}}{\text{mol}}}{\frac{10^3 \text{ mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23 \text{ mL NaOH} \times \frac{0.250 \text{ mmol NaOH}}{\text{mL NaOH}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{50.00 \text{ mL solution}} = 0.176 \, M \text{ HCl}$$

Check Your Learning

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-*M* solution of potassium permanganate, $KMnO_4$ (see net ionic equation below).

$$2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer

0.2648 *M*

Learning Objectives

By the end of this section, you will be able to:

- Interpret titration curves for strong acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

28.2 Titration Curves

A titration curve is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the

computation of pH for a titration solution after additions of several specified titrant volumes. The following example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH.

EXAMPLE 28.2.1

Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH (the titration curve is shown in Figure 14.18). Calculate the pH at these volumes of added base solution:

(a) 0.00 mL

(b) 12.50 mL

(c) 25.00 mL

(d) 37.50 mL

Solution

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 *M*. The pH of the solution is then

$$\text{pH} = -\log(0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the intial amount and then dividing by the solution volume:

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times 12.50\ \text{mL}}{25.00\ \text{mL} + 12.50\ \text{mL}} = 0.0333\ M$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

$$\text{n}(\text{OH}^-)_0 > \text{n}(\text{H}^+)_0$$

$$[\text{OH}^-] = \frac{\text{n}(\text{OH}^-)}{V} = \frac{0.100\ M \times 37.50\ \text{mL} - 0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL} + 37.50\ \text{mL}} = 0.0200\ M$$

pH = 14 − pOH = 14 + log([OH^-]) = 14 + log(0.0200) = 12.30

Check Your Learning

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $HNO_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

Answer

0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

28.3 Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called acid-base indicators. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underset{\text{red}}{\mathrm{HIn}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \underset{\text{yellow}}{\mathrm{In^-}(aq)}$$

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, In^-, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Châtelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species In^- and HIn. If most of the indicator (typically about 60–90% or more) is present as In^-, the perceived color of the solution is yellow. If most is present as HIn, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

$$\mathrm{pH} = \mathrm{p}K\mathrm{a} + \log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right)$$

In solutions where pH > pK_a, the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When pH < pK_a, the log term must be negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pKa, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The color

change interval (or *pH interval*) for an acid-base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately pK_a ± 1.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure 29.2 presents several indicators, their colors, and their color-change intervals.

Figure 28.2

This chart illustrates the color change intervals for several acid-base indicators.

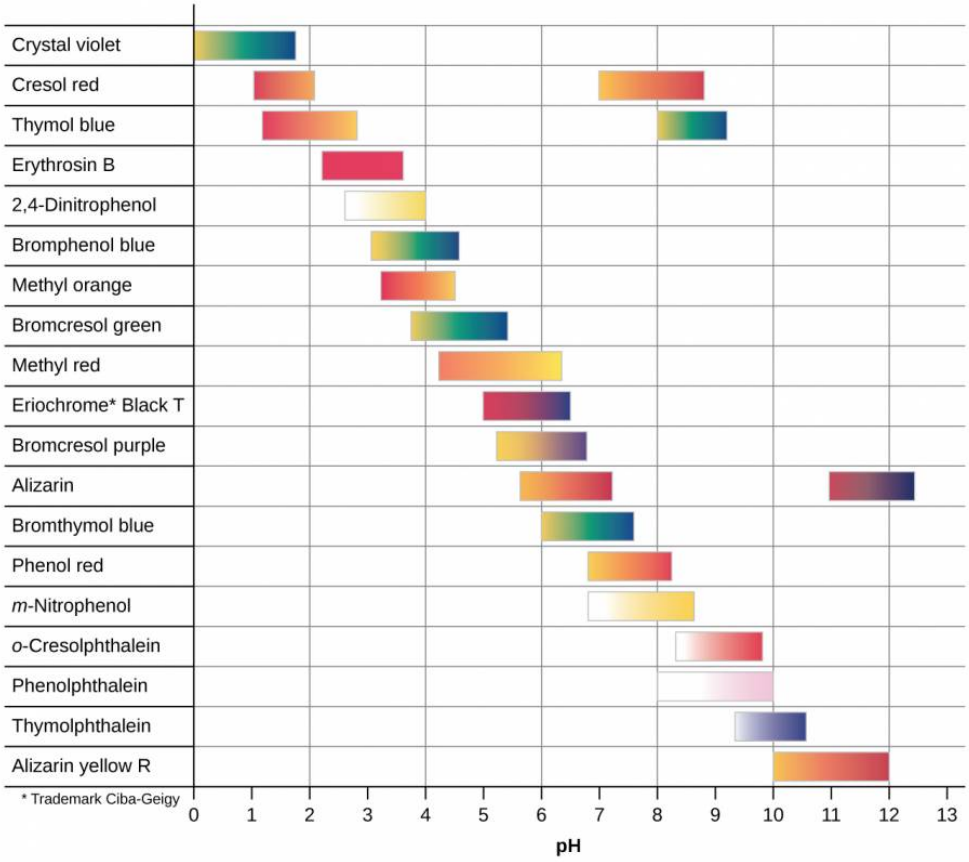
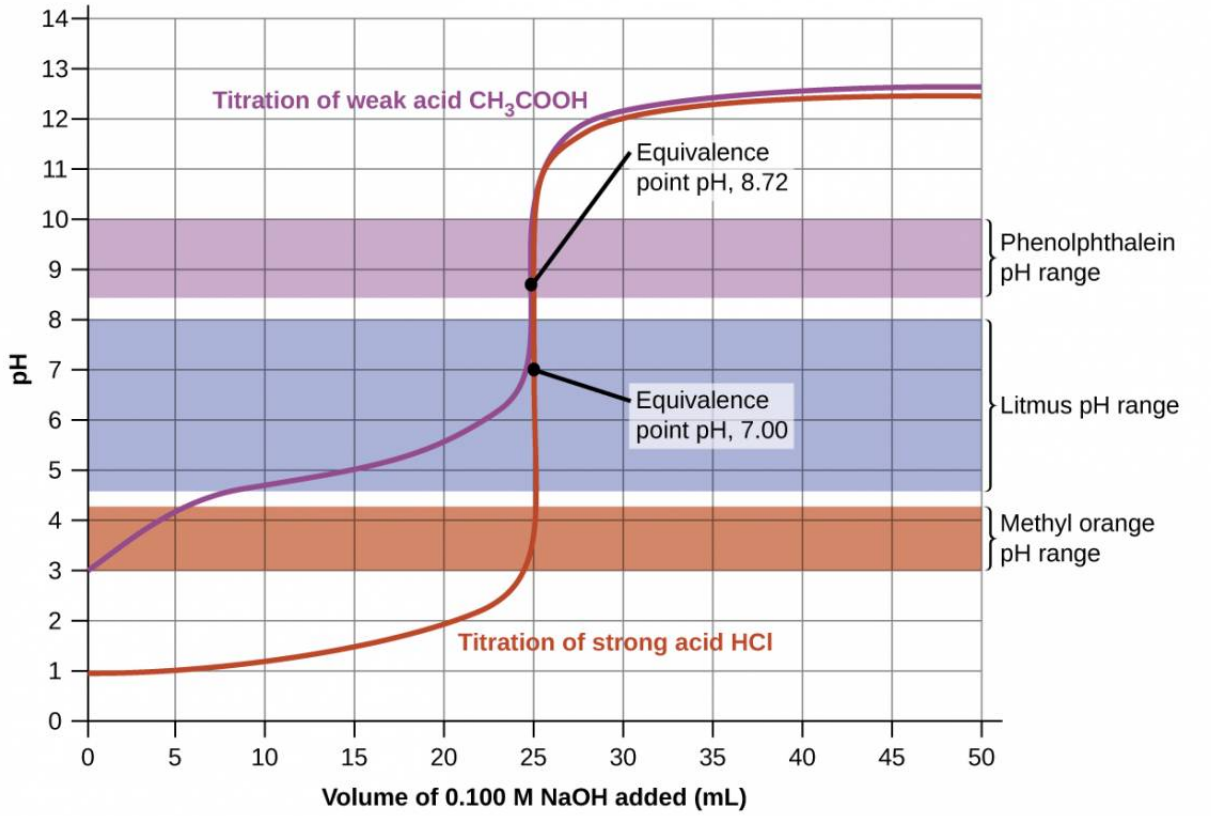


Figure 28.3

Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.



The titration curves shown in Figure 28.3 illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

The weak acid titration curve in Figure 28.3 shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

Files

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29

Titrations II

Learning Objectives

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration

EXAMPLE 29.0.1

Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$$

Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

(a) 0.00 mL

(b) 25.00 mL

(c) 12.50 mL

(d) 37.50 mL

Solution

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} \approx \frac{[H_3O^+]^2}{[CH_3CO_2H]_0},$$

and

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

$$\frac{0.00250\ \text{mol}}{0.0500\ \text{L}} = 0.0500\ M CH_3CO_2^-$$

Base ionization of acetate is represented by the equation

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

$$K_b = \frac{[H^+][OH^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming x << 0.0500, the pH may be calculated via the usual ICE approach:

$$K_b = \frac{x^2}{0.0500\ M}$$

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]} = -\log(K_a) + \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = -\log(1.8 \times 10^{-5}) + \log(1)$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

(pH = pK_a at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

$$[OH^-] = \frac{(0.003750\ \text{mol} - 0.00250\ \text{mol})}{0.06250\ \text{L}} = 2.00 \times 10^{-2}\ M$$

$$\text{pOH} = -\log(2.00 \times 10^{-2}) = 1.70, \text{ and pH} = 14.00 - 1.70 = 12.30$$

Check Your Learning

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

Answer

0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Performing calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in Table 29.1 and plotted as titration curves in Figure 29.1. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH

pre-equivalence point (0 mL < V < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction product, its conjugate base

equivalence point (V = 25 mL): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid

postequivalence point (V > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

Table 29.1

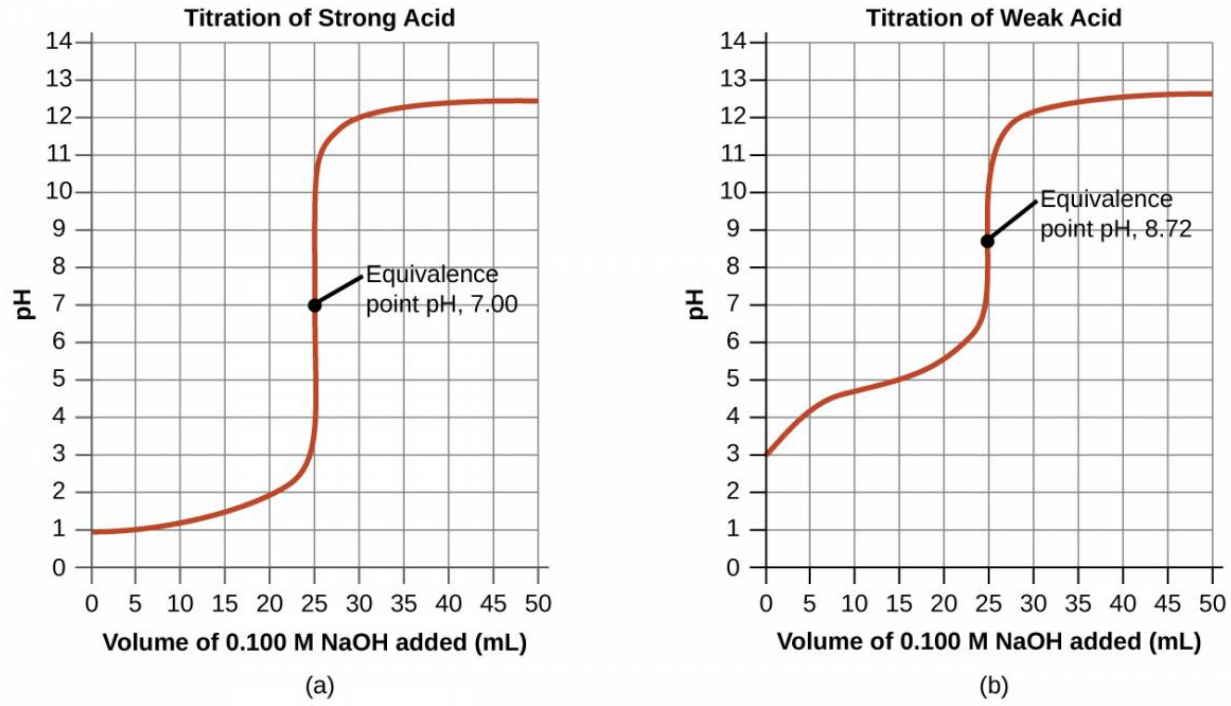
pH Values in the Titrations of a Strong Acid and of a Weak Acid

Volume of 0.100 *M* NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 *M* HCl[1]	pH Values 0.100 *M* CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96

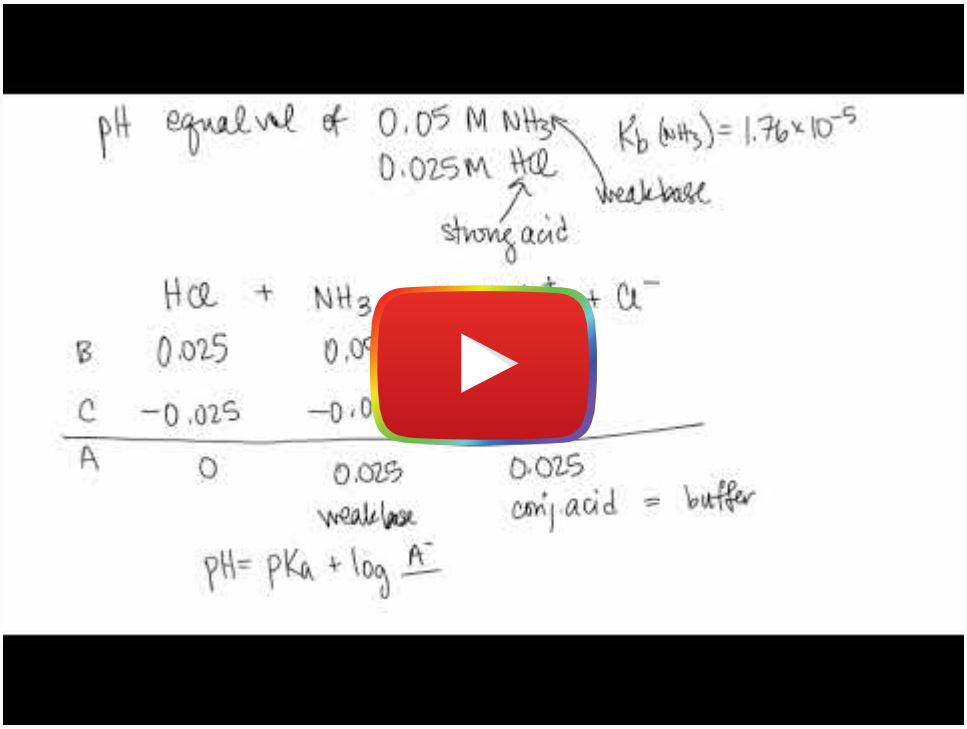
Volume of 0.100 *M* NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 *M* HCl[1]	pH Values 0.100 *M* CH_3CO_2H[2]
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

Figure 29.2

(a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M acetic acid (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.



29.0.2 Strong Acid + Weak Base



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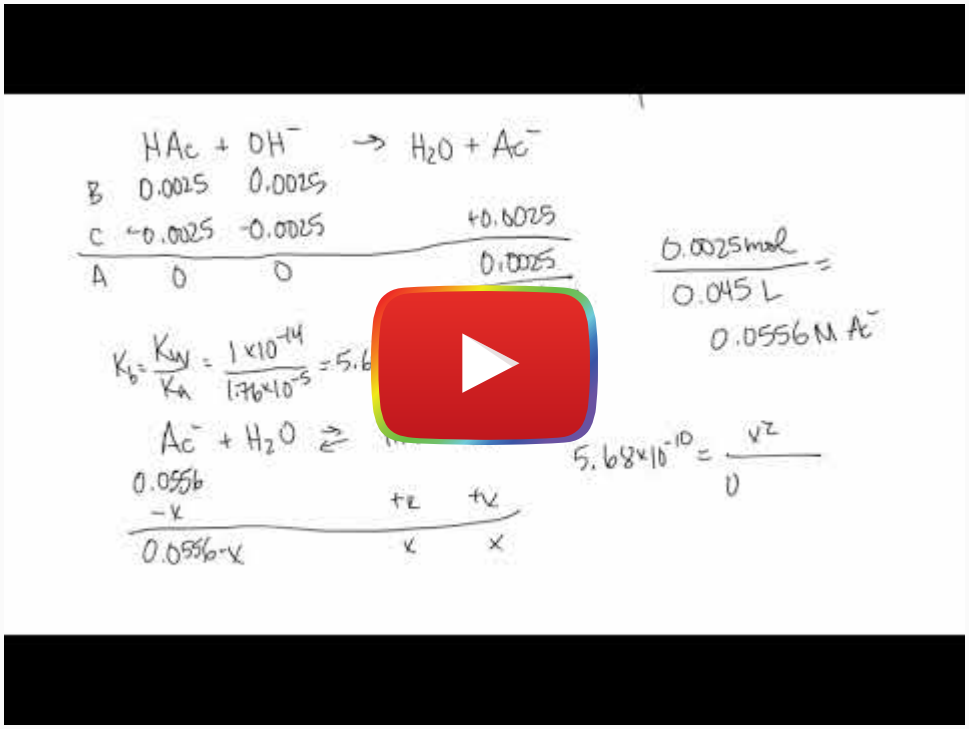
29.0.3 Weak Acid + Strong Base



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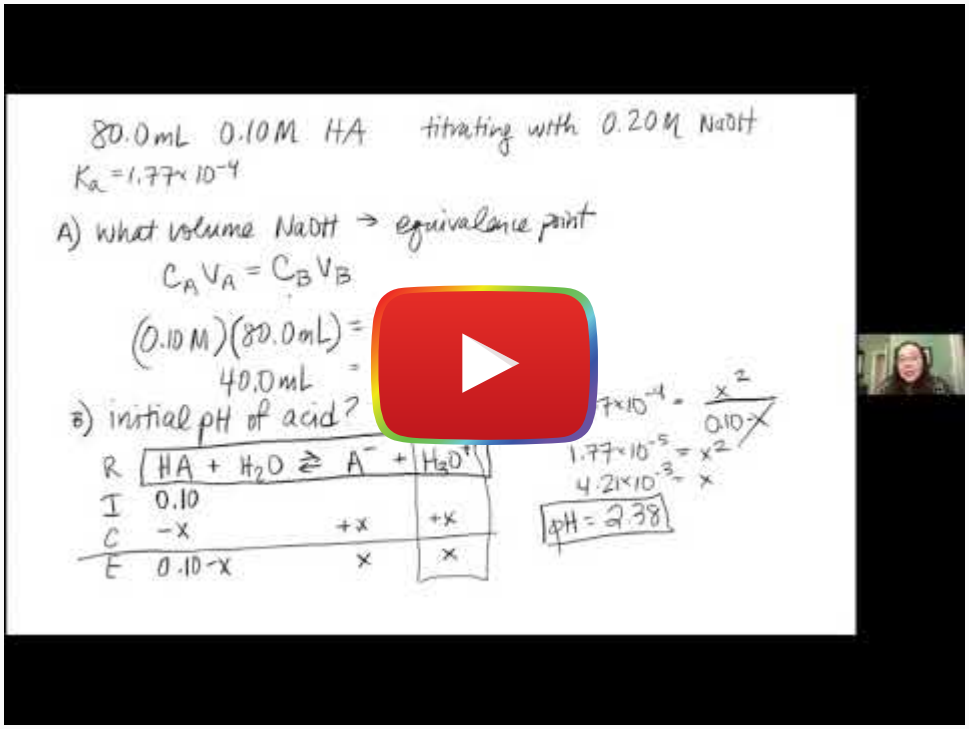
29.0.4 Weak Acid Strong Base Titration



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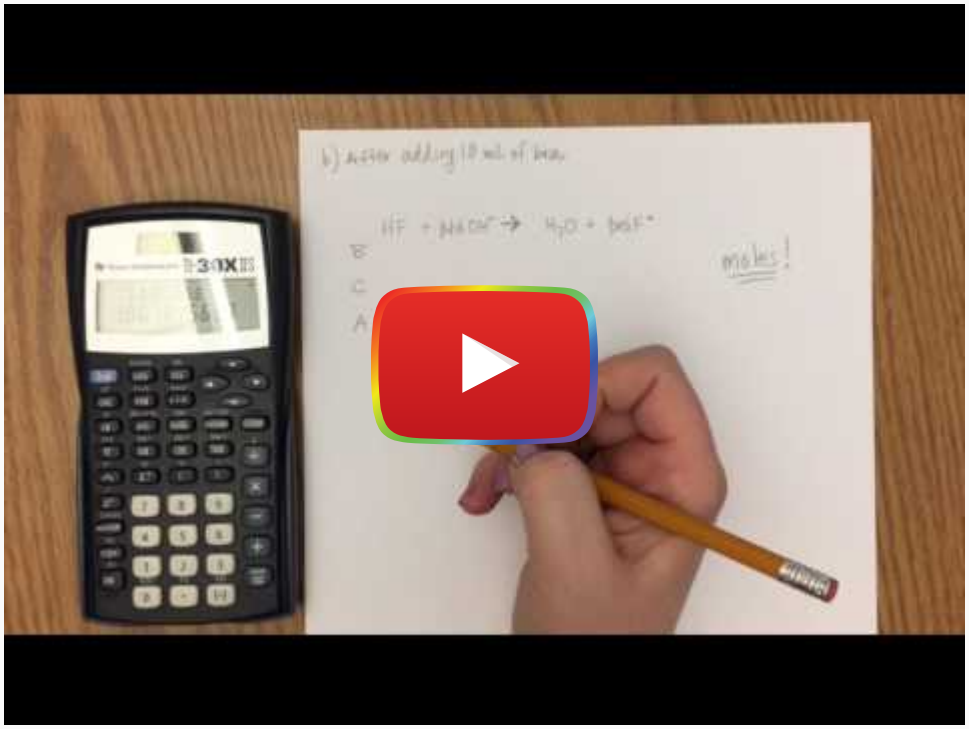
29.0.5 Weak Acid Titration Example



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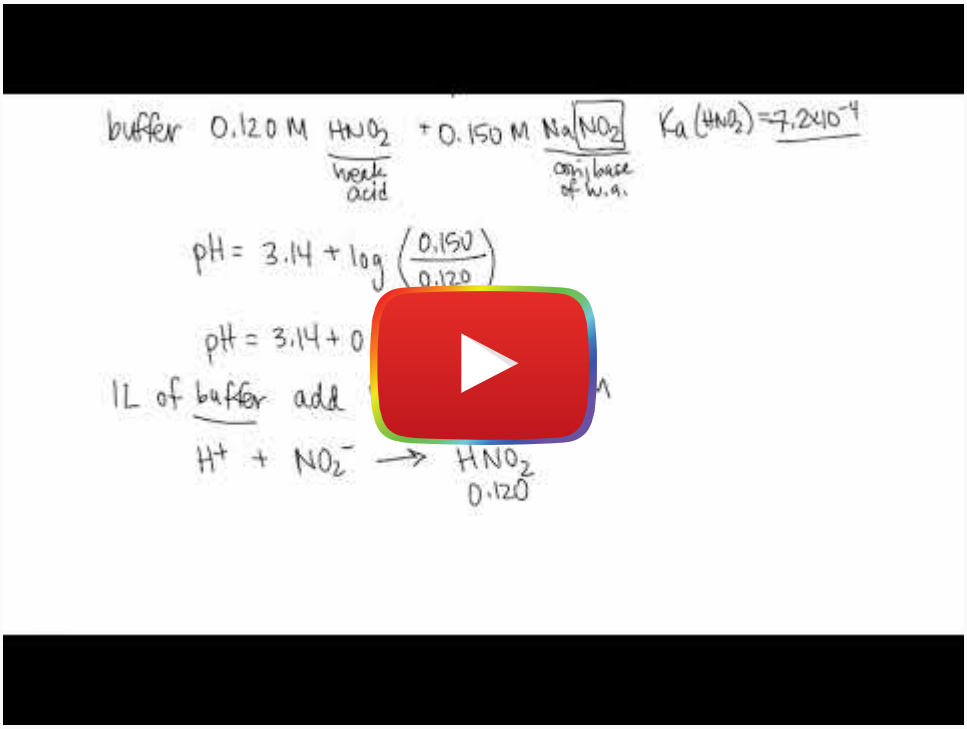
29.0.6 Strong Acid + Buffer



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Unit 6

Solubility and Complex Ion Equilibria

Solubility Equilibria
Complex Ion Equilibria
Chelation, Biological Effects
Crystal Field Theory
Isomerism, Equilibria and Biological Systems

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30

Solubility Equilibria

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, Ksp, of the solid. For a heterogeneous equilibrium involving the slightly soluble solid $MpXq$ *and its ions* M^{m+} *and* X^{n-}*:* $MpXq(s) \rightleftharpoons pM^{m+}(aq)+qX^{n-}(aq)$ *the solubility product expression is:* $K_{sp}=[M^{m+}]^p[X^{n-}]^q$ *The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its Ksp, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions. A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.*

30.1 Precipitation and Dissolution

Learning Objectives

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

30.1.1 The Solubility Product

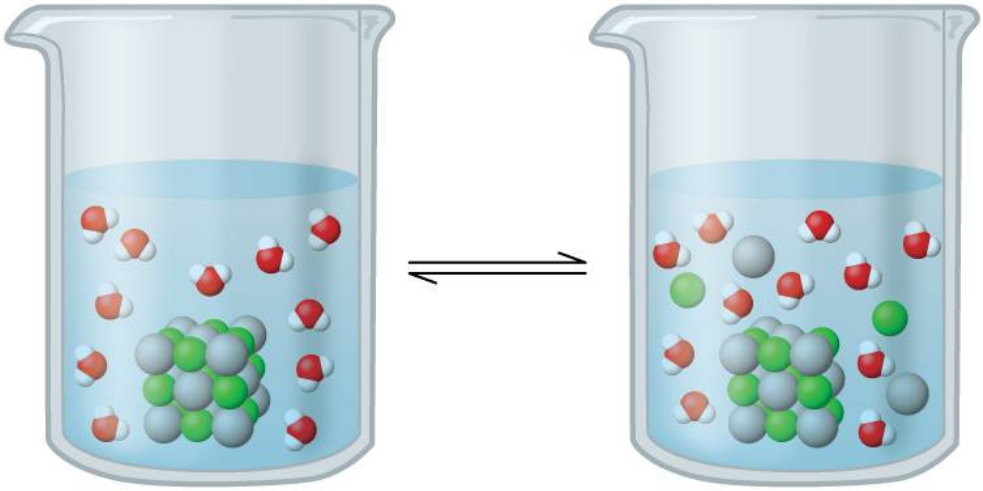
Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute. For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

$$\mathrm{AgCl}(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous Ag^+ and Cl^- ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (Figure 30.1). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.

Figure 30.1

Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.



The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant, K_{sp},** in this case

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq) \qquad K_{\text{sp}} = [\mathrm{Ag}^{+}(aq)][\mathrm{Cl}^{-}(aq)]$$

Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in Appendix J.

EXAMPLE 30.1.2

Writing Equations and Solubility Products

Write the dissolution equation and the solubility product expression for each of the following slightly soluble ionic compounds:
(a) AgI, silver iodide, a solid with antiseptic properties

(b) $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids

(c) $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia

(d) $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium

(e) $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

Solution

$$\text{(a) } AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad K_{sp} = [Ag^+][I^-$$

$$\text{(b) } CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][CO_3$$

$$\text{(c) } Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = [Mg^{2+}][OH^-]^2$$

$$\text{(d) } Mg(NH_4)PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4{}^+(aq) + PO_4{}^{3-}(aq) \qquad K_{sp} = [Mg^{2+}][NH_4{}^+][PO_4{}^{3-}]$$

$$\text{(e) } Ca_5(PO_4)3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4{}^{3-}(aq) + OH^-(aq) \qquad K_{sp} = [Ca^{2+}]^5[PO_4{}^{3-}]^3[OH^-]$$

Check Your Learning

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds:
(a) $BaSO_4$

(b) Ag_2SO_4

(c) $Al(OH)_3$

(d) Pb(OH)Cl

Answer

$$\text{(a) } BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ba^{2+}][SO_4{}^{2-}];$$

$$\text{(b) } Ag_2SO_4(s) \rightleftharpoons 2Ag^{+}(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ag^{+}]^2[SO_4{}^{2-}];$$

$$\text{(c) } Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^{-}(aq) \qquad K_{sp} = [Al^{3+}][OH^{-}]^3;$$

$$\text{(d) } Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^{-}(aq) + Cl^{-}(aq) \qquad K_{sp} = [Pb^{2+}][OH^{-}][Cl^{-}]$$

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

$$M_pX_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$$

For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

EXAMPLE 30.1.3

Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} *M*. What is the solubility product of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a CaF_2 solution is equal to twice its calcium ion molarity:

$$[F^-] = (2\text{ mol } F^-\ /\ 1\text{ mol } Ca^{2+}) = (2)(2.15 \times 10^{-4}\ M) = 4.30 \times 10^{-4}\ M$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.15 \times 10^{-4})(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

Check Your Learning

In a saturated solution of $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31×10^{-4} *M*. What is the solubility product for $Mg(OH)_2$?

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^-\,(aq)$$

Answer

8.99

×

10^{-12}

EXAMPLE 30.1.4

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3

×

10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The dissolution equation and solubility product expression are

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu}^{+}(aq) + \mathrm{Br}^{-}(aq)$$

$$K_{sp} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$

Following the ICE approach to this calculation yields the table

	$\mathrm{CuBr}\ (s) \rightleftharpoons \mathrm{Cu}^{+}\ (aq) + \mathrm{Br}^{-}\ (aq)$		
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		x	x

Substituting the equilibrium concentration terms into the solubility product expression and solving for x yields

$$K_{sp} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$

$$6.3 \times 10^{-9} = (x)(x) = x^2$$

$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}\ M$$

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of Br dissolved, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Check Your Learning

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

1.2

$\times$

$10^{-8}\ M$

EXAMPLE 30.1.5

Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2OH^-\,(aq)$$

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

The ICE table for this system is

	$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq)$	+	$2OH^-\,(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for x gives

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$

$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3}\ M$$

As defined in the ICE table, x is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is 6.9×10^{-3} *M*.

Check Your Learning

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer

1.5

×

10^{-3} *M*

EXAMPLE 30.1.6

Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 30.2) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product for $PbCrO_4$.

Figure 30.2

Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$[PbCrO_4] = \frac{4.6 \times 10^{-6}\ \text{g PbCrO}_4}{1\ \text{L}} \times \frac{1\ \text{mol PbCrO}_4}{323.2\ \text{g PbCrO}_4}$$

$$= \frac{1.4 \times 10^{-8}\ \text{mol PbCrO}_4}{1\ \text{L}}$$

$$= 1.4 \times 10^{-8}\ M$$

The dissolution equation for this compound is

$$PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4{}^{2-}(aq)$$

The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[Pb^{2+}]$ and

$$[CrO_4{}^{2-}]$$

are equal to the molar solubility of $PbCrO_4$:

$$[Pb^{2+}] = [CrO_4{}^{2-}] = 1.4 \times 10^{-8}\,M$$

$K_{sp} = [Pb^{2+}]$

$$[CrO_4{}^{2-}]$$

$= (1.4\times10^{-8})(1.4\times10^{-8}) = 2.0\times10^{-16}$

Check Your Learning

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

Answer

1.69

×

10^{-4}

EXAMPLE 30.1.7

Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I),

$$Hg_2^{2+},$$

and chloride ions, Cl^-. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel has a very low solubility, as suggested by its very small K_{sp}:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 1.1 \times 10^{-18}$$

Calculate the molar solubility of Hg_2Cl_2.

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of

$$Hg_2^{2+}$$

ions
Following the ICE approach results in

	$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq)$	+	$2Cl^-(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$1.1 \times 10^{-18} = (x)(2x)^2$$

$$4x^3 = 1.1 \times 10^{-18}$$

$$x = \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7}\ M$$

$$[Hg_2^{2+}] = 6.5 \times 10^{-7}\ M = 6.5 \times 10^{-7}\ M$$

$$[Cl^-] = 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6}\ M$$

The dissolution stoichiometry shows the molar solubility of Hg_2Cl_2 is equal to

$[Hg_2^{2+}]$,

or 6.5×10^{-7} *M*.

Check Your Learning

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Answer

1.2

×

10^{-3} *M*

30.1.8 HOW SCIENCES INTERCONNECT

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 2.3×10^{-8}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 30.3).

Figure 30.3

A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit this website for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

30.1.9 Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}\,(s) \rightleftharpoons \mathrm{Ca^{2+}}\,(aq) + \mathrm{CO_3}^{2-}\,(aq) \qquad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{CO_3}^{2-}] = 8.7 \times 10^{-9}$$

It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and CO_3^{2-} ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate. If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp}, that exceeds the solubility product, K_{sp}, then no precipitation will occur. If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{sp}$). The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

$Q_{sp} < K_{sp}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)

$Q_{sp} > K_{sp}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

EXAMPLE 30.1.10

Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^-\,(aq) \qquad K_{sp} = 8.9 \times 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

Calculation of the reaction quotient under these conditions is shown here:

$$Q = [Mg^{2+}][OH^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4\times10^{-8}$ is larger than $K_{sp} = 8.9\times10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Check Your Learning

Predict whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}] = 0.0001$ *M* and

$[HPO_4{}^{2-}]$

= 0.001 *M*.

Answer

No precipitation of $CaHPO_4$; $Q = 1$

×

10^{-7}, which is less than K_{sp} (7×10^{-7})

EXAMPLE 30.1.11

Precipitation of AgCl

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-*M* solution of $AgNO_3$ and a 2.0×10^{-4}-*M* solution of NaCl are mixed?

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility product is 1.6×10^{-10} (see Appendix J).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. Because the volume doubles when equal volumes of $AgNO_3$ and NaCl solutions are mixed, each concentration is reduced to half its initial value

$$\frac{1}{2}(2.0 \times 10^{-4})\,M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, *Q*, is greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [Ag^+][Cl^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

AgCl will precipitate from the mixture until the dissolution equilibrium is established, with *Q* equal to K_{sp}.

Check Your Learning

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of

ClO_4^- ?

(Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

Answer

No, *Q* = 4.0

×

10^{-3}, which is less than K_{sp} = 1.05

×

10^{-2}

EXAMPLE 30.1.12

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion,

$$C_2O_4^{2-},$$

for this purpose (Figure 30.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of

$$C_2O_4^{2-}$$

ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?

Figure 30.4

Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4{}^{2-}(aq)$$

For this reaction:

$$K_{sp} = [Ca^{2+}][C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$

(see Appendix J)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$Q = K_{sp} = [Ca^{2+}][C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$

$$(2.2 \times 10^{-3})[C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$

$$[C_2O_4{}^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}\ M$$

A concentration of

$[C_2O_4{}^{2-}]$

= 8.9×10^{-6} *M* is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Check Your Learning

If a solution contains 0.0020 mol of

$CrO_4{}^{2-}$

per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer

6.7

×

10^{-5} *M*

EXAMPLE 30.1.13

Concentrations Following Precipitation

Clothing washed in water that has a manganese [$Mn^{2+}(aq)$] concentration exceeding 0.1 mg/L (1.8×10^{-6} *M*) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. What pH is required to keep [Mn^{2+}] equal to 1.8×10^{-6} *M*?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}\,(s) \rightleftharpoons \mathrm{Mn^{2+}}\,(aq) + 2\mathrm{OH^-}\,(aq) \qquad K_{sp} = 2 \times 10^{-13}$$

At equilibrium:

$$K_{sp} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2$$

or

$$(1.8 \times 10^{-6})[\mathrm{OH^-}]^2 = 2 \times 10^{-13}$$

so

$$[\mathrm{OH^-}] = 3.3 \times 10^{-4}\ M$$

Calculate the pH from the pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(3.3 \times 10 - 4) = 3.48$$
$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 3.48 = 10.52$$

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

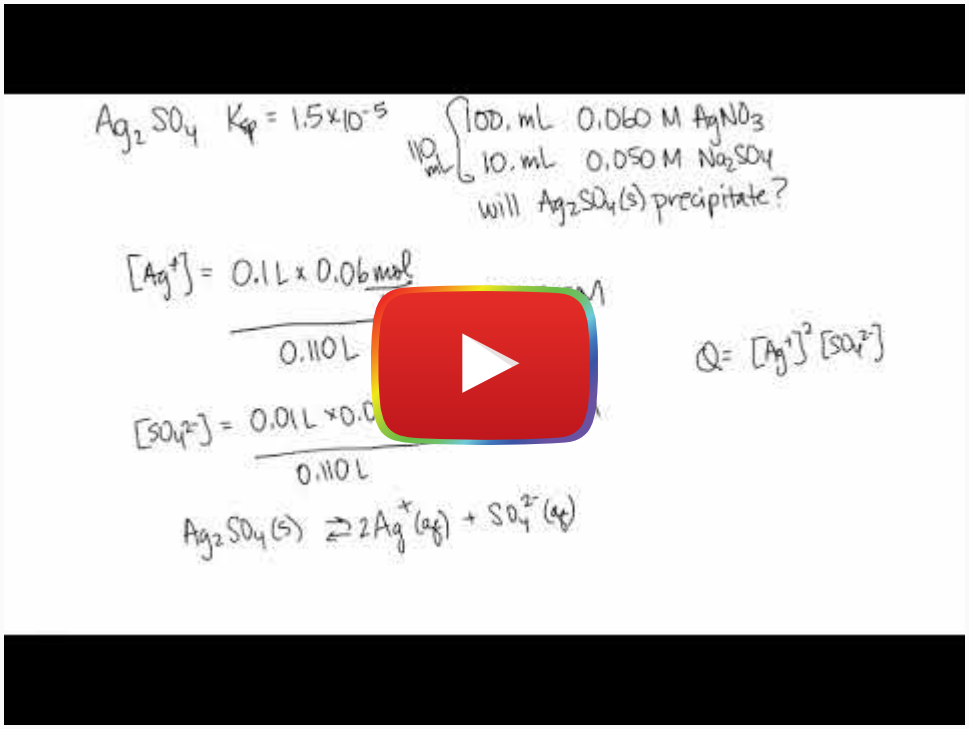
Check Your Learning

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which [Mg^{2+}] is decreased to 1.0×10^{-5} *M*

Answer

10.97

30.1.14 Predicting Precipitation Q vs. Ksp



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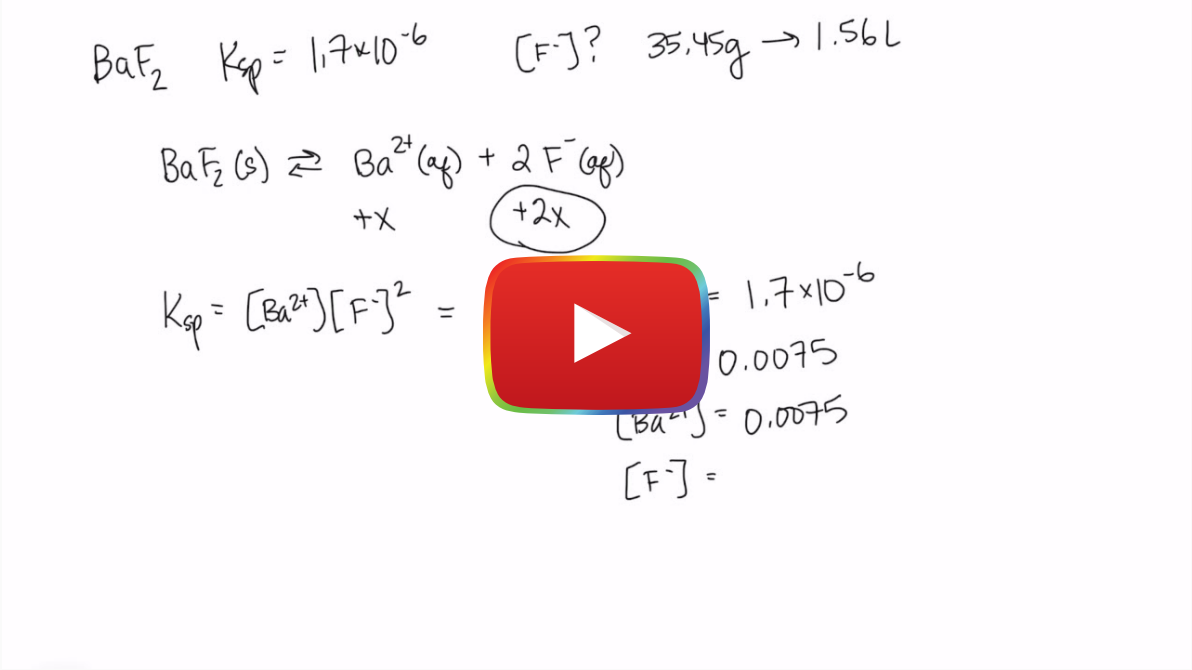
30.1.15 Ksp: Concentration of Ions in Solution



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In solutions containing two or more ions that may form insoluble compounds with the same counter ion, an experimental strategy called selective precipitation may be used to remove individual ions from solution. By increasing the counter ion concentration in a controlled manner, ions in solution may be precipitated individually, assuming their compound solubilities are adequately different. In solutions with equal concentrations of target ions, the ion forming the least soluble compound will precipitate first (at the lowest concentration of counter ion), with the other ions subsequently precipitating as their compound's solubilities are reached. As an illustration of this technique, the next example exercise describes separation of a two halide ions via precipitation of one as a silver salt.

30.1.16 CHEMISTRY IN EVERYDAY LIFE

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 30.5). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions

$$(PO_4^{3-})$$

are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 30.5

Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightleftharpoons Ca_5(PO_4)_3 \cdot OH(s)$$

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this site for more information on how phosphorus is removed from wastewater.

EXAMPLE 30.1.17

Precipitation of Silver Halides

A solution contains 0.00010 mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Solution

The two equilibria involved are:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$
$$\mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Br}^-(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$$

If the solution contained about *equal* concentrations of Cl^- and Br^-, then the silver salt with the smaller K_{sp} (AgBr) would precipitate first. The concentrations are not equal, however, so the $[Ag^+]$ at which AgCl begins to precipitate and the $[Ag^+]$ at which AgBr begins to precipitate must be calculated. The salt that forms at the lower $[Ag^+]$ precipitates first.

AgBr precipitates when Q equals K_{sp} for AgBr

$$Q_{sp} = K_{sp} = [\mathrm{Ag}^+][\mathrm{Br}^-] = [\mathrm{Ag}^+](0.00010) = 5.0 \times 10^{-13}$$

$$[\mathrm{Ag}^+] = \frac{5.0 \times 10^{-13}}{0.00010} = 5.0 \times 10^{-9}\ M$$

AgBr begins to precipitate when $[Ag^+]$ is 5.0×10^{-9} *M*.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[Cl^-]$ = 0.10 *M*:

$$Q_{sp} = K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-] = [\mathrm{Ag}^+](0.10) = 1.6 \times 10^{-10}$$

$$[\mathrm{Ag}^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9}\ M$$

AgCl begins to precipitate when $[Ag^+]$ is 1.6×10^{-9} *M*.

AgCl begins to precipitate at a lower $[Ag^+]$ than AgBr, so AgCl begins to precipitate first. Note the chloride ion concentration of the initial mixture was significantly greater than the bromide ion concentration, and so silver chloride precipitated first despite having a K_{sp} greater than that of silver bromide.

Check Your Learning

If silver nitrate solution is added to a solution which is 0.050 *M* in both Cl^- and Br^- ions, at what $[Ag^+]$ would precipitation begin, and what would be the formula of the precipitate?

Answer

$[Ag^+] = 1.0$

×

10^{-11} *M*; AgBr precipitates first

Files

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Previous Citation(s)

Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (15.1)

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https://open.byu.edu/general_college_chemistry_2/30_solubility_equili.

31

Complex Ion Equilibria

A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts and comprise central metal atoms or ions acting as Lewis acids bonded to molecules or ions called ligands that act as Lewis bases. The equilibrium constant for the reaction between a metal ion and ligands produces a complex ion called a formation constant; for the reverse reaction, it is called a dissociation constant.

Learning Objectives

By the end of this section, you will be able to:

- Explain the common ion effect
- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

31.0.1 Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le ChÂtelier's principle. Consider the dissolution of silver iodide:

$$\mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{I}^{-}(aq)$$

This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved Ag^{+} and I^{-}. In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

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

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

LINK TO LEARNING

View this simulation to explore various aspects of the common ion effect.

EXAMPLE 31.0.2

Common Ion Effect on Solubility

What is the effect on the amount of solid $Mg(OH)_2$ and the concentrations of Mg^{2+} and OH^- when each of the following are added to a saturated solution of $Mg(OH)_2$?
(a) $MgCl_2$

(b) KOH

(c) $NaNO_3$

(d) $Mg(OH)_2$

Solution

The solubility equilibrium is

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

(a) Adding a common ion, Mg^{2+}, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.

(b) Adding a common ion, OH^-, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.

(c) The added compound does not contain a common ion, and no effect on the magnesium hydroxide solubility equilibrium is expected.

(d) Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

$$Q = [Mg^{2+}][OH^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q, and no shift is required to restore Q to the value of the equilibrium constant.

Check Your Learning

What is the effect on the amount of solid $NiCO_3$ and the concentrations of Ni^{2+} and

CO_3^{2-}

when each of the following are added to a saturated solution of $NiCO_3$
(a) $Ni(NO_3)_2$

(b) $KClO_4$

(c) $NiCO_3$

(d) K_2CO_3

Answer

(a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases,

$[CO_3^{2-}]$

decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid $NiCO_3$; (d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases,

$[CO_3^{2-}]$

increases;

EXAMPLE 31.0.3

Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide ($CdBr_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

This calculation can be performed using the ICE approach:

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$$

	$CdS\ (s) \rightleftharpoons Cd^{2+}\ (aq) + S^{2-}\ (aq)$		
Initial concentration (*M*)		0.010	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		$0.010 + x$	x

$$K_{sp} = [Cd^{2+}][S^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because K_{sp} is very small, assume $x << 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28}$$

$$x = 1.0 \times 10^{-26}\ M$$

The molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Check Your Learning

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015-*M* solution of aluminum nitrate, $Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Answer

4

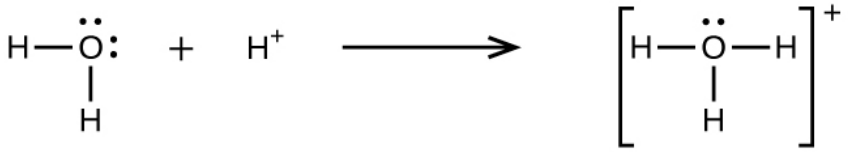
×

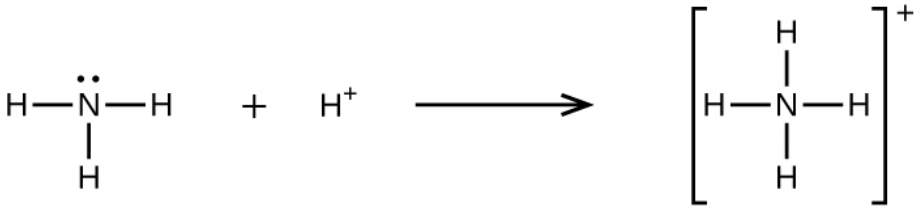
10^{-11} *M*

31.1 Lewis Acids and Bases

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

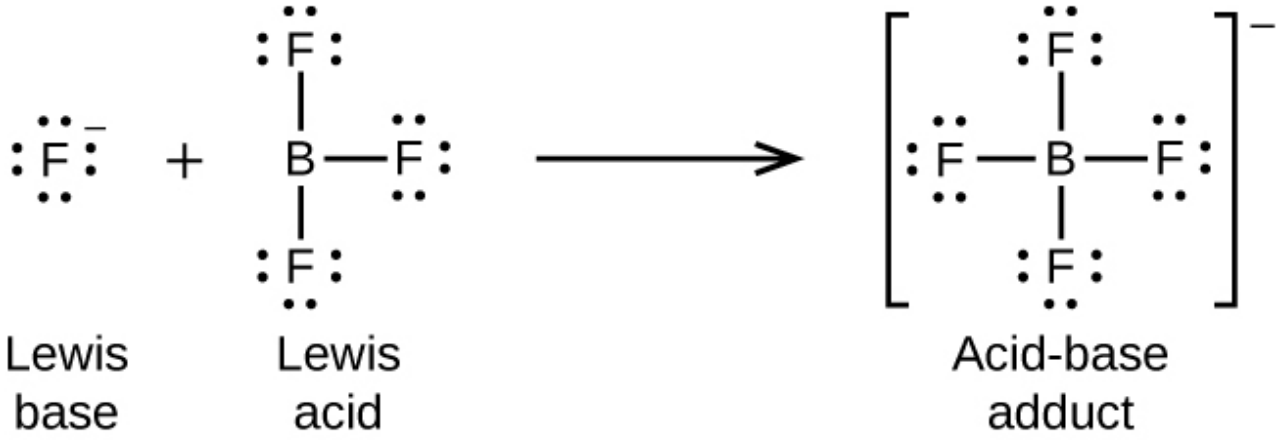
A coordinate covalent bond (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



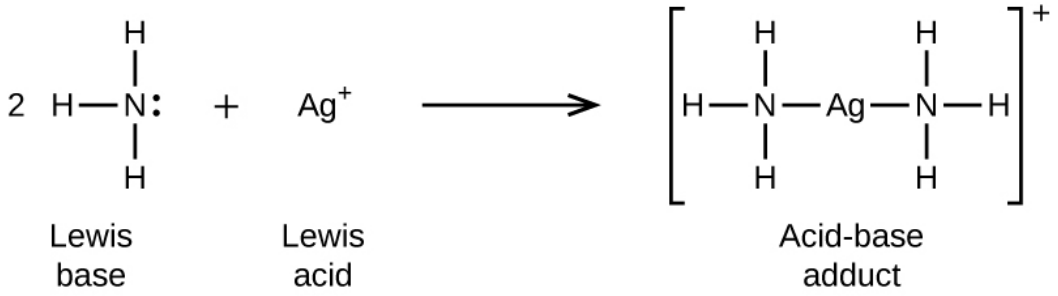


Reactions involving the formation of coordinate covalent bonds are classified as Lewis acid-base chemistry. The species donating the electron pair that compose the bond is a Lewis base, the species accepting the electron pair is a Lewis acid, and the product of the reaction is a Lewis acid-base adduct. As the two examples above illustrate, Brønsted-Lowry acid-base reactions represent a subcategory of Lewis acid reactions, specifically, those in which the acid species is H^+. A few examples involving other Lewis acids and bases are described below.

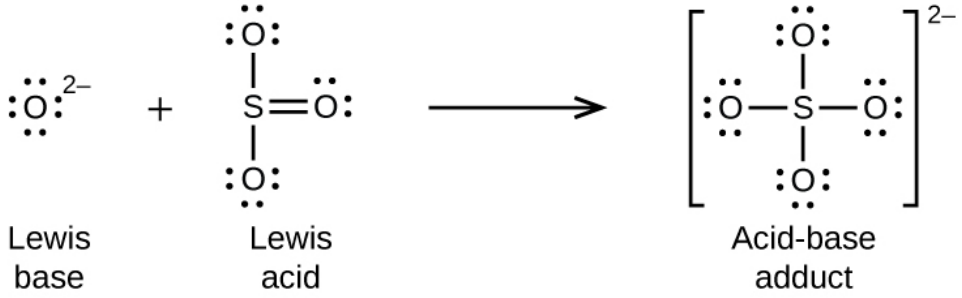
The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



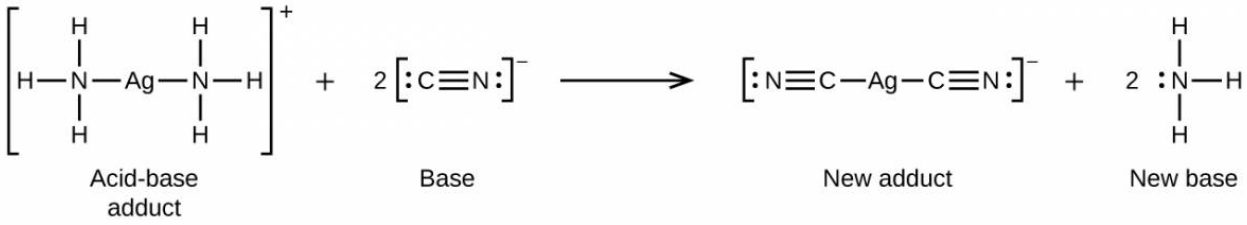
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:

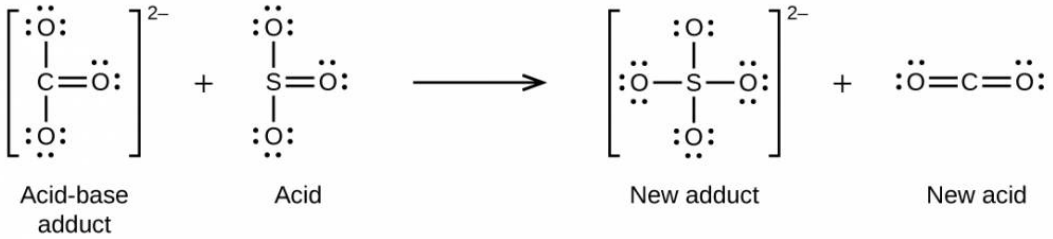


Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:



Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:

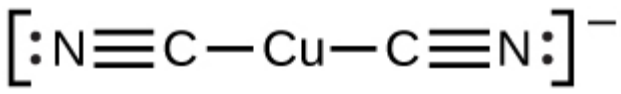




Another type of Lewis acid-base chemistry involves the formation of a complex ion (or a coordination complex) comprising a central atom, typically a transition metal cation, surrounded by ions or molecules called ligands. These ligands can be neutral molecules like H_2O or NH_3, or ions such as CN^- or OH^-. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. These types of Lewis acid-base reactions are examples of a broad subdiscipline called *coordination chemistry*—the topic of another chapter in this text.

The equilibrium constant for the reaction of a metal ion with one or more ligands to form a coordination complex is called a formation constant (K_f) (sometimes called a stability constant). For example, the complex ion

$Cu(CN)_2^-$



is produced by the reaction

$$Cu^+(aq) + 2CN^-(aq) \rightleftharpoons Cu(CN)_2^-(aq)$$

The formation constant for this reaction is

$$K_f = \frac{[Cu(CN)_2^-]}{[Cu^+][CN^-]^2}$$

Alternatively, the reverse reaction (decomposition of the complex ion) can be considered, in which case the equilibrium constant is a dissociation constant (K_d). Per the relation between equilibrium constants for reciprocal reactions described, the dissociation constant is the mathematical inverse of the formation constant, $K_d = K_f^{-1}$. A tabulation of formation constants is provided in Appendix K.

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[Ag^+] = 1.3\times10^{-5}$ *M*):

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

However, if NH_3 is present in the water, the complex ion,

$Ag(NH_3)_2^+$,

can form according to the equation:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

with

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form

$Ag(NH_3)_2^+$.

As a consequence, the concentration of silver ions, $[Ag^+]$, is reduced, and the reaction quotient for the dissolution of silver chloride, $[Ag^+][Cl^-]$, falls below the solubility product of AgCl:

$$Q = [Ag^+][Cl^-] < K_{sp}$$

More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

EXAMPLE 31.1.1

Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 *M* with respect to

$Ag(NH_3)_2^+$.

Solution

Applying the standard ICE approach to this reaction yields the following:

	Ag^+ +	$2NH_3$ ⇌	$Ag(NH_3)_2^+$
Initial concentration (*M*)	0	0	0.10
Change (*M*)	$+x$	$+2x$	$-x$
Equilibrium concentration (*M*)	x	$2x$	$0.10 - x$

Substituting these equilibrium concentration terms into the K_f expression gives

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$$

$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

The very large equilibrium constant means the amount of the complex ion that will dissociate, *x*, will be very small. Assuming $x << 0.1$ permits simplifying the above equation:

$$1.7 \times 10^7 = \frac{0.10}{(x)(2x)^2}$$

$$x^3 = \frac{0.10}{4(1.7 \times 10^7)} = 1.5 \times 10^{-9}$$

$$x = \sqrt[3]{1.5 \times 10^{-9}} = 1.1 \times 10^{-3}$$

Because only 1.1% of the

$Ag(NH_3)_2^+$

dissociates into Ag^+ and NH_3, the assumption that x is small is justified.

Using this value of x and the relations in the above ICE table allows calculation of all species' equilibrium concentrations:

$$[Ag^+] = 0 + x = 1.1 \times 10^{-3}\ M$$

$$[NH_3] = 0 + 2x = 2.2 \times 10^{-3}\ M$$

$$[Ag(NH_3)_2{}^+] = 0.10 - x = 0.10 - 0.0011 = 0.099$$

The concentration of free silver ion in the solution is 0.0011 *M*.

Check Your Learning

Calculate the silver ion concentration, $[Ag^+]$, of a solution prepared by dissolving 1.00 g of $AgNO_3$ and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because K_f is very large, assume the reaction goes to completion then calculate the $[Ag^+]$ produced by dissociation of the complex.)

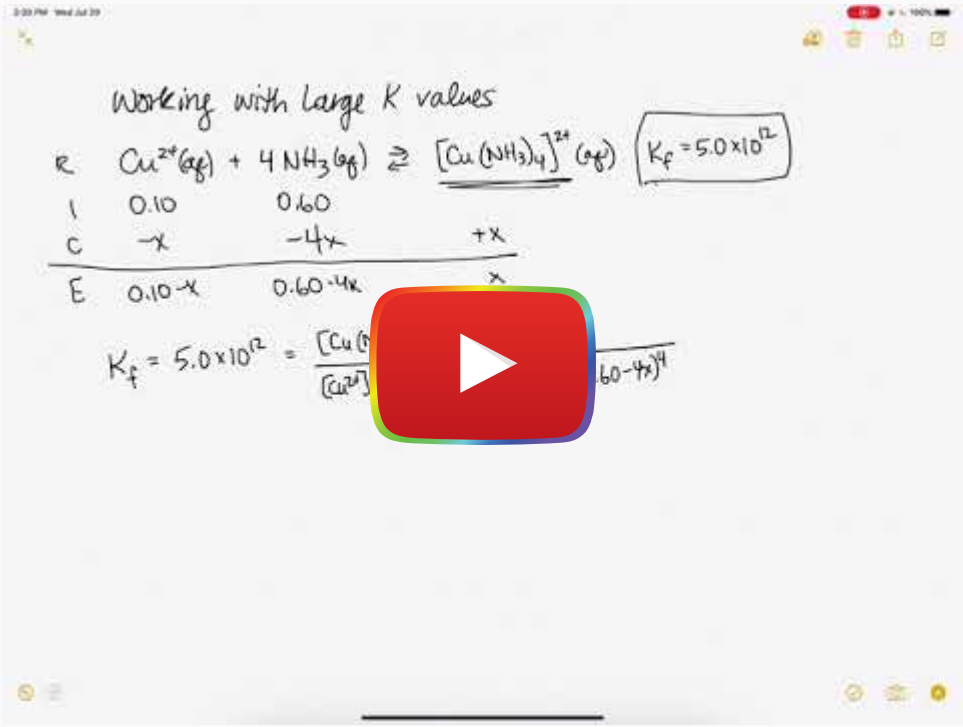
Answer

2.9

×

$10^{-22}\ M$

31.1.2 Working with Large K Values



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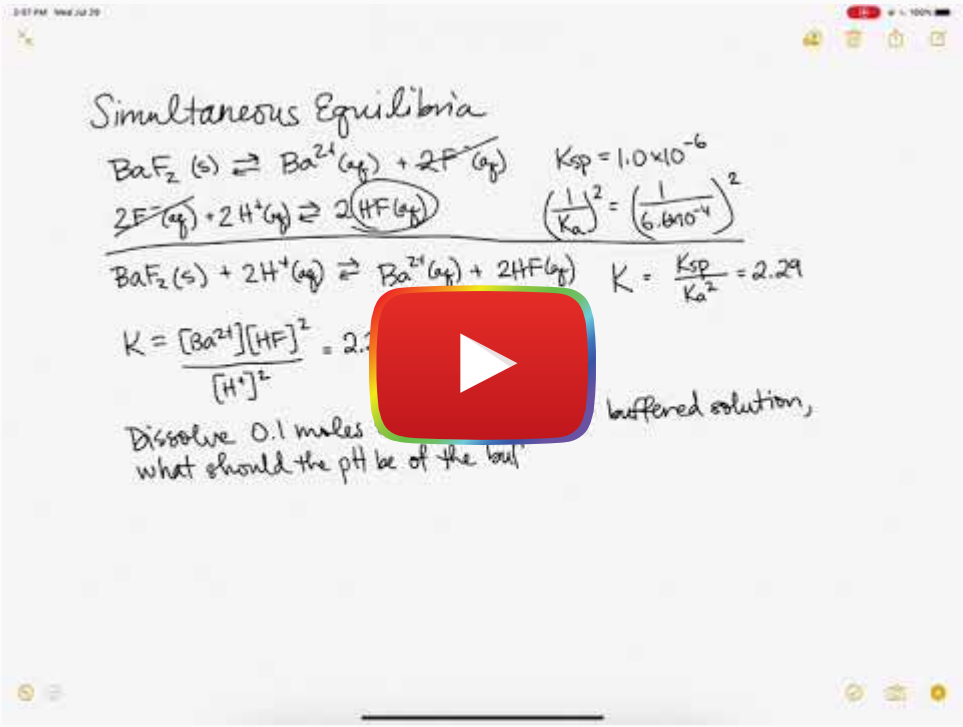
31.1.3 Simultaneous Equilibria Ksp/Ka



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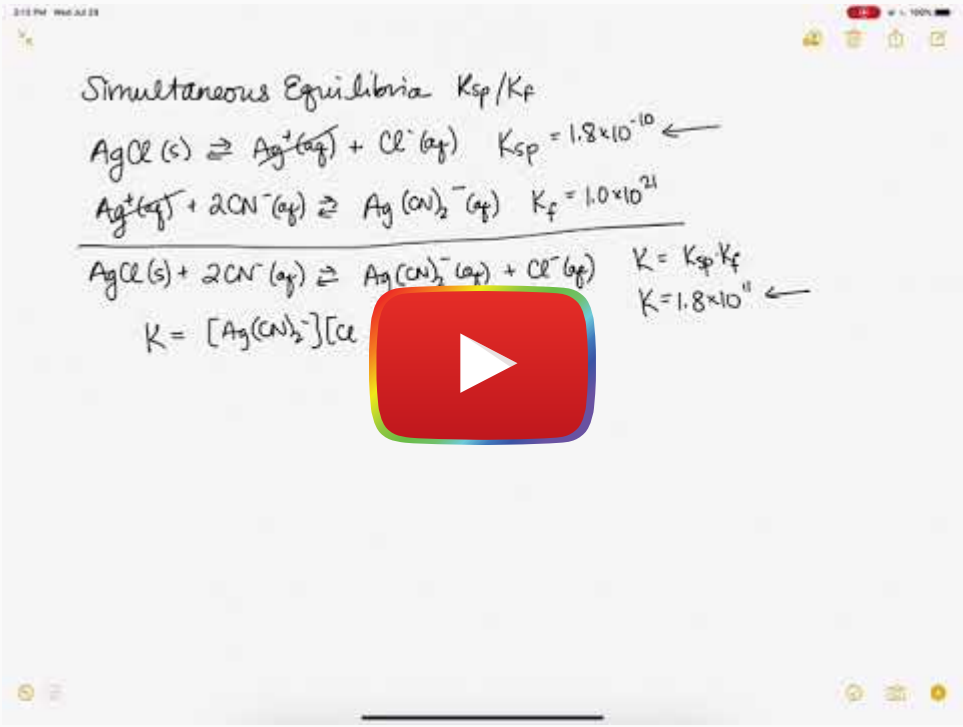
31.1.4 Simultaneous Equilibria Ksp/Kf



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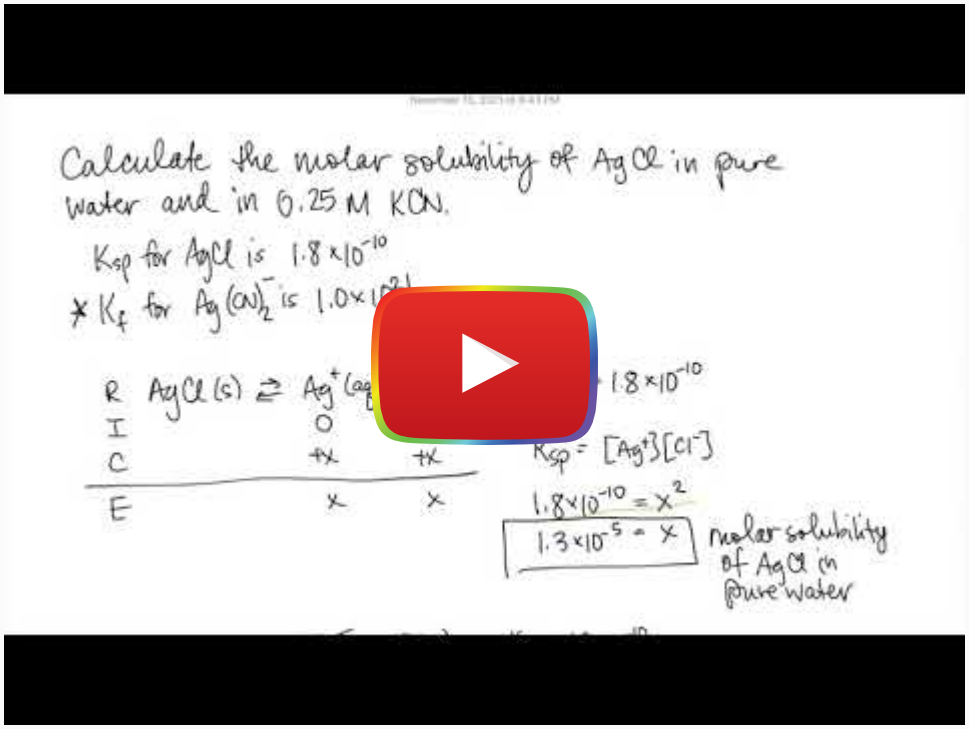
31.1.5 Simultaneous Equilibria Ksp/Kf Part 2



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https://open.byu.edu/general_college_chemistry_2/complex_ion_formatio.

32

Chelation, Biological Effects

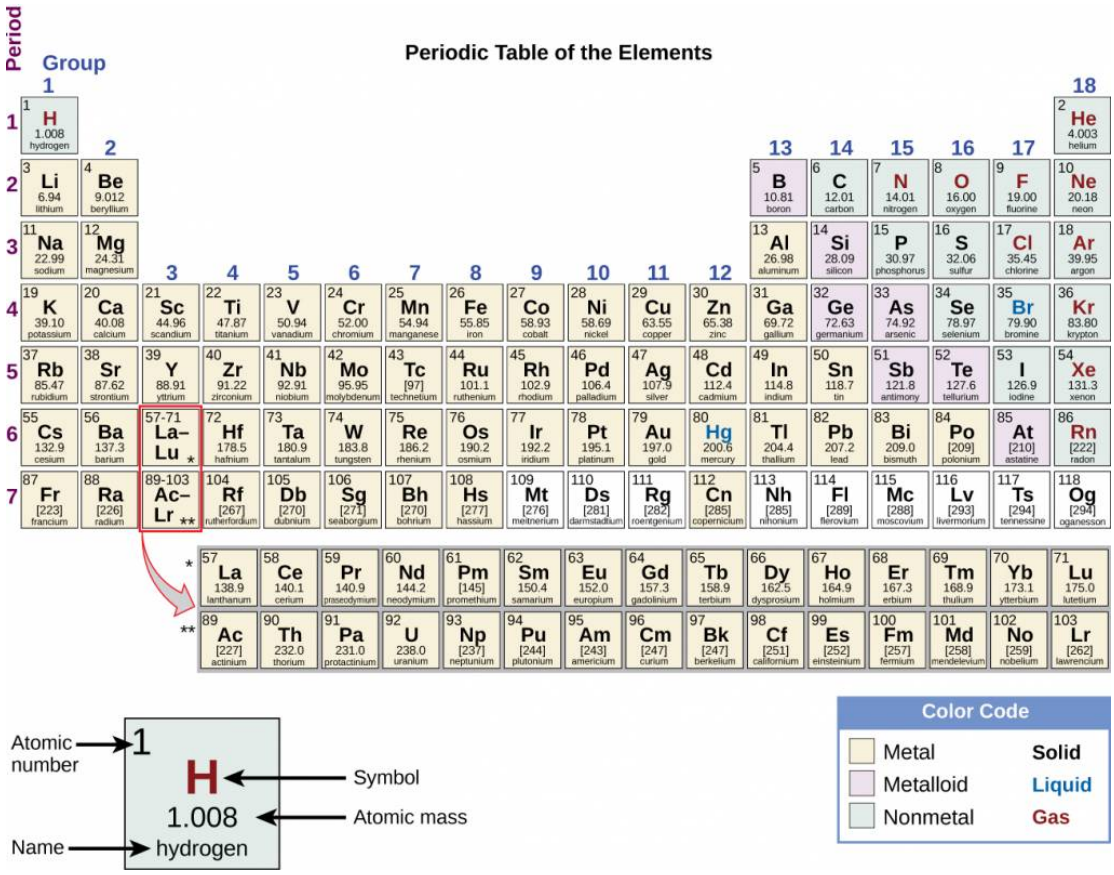
The transition metals are elements with partially filled d orbitals, located in the d-block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals. The type of chemistry used 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. The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds.

32.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure 32.1, 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 32.1

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 *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.

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 32.1.1

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) $Pb^{2+}[Xe]6s^{2}5d^{10}4f^{14}$; 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

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+}.

32.1.2 CHEMISTRY IN EVERYDAY LIFE

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

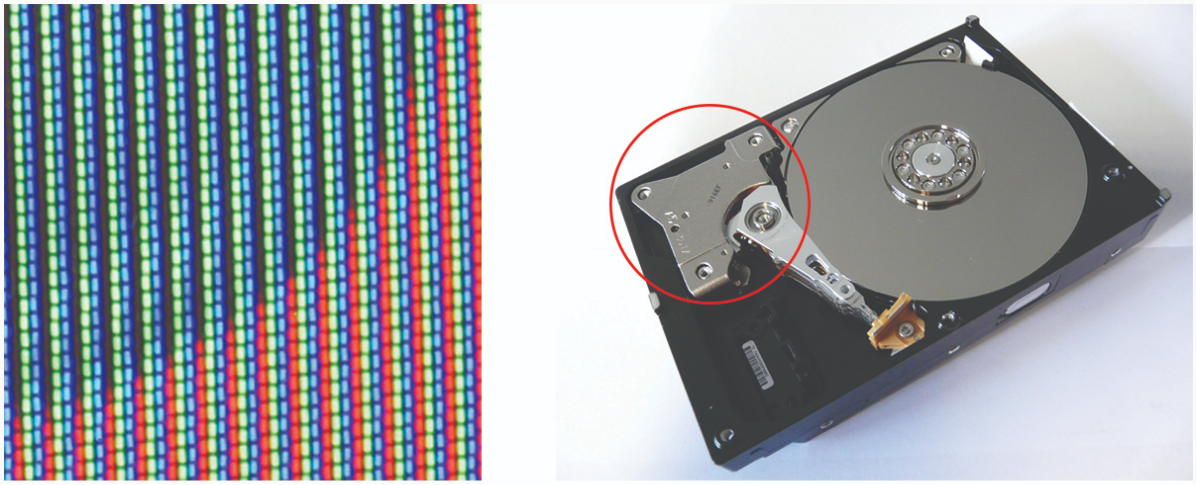
×

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 32.2). 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 32.2

(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)



(a) (b)

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.

32.1.3 Properties of the Transition Elements

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (see Appendix H), 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 32.3. 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+).

Figure 32.3

Transition metals of the first transition series can form compounds with varying oxidation states.

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+					

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 32.1.4

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 (in Appendix L) for each oxide in the specified oxidation state:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad +1.33\ V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + H_2O \qquad +1.51\ V$$

$$TiO_2 + 4H^+ + 2e^- \longrightarrow Ti^{2+} + 2H_2O \qquad -0.50\ V$$

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.

Check Your Learning

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 Appendix L.

Answer

$$Co(s) + 2HCl \longrightarrow H_2 + CoCl_2(aq);$$

no reaction because Pt(*s*) will not be oxidized by H^+

32.1.5 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 32.4). 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 32.4

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)

(a) (b) (c)

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.

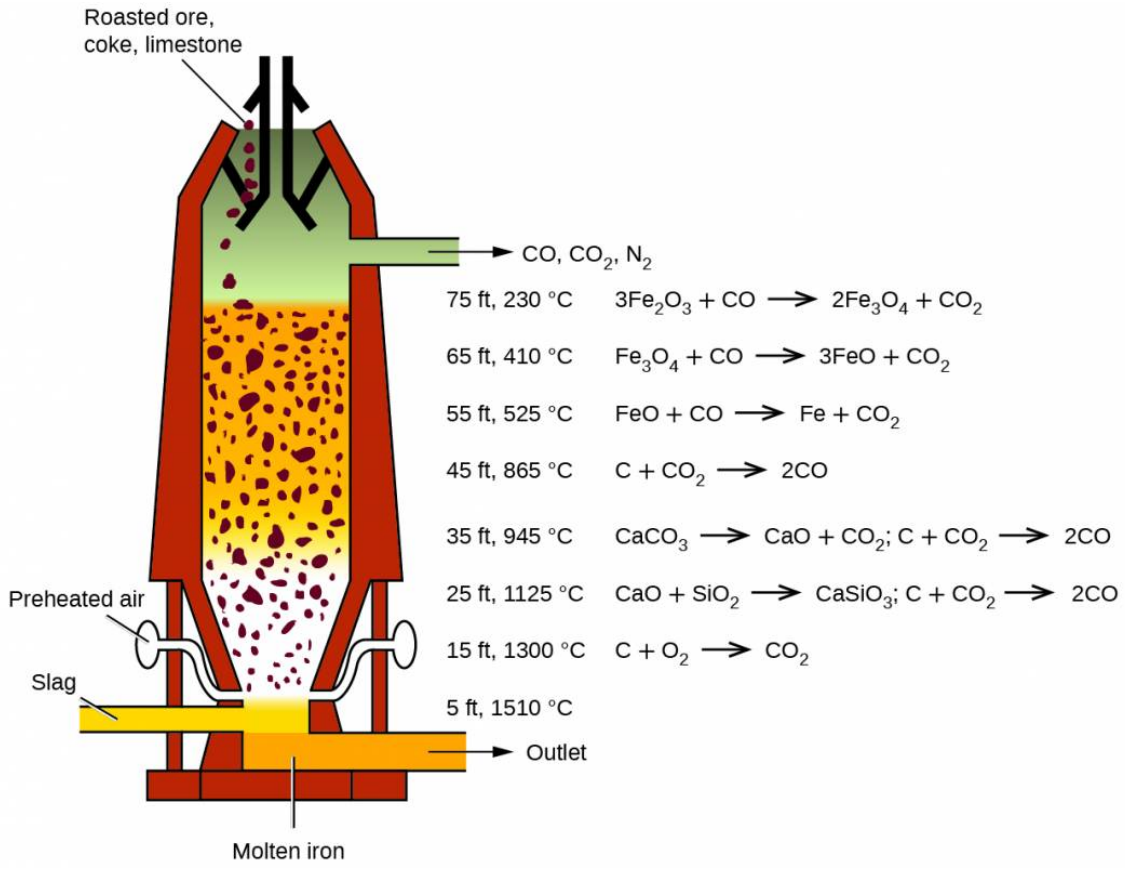
32.1.6 Isolation of Iron

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 32.5) 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 32.5

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:

$$\mathrm{CO_2}\,(g) + \mathrm{C}(s) \longrightarrow 2\mathrm{CO}(g)$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 32.5.

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:

$$\mathrm{CaO}(s) + \mathrm{SiO_2}\,(s) \longrightarrow \mathrm{CaSiO_3}\,(l)$$

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 32.6).

Figure 32.6

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.

LINK TO LEARNING

You can watch an animation of steelmaking that walks you through the process.

32.1.7 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:

$$\mathrm{CaCO_3}\,(s) + \mathrm{SiO_2}\,(s) \longrightarrow \mathrm{CaSiO_3}\,(l) + \mathrm{CO_2}\,(g)$$

$$\mathrm{FeO}(s) + \mathrm{SiO_2}\,(s) \longrightarrow \mathrm{FeSiO_3}\,(l)$$

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:

$$2\mathrm{Cu_2\,S}(l) + 3\mathrm{O_2}\,(g) \longrightarrow 2\mathrm{Cu_2\,O}(l) + 2\mathrm{SO_2}\,(g)$$

$$2\mathrm{Cu_2\,O}(l) + \mathrm{Cu_2\,S}(l) \longrightarrow 6\mathrm{Cu}(l) + \mathrm{SO_2}\,(g)$$

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 32.7). 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 32.7

Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: "Tortie tude"/Wikimedia Commons)

32.1.8 Isolation of Silver

Silver sometimes occurs in large nuggets (Figure 32.8) 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. 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,

$$[\mathrm{Ag(CN)_2}]^-,$$

from silver metal or silver-containing compounds such as Ag_2S and AgCl. Representative equations are:

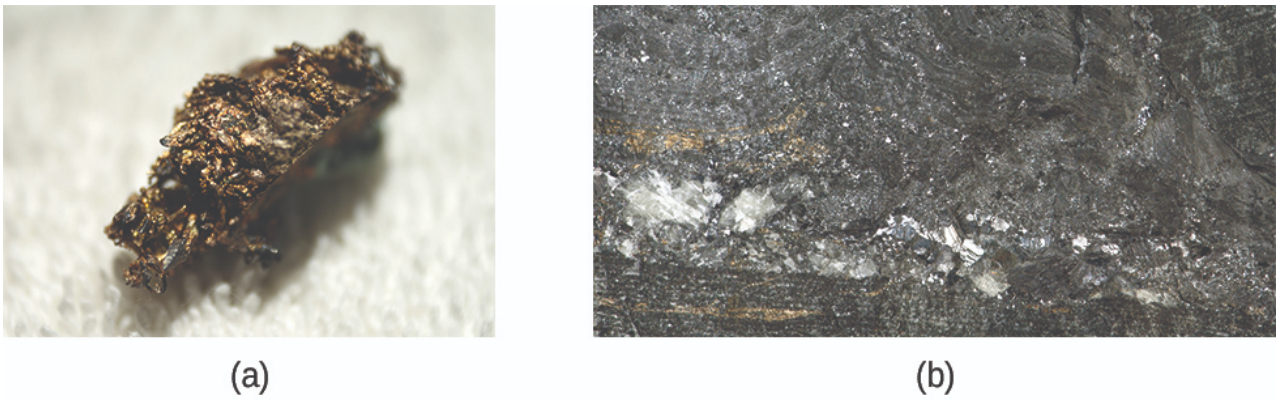
$$4\mathrm{Ag}(s) + 8\mathrm{CN}^-(aq) + \mathrm{O_2}(g) + 2\mathrm{H_2O}(l) \longrightarrow 4[\mathrm{Ag(CN)_2}]^-(aq) + 4\mathrm{OH}^-(aq)$$

$$2\mathrm{Ag_2S}(s) + 8\mathrm{CN}^-(aq) + \mathrm{O_2}(g) + 2\mathrm{H_2O}(l) \longrightarrow 4[\mathrm{Ag(CN)_2}]^-(aq) + 2\mathrm{S}(s) + 4\mathrm{OH}^-(aq)$$

$$\mathrm{AgCl}(s) + 2\mathrm{CN}^-(aq) \longrightarrow [\mathrm{Ag(CN)_2}]^-(aq) + \mathrm{Cl}^-(aq)$$

Figure 32.8

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)



(a) (b)

The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:

$$2[\mathrm{Ag(CN)_2}]^-(aq) + \mathrm{Zn}(s) \longrightarrow 2\mathrm{Ag}(s) + [\mathrm{Zn(CN)_4}]^{2-}(aq)$$

EXAMPLE 32.1.9

Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargenate(I) ions:

$$4\text{Ag}(s) + 8\text{CN}^{-}(aq) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4[\text{Ag}(\text{CN})_2]^{-}(aq) + 4\text{OH}^{-}(aq)$$

Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:

$$4\text{Ag}(s) + 8\text{CN}^{-}(aq) \longrightarrow 4[\text{Ag}(\text{CN})_2]^{-}(aq)?$$

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.

Check Your Learning

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).

32.1.10 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.

32.1.10.1 Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:

$$2\text{Fe}(s) + 3\text{Cl}_2(g) \longrightarrow 2\text{FeCl}_3(s)$$

Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:

$$\mathrm{Fe}(s) + 2\mathrm{FeCl_3}\,(s) \longrightarrow 3\mathrm{FeCl_2}\,(s)$$

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:

$$\mathrm{NiCO_3}\,(s) + 2\mathrm{HF}(aq) \longrightarrow \mathrm{NiF_2}\,(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}\,(g)$$

$$\mathrm{Co(OH)_2}\,(s) + 2\mathrm{HBr}(aq) \longrightarrow \mathrm{CoBr_2}\,(aq) + 2\mathrm{H_2O}(l)$$

Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:

$$\mathrm{Cr}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{CrCl_2}\,(aq) + \mathrm{H_2}\,(g)$$

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 ($\mathrm{TiCl_2}$ and $\mathrm{TiCl_3}$) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride ($\mathrm{TiCl_4}$) 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:

$$\mathrm{SiCl_4}\,(l) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{SiO_2}\,(s) + 4\mathrm{HCl}(aq)$$

$$\mathrm{TiCl_4}\,(l) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{TiO_2}\,(s) + 4\mathrm{HCl}(aq)$$

32.1.10.2 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:

$$\mathrm{FeC_2O_4}(s) \longrightarrow \mathrm{FeO}(s) + \mathrm{CO}(g) + \mathrm{CO_2}(g)$$

$$\mathrm{Co(OH)_2}(s) \longrightarrow \mathrm{CoO}(s) + \mathrm{H_2O}(g)$$

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:

$$\mathrm{CoO}(s) + 2\mathrm{HNO_3}(aq) \longrightarrow \mathrm{Co(NO_3)_2}(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{Sc_2O_3}(s) + 6\mathrm{HCl}(aq) \longrightarrow 2\mathrm{ScCl_3}(aq) + 3\mathrm{H_2O}(l)$$

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:

$$\mathrm{CrO_3}(s) + 2\mathrm{Na^+}(aq) + 2\mathrm{OH^-}(aq) \longrightarrow 2\mathrm{Na^+}(aq) + \mathrm{CrO_4}^{2-}(aq) + \mathrm{H_2O}(l)$$

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and $HMnO_4$, respectively.

32.1.10.3 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:

$$\mathrm{Co^{2+}}(aq) + 2\mathrm{OH^-}(aq) \longrightarrow \mathrm{Co(OH)_2}(s)$$

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:

$$4\mathrm{Fe^{3+}}(aq) + 6\mathrm{OH^-}(aq) + \mathrm{n\ H_2O}(l) \longrightarrow 2\mathrm{Fe_2O_3} \cdot (\mathrm{n} + 3)\mathrm{H_2O}(s)$$

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.

32.1.10.4 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:

$$\mathrm{Ni^{2+}}(aq) + \mathrm{CO_3^{2-}} \longrightarrow \mathrm{NiCO_3}(s)$$

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.

32.1.10.5 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:

$$2\mathrm{Sc}(s) + 6\mathrm{HBr}(aq) \longrightarrow 2\mathrm{ScBr_3}(aq) + 3\mathrm{H_2}(g)$$

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:

$$\mathrm{Ni(OH)_2}(s) + 2\mathrm{H_3O^+}(aq) + 2\mathrm{ClO_4^-}(aq) \longrightarrow \mathrm{Ni^{2+}}(aq) + 2\mathrm{ClO_4^-}(aq) + 4\mathrm{H_2O}(l)$$

Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

$$\mathrm{Ba^{2+}}(aq) + 2\mathrm{Cl^-}(aq) + 2\mathrm{K^+}(aq) + \mathrm{CrO_4^{2-}}(aq) \longrightarrow \mathrm{BaCrO_4}(s) + 2\mathrm{K^+}(aq) + 2\mathrm{Cl^-}(aq)$$

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.

32.1.11 HOW SCIENCES INTERCONNECT

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.

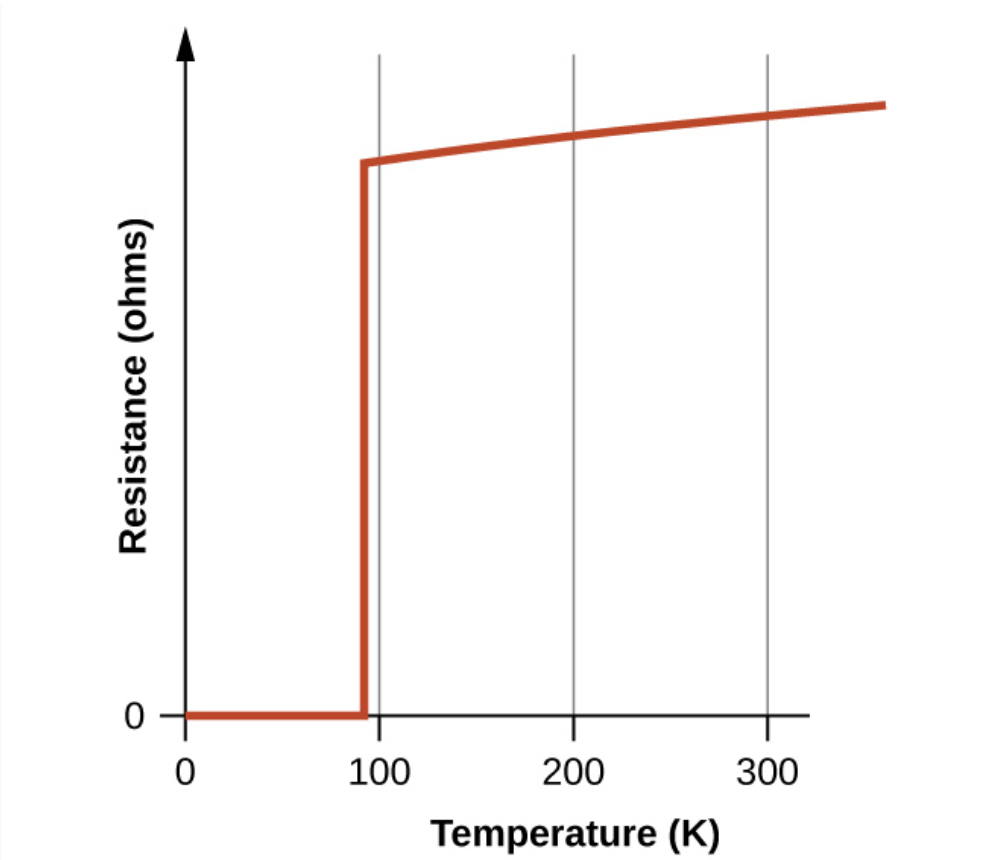
Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium 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 32.9), 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.

Further advances during the same period included materials that became superconducting at even higher temperatures and with a wider array of materials. The DuPont team led by Uma Chowdry and Arthur Sleight identified Bismouth-Strontium-Copper-Oxides that became superconducting at temperatures as high as 110 K and, importantly, did not contain rare earth elements. Advances continued through the subsequent decades until, in 2020, a team led by Ranga Dias at University of Rochester announced the development of a room-temperature superconductor, opening doors to widespread applications. More research and development is needed to realize the potential of these materials, but the possibilities are very promising.

Figure 32.9
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.

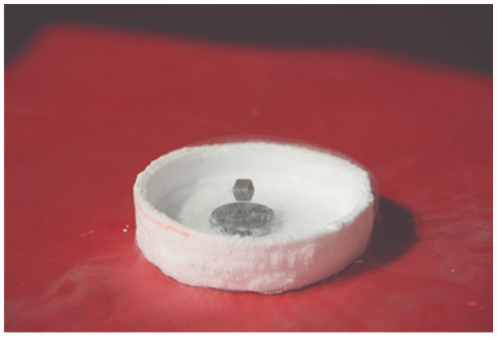


Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss 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.

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 32.10).

Figure 32.10
(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)

(a)



(b)

LINK TO LEARNING

Watch how a high-temperature superconductor levitates around a magnetic racetrack in the video.

32.2 Coordination Chemistry of Transition Metals

Learning Objectives

By the end of this section, you will be able to:

- List the defining traits of coordination compounds
- Describe the structures of complexes containing monodentate and polydentate ligands
- Use standard nomenclature rules to name coordination compounds

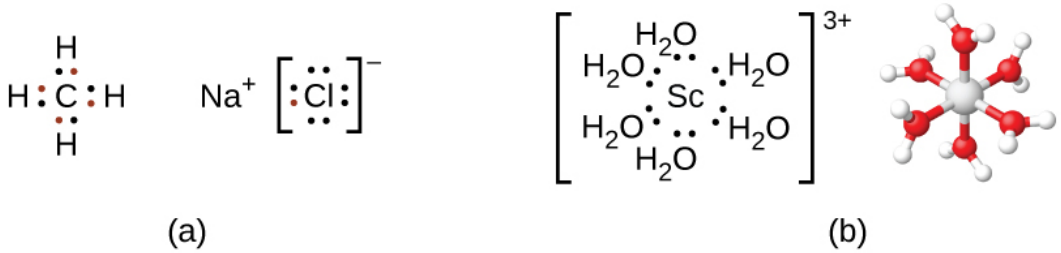
The hemoglobin in your blood, the chlorophyll in green plants, vitamin B-12, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure 32.11). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

Figure 32.11
Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with M = $Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure 32.12). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a central metal ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form coordination compounds. The Lewis base donors, called ligands, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a donor atom with a lone pair of electrons that can form a coordinate bond to the metal.

Figure 32.12

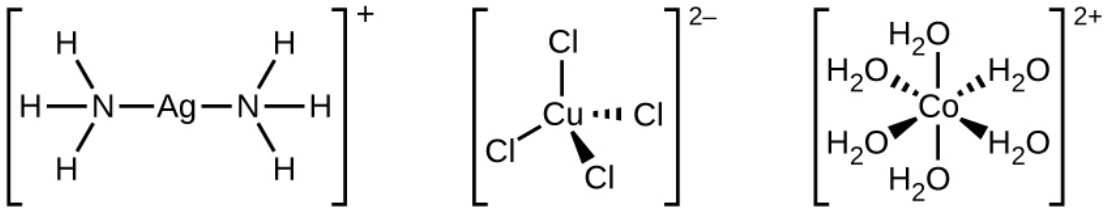
(a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)



The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure 32.13). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for "one toothed," meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

Figure 32.13

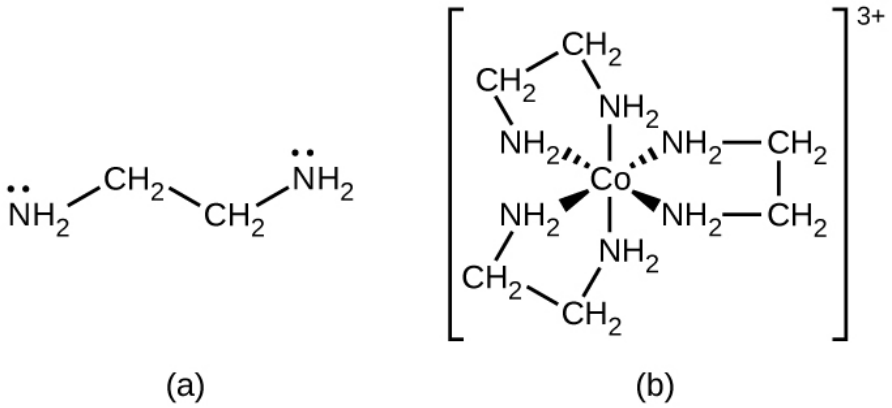
The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.



Many other ligands coordinate to the metal in more complex fashions. Bidentate ligands are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 32.14). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

Figure 32.14

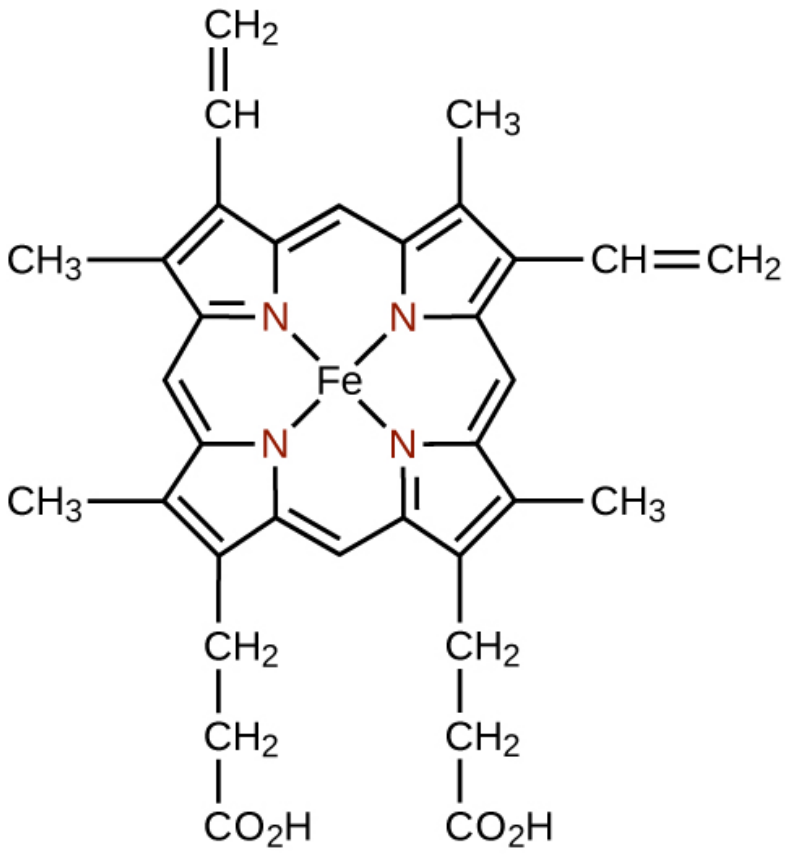
(a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex $[Co(en)_3]^{3+}$ contains three of these ligands, each forming two bonds to the cobalt ion.



Any ligand that bonds to a central metal ion by more than one donor atom is a polydentate ligand (or "many teeth") because it can bite into the metal center with more than one bond. The term chelate (pronounced "KEY-late") from the Greek for "claw" is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab's claw would hold a marble. Figure 32.14 showed one example of a chelate. The heme complex in hemoglobin is another important example (Figure 32.15). It contains a polydentate ligand with four donor atoms that coordinate to iron.

Figure 32.15

The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.



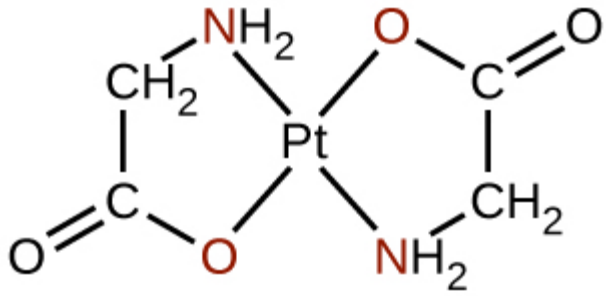
Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $H_2NCH_2CH_2NH_2$, and the anion of the acid glycine,

$$NH_2\,CH_2\,CO_2^-$$

(Figure 32.16) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The ligand in heme (Figure 32.15) is a tetradentate ligand.

Figure 32.16

Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.



32.2.1 The Naming of Complexes

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds. The following five rules are used for naming complexes:

1. If a coordination compound is ionic, name the cation first and the anion second, in accordance with the usual nomenclature.
2. Name the ligands first, followed by the central metal. Name the ligands alphabetically. Negative ligands (anions) have names formed by adding *-o* to the stem name of the group. For examples, see Table 32.1. For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *ammine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO). For example, name $[Pt(NH_3)_2Cl_4]$ as diamminetetrachloroplatinum(IV).
   Table 32.17

   Examples of Anionic Ligands

Anionic Ligand	Name
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
NO_3^-	nitrato
OH^-	hydroxo
O^{2-}	oxo
$C_2O_4^{2-}$	oxalato
CO_3^{2-}	carbonato

3. If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes, the prefixes *bis-* (for two), *tris-* (for three), and *tetrakis-* (for four) are used when the name of the ligand already includes *di-*, *tri-*, or *tetra-*, or when the ligand name begins with a vowel. For example, the ion bis(bipyridyl)osmium(II) uses bis- to signify that there are two ligands attached to Os, and each bipyridyl ligand contains two pyridine groups (C_5H_4N).

When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly like the name of the element and is followed by a Roman numeral in parentheses to indicate its oxidation state (Table 32.2 and Table 32.3). When the complex is an anion, the suffix -ate is added to the stem of the name of the metal, followed by the Roman numeral designation of its oxidation state (Table 32.4). Sometimes, the Latin name of the metal is used when the English name is clumsy. For example, *ferrate* is used instead of *ironate*, *plumbate* instead *leadate*, and *stannate* instead of *tinate*. The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[Cr(H_2O)_4Cl_2]Br$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: +1 = −2 + *x*, so the oxidation state (*x*) is equal to 3+.

Table 32.18

Examples in Which the Complex Is a Cation

$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) chloride
$[Pt(NH_3)_4Cl_2]^{2+}$	tetraamminedichloroplatinum(IV) ion
$[Ag(NH_3)_2]^+$	diamminesilver(I) ion
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichlorochromium(III) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate

Table 32.19

Examples in Which the Complex Is Neutral

$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
$[Ni(H_2NCH_2CH_2NH_2)_2Cl_2]$	dichlorobis(ethylenediamine)nickel(II)

Table 32.20

Examples in Which the Complex Is an Anion

$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion
$Na_2[SnCl_6]$	sodium hexachlorostannate(IV)

LINK TO LEARNING

Do you think you understand naming coordination complexes? You can look over more examples and test yourself with online quizzes at the University of Sydney's site.

EXAMPLE 32.2.2

Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.
(a) $Na_2[PtCl_6]$

(b) $K_3[Fe(C_2O_4)_3]$

(c) $[Co(NH_3)_5Cl]Cl_2$

Solution

(a) There are two Na^+ ions, so the coordination sphere has a negative two charge: $[PtCl_6]^{2-}$. There are six anionic chloride ligands, so $-2 = -6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six. (b) The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $-3 = -6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six. (c) In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = -1 + x$ and is 3+, so the complex is pentaamminechlorocobalt(III) chloride and the coordination number is six.

Check Your Learning

The complex potassium dicyanoargenate(I) is used to make antiseptic compounds. Give the formula and coordination number.

Answer

$K[Ag(CN)_2]$; coordination number two

Files

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33

Crystal Field Theory

Crystal field theory treats interactions between the electrons on the metal and the ligands as a simple electrostatic effect. The presence of the ligands near the metal ion changes the energies of the metal d orbitals relative to their energies in the free ion. Both the color and the magnetic properties of a complex can be attributed to this crystal field splitting. The magnitude of the splitting (Δoct) depends on the nature of the ligands bonded to the metal. Strong-field ligands produce large splitting and favor low-spin complexes, in which the t2g orbitals are completely filled before any electrons occupy the eg orbitals. Weak-field ligands favor formation of high-spin complexes. The t2g and the eg orbitals are singly occupied before any are doubly occupied.

33.1 The Structures of Complexes

Learning Objectives

By the end of this section, you will be able to:

- Predict geometries of coordination compounds using coordination number and electron configuration

For transition metal complexes, the coordination number determines the geometry around the central metal ion. The most common structures of the complexes in coordination compounds are square planar, tetrahedral, and octahedral, corresponding to coordination numbers of four, four, and six, respectively. Coordination numbers greater than six are less common and yield a variety of structures (see Figure 33.1 and Table 33.1):

Figure 33.1

These are geometries of some complexes with coordination numbers of seven and eight.

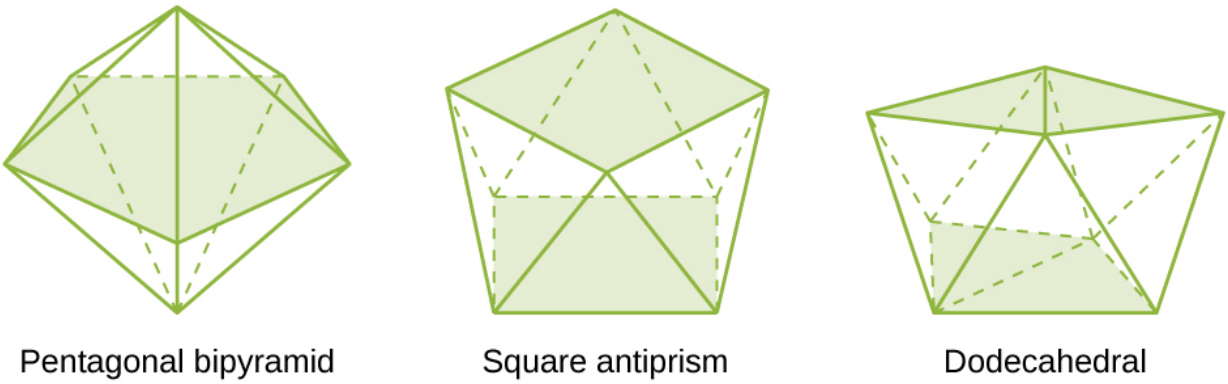


Table 33.2

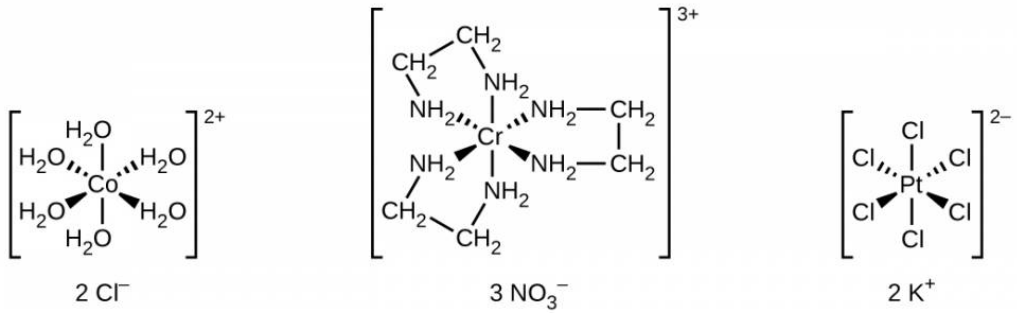
Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Ni(CO)_4]$
4	square planar (d^8)	$[Ni(CN)_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding *d*-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in Figure 33.2. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.

Figure 33.3

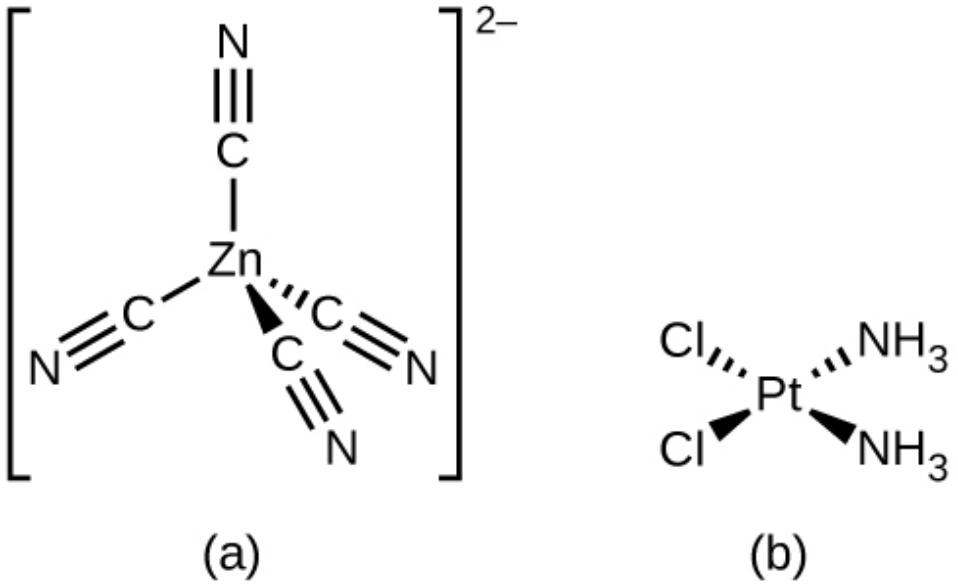
Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.



For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (Figure 33.2), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.

Figure 33.4

Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$.



33.2 Spectroscopic and Magnetic Properties of Coordination Compounds

Learning Objectives

By the end of this section, you will be able to:

- Outline the basic premise of crystal field theory (CFT)
- Identify molecular geometries associated with various d-orbital splitting patterns
- Predict electron configurations of split d orbitals for selected transition metal atoms or ions
- Explain spectral and magnetic properties in terms of CFT concepts

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the *d* orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three *p* orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

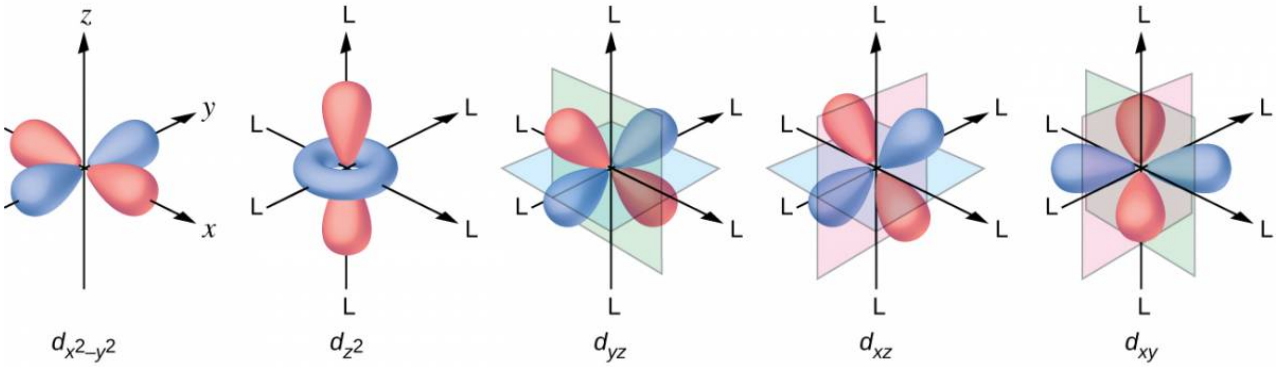
33.2.1 Crystal Field Theory

To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized *d* orbitals of the central metal atom has been developed. This electrostatic model is crystal field theory (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized *d* orbitals in an octahedral complex. The five *d* orbitals consist of lobe-shaped regions and are arranged in space, as shown in Figure 33.4. In an octahedral complex, the six ligands coordinate along the axes.

Figure 33.5
The directional characteristics of the five d orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the $d_{x^2-y^2}$ *orbital so that the axis labels could be shown.*



In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five *d* orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the *d* orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five *d* orbitals, the

d_{z^2}

and

$d_{x^2-y^2}$

orbitals, point toward the ligands (Figure 33.4). These two orbitals are called the e_g orbitals (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the d_{xy}, d_{xz}, and d_{yz} orbitals, have lobes that point between the ligands and are called the t_{2g} orbitals (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the *d* orbitals of the metal ion. However, the repulsions between the electrons in the e_g orbitals (the

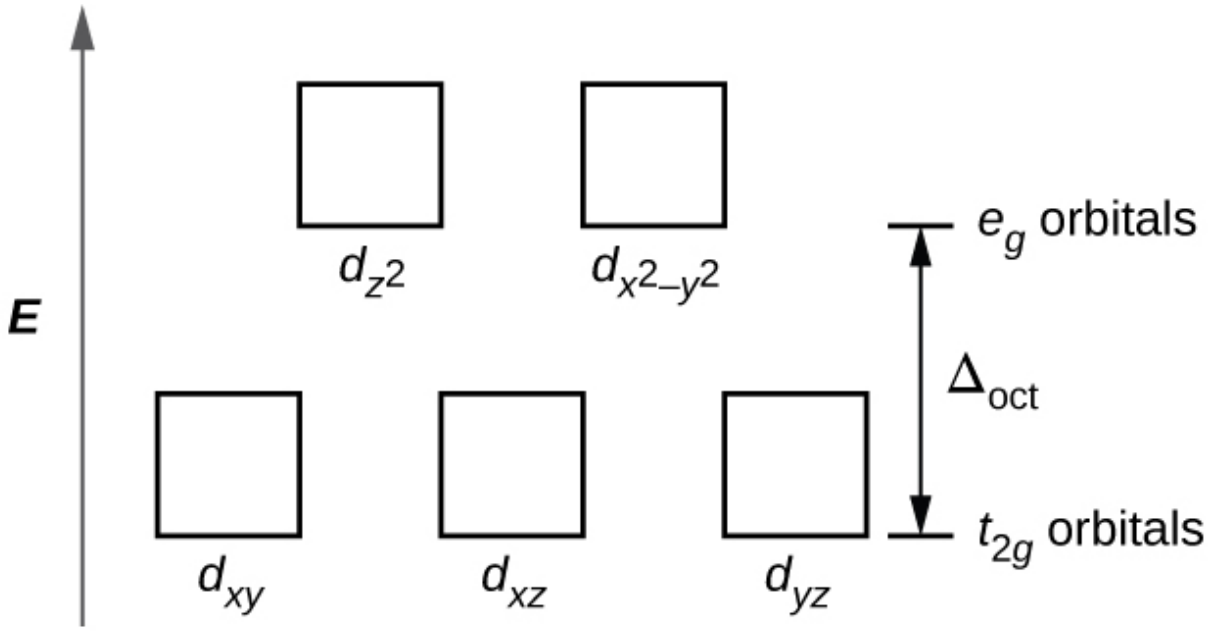
d_{z^2}

and

$d_{x^2-y^2}$

orbitals) and the ligands are greater than the repulsions between the electrons in the t_{2g} orbitals (the d_{zy}, d_{xz}, and d_{yz} orbitals) and the ligands. This is because the lobes of the e_g orbitals point directly at the ligands, whereas the lobes of the t_{2g} orbitals point between them. Thus, electrons in the e_g orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the t_{2g} orbitals. The difference in energy may be represented as shown in Figure 33.5.

Figure 33.6
In octahedral complexes, the e_g orbitals are destabilized (higher in energy) compared to the t_{2g} orbitals because the ligands interact more strongly with the d orbitals at which they are pointed directly.



The difference in energy between the e_g and the t_{2g} orbitals is called the crystal field splitting and is symbolized by Δ_{oct}, where oct stands for octahedral.

The magnitude of Δ_{oct} depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using 3*d*, 4*d*, or 5*d* orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the spectrochemical series, a short version of which is given here:

$$I^- < Br^- < Cl^- < F^- < H_2O < C_2O_4^{2-} < NH_3 < en < NO_2^- < CN^-$$

a few ligands of the spectrochemical series, in order of increasing field strength of the ligand

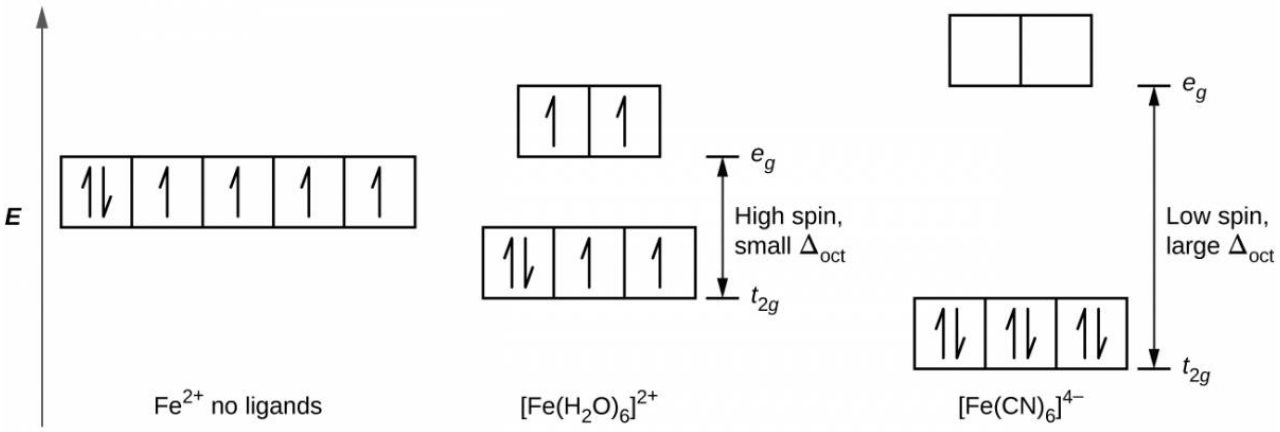
In this series, ligands on the left cause small crystal field splittings and are weak-field ligands, whereas those on the right cause larger splittings and are strong-field ligands. Thus, the Δ_{oct} value for an octahedral complex with iodide ligands (I^-) is much smaller than the Δ_{oct} value for the same metal with cyanide ligands (CN^-).

Electrons in the *d* orbitals follow the aufbau ("filling up") principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the pairing energy (P). Electrons will always singly occupy each orbital in a degenerate set before pairing. P is similar in magnitude to Δ_{oct}. When electrons fill the *d* orbitals, the relative magnitudes of Δ_{oct} and P determine which orbitals will be occupied.

In $[Fe(CN)_6]^{4-}$, the strong field of six cyanide ligands produces a large Δ_{oct}. Under these conditions, the electrons require less energy to pair than they require to be excited to the e_g orbitals ($\Delta_{oct} > P$). The six 3*d* electrons of the Fe^{2+} ion pair in the three t_{2g} orbitals (Figure 33.6). Complexes in which the electrons are paired because of the large crystal field splitting are called low-spin complexes because the number of unpaired electrons (spins) is minimized.

Figure 33.7

Iron(II) complexes have six electrons in the 5d orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as $[Fe(CN)_6]^{4-}$, Δ_{oct} is greater than P, and the electrons pair in the lower energy t_{2g} orbitals before occupying the eg orbitals. With weak-field ligands such as H_2O, the ligand field splitting is less than the pairing energy, Δ_{oct} less than P, so the electrons occupy all d orbitals singly before any pairing occurs.



In $[Fe(H_2O)_6]^{2+}$, on the other hand, the weak field of the water molecules produces only a small crystal field splitting ($\Delta_{oct} < P$). Because it requires less energy for the electrons to occupy the e_g orbitals than to pair together, there will be an electron in each of the five 3*d* orbitals before pairing occurs. For the six *d* electrons on the iron(II) center in $[Fe(H_2O)_6]^{2+}$, there will be one pair of electrons and four unpaired electrons (Figure 33.6). Complexes such as the $[Fe(H_2O)_6]^{2+}$ ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called high-spin complexes because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the $[Fe(CN)_6]^{3-}$ ion is a low-spin complex with only one unpaired electron, whereas both the $[Fe(H_2O)_6]^{3+}$ and $[FeF_6]^{3-}$ ions are high-spin complexes with five unpaired electrons.

EXAMPLE 33.2.2

High- and Low-Spin Complexes

Predict the number of unpaired electrons.
(a) $K_3[CrI_6]$

(b) $[Cu(en)_2(H_2O)_2]Cl_2$

(c) $Na_3[Co(NO_2)_6]$

Solution

The complexes are octahedral.
(a) Cr^{3+} has a d^3 configuration. These electrons will all be unpaired.

(b) Cu^{2+} is d^9, so there will be one unpaired electron.

(c) Co^{3+} has d^6 valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the t_{2g} orbitals, leaving 0 unpaired.

Check Your Learning

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which *d*-electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

Answer

d^4, d^5, d^6, and d^7

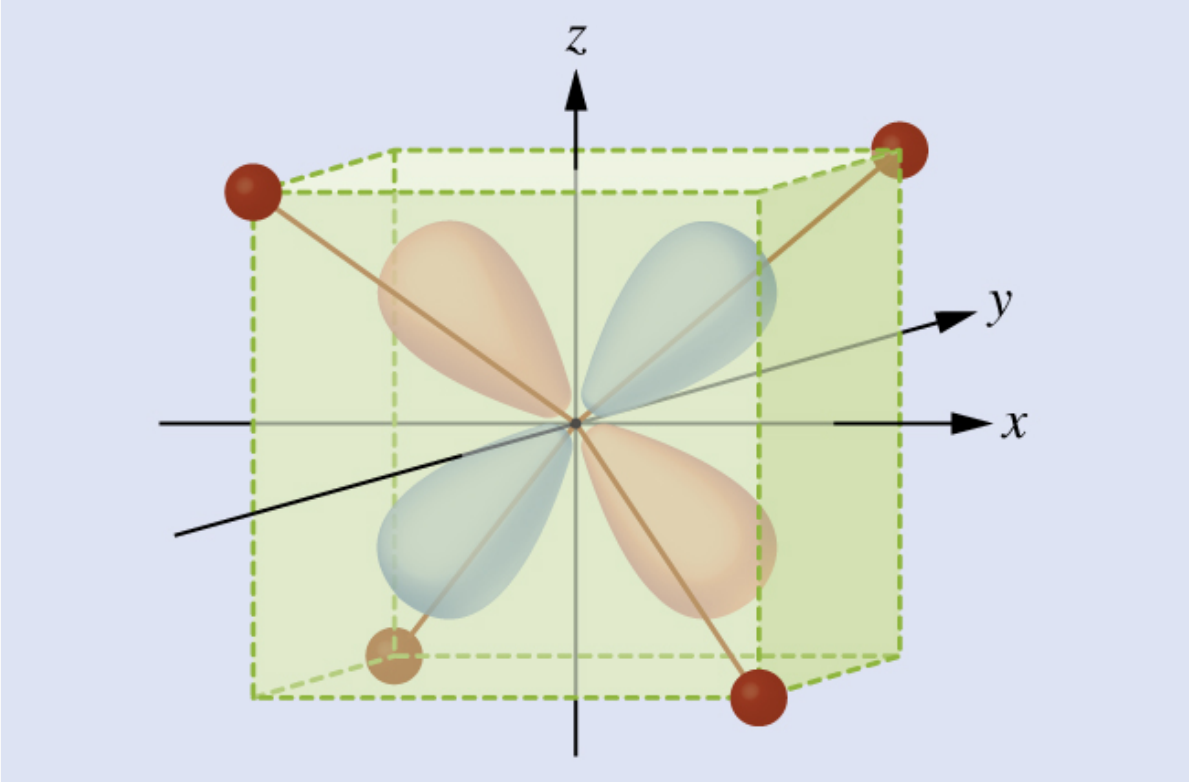
EXAMPLE 33.2.3

CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the e_g set point directly at the ligands. For tetrahedral complexes, the *d* orbitals remain in place, but now we have only four ligands located between the axes (Figure 33.7). None of the orbitals points directly at the tetrahedral ligands. However, the e_g set (along the Cartesian axes) overlaps with the ligands less than does the t_{2g} set. By analogy with the octahedral case, predict the energy diagram for the *d* orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral e_g set becomes a tetrahedral *e* set, and the octahedral t_{2g} set becomes a t_2 set.

Figure 33.8

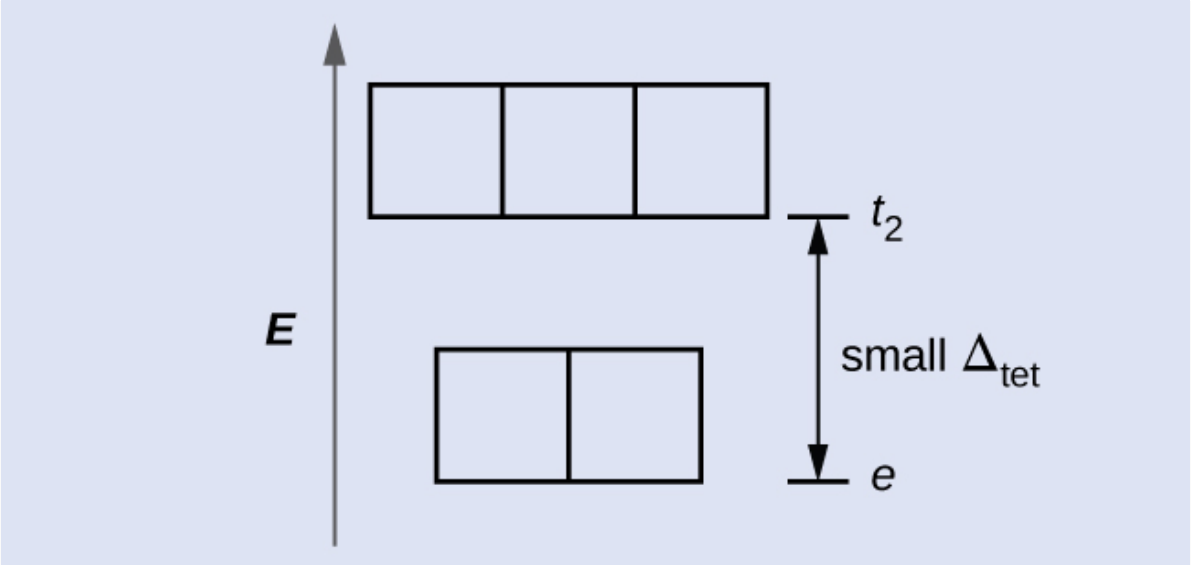
This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.



Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so Δ_{tet} is usually small

$(\Delta_{tet} = \frac{4}{9}\Delta_{oct})$:



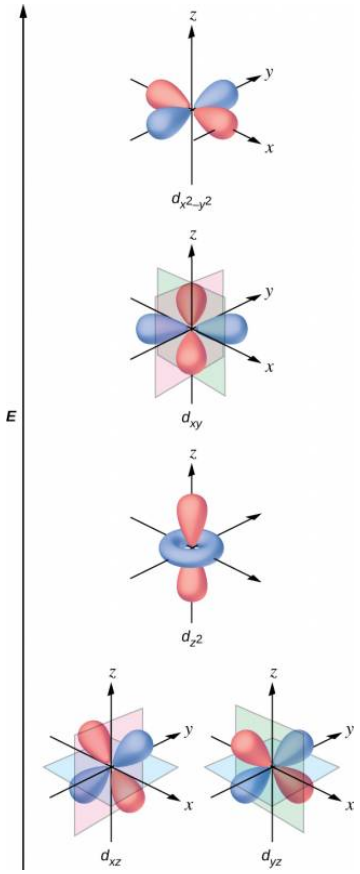
Check Your Learning

Explain how many unpaired electrons a tetrahedral d^4 ion will have.

Answer

4; because Δ_{tet} is small, all tetrahedral complexes are high spin and the electrons go into the t_2 orbitals before pairing

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the *z*-axis. This changes the distribution of the *d* orbitals, as orbitals on or near the *z*-axis become more stable, and those on or near the *x*- or *y*-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated pattern, as depicted below:



33.2.4 Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

33.2.5 Colors of Transition Metal Complexes

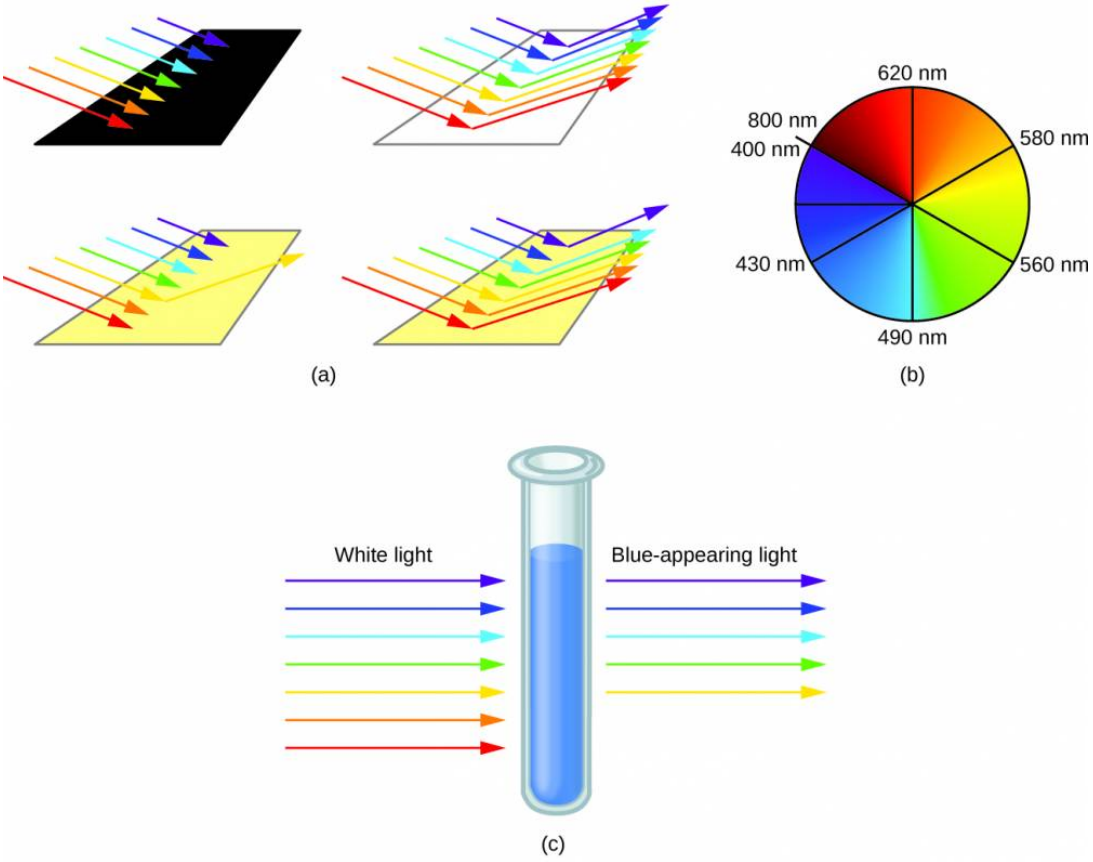
When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue

color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 33.8).

Figure 33.9

(a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.



EXAMPLE 33.2.6

Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{oct} and occurs at 499 nm. Calculate the value of Δ_{oct} in Joules and predict what color the solution will appear.

Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

$$\upsilon = \frac{c}{\lambda} \text{ so } \frac{3.00 \times 10^8 \text{ m/s}}{\frac{499 \text{ nm} \times 1 \text{ m}}{10^9 \text{ nm}}} = 6.01 \times 10^{14} \text{ Hz}$$

$$E = h\nu \text{ so } 6.63 \times 10^{-34} \text{ J·s} \times 6.01 \times 10^{14} \text{ Hz} = 3.99 \times 10^{-19} \text{ Joules/ion}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Check Your Learning

A complex that appears green, absorbs photons of what wavelengths?

Answer

red, 620–800 nm

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 33.9, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.

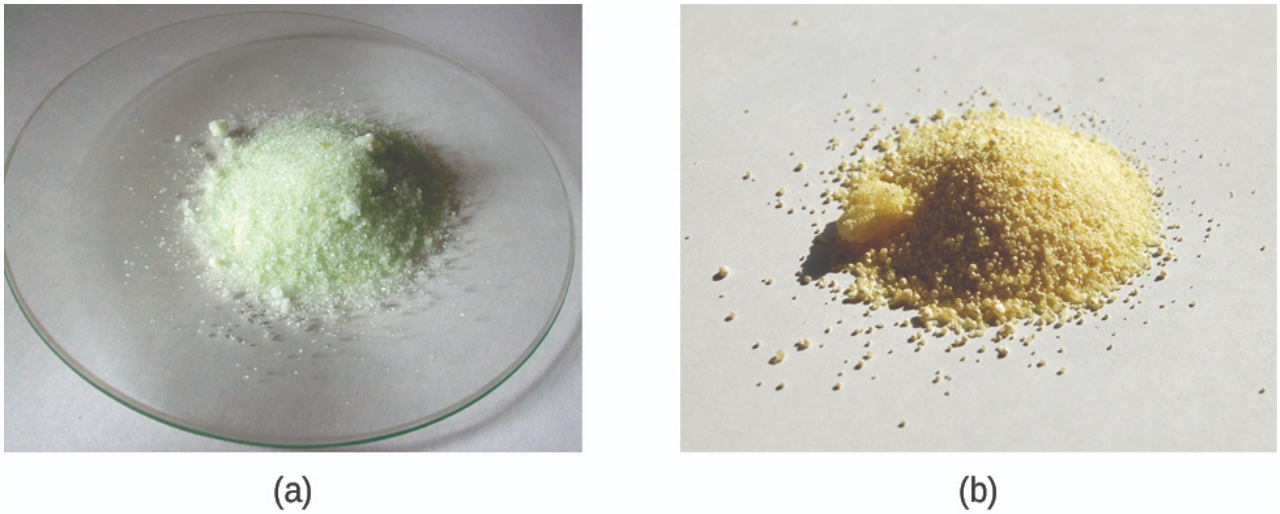
Figure 33.10

The partially filled d orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 33.10). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.

Figure 33.11

Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.



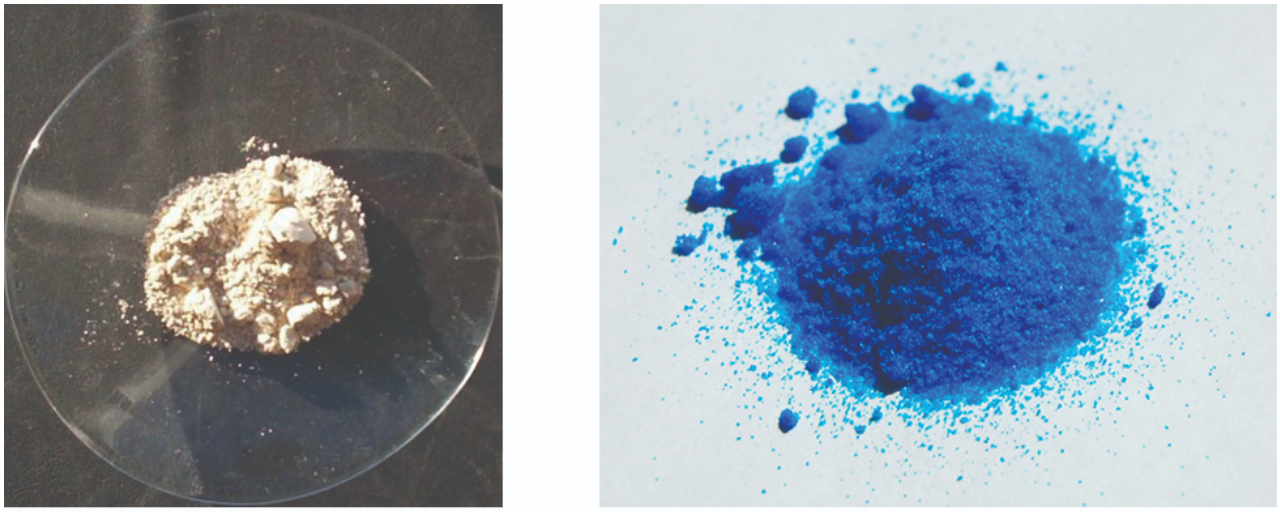
LINK TO LEARNING

Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 33.11). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

Figure 33.12
(a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored.



(a) (b)

Files

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34

Isomerism, Equilibria and Biological Systems

Cis and trans configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

34.1 Isomerism in Complexes

Learning Objectives

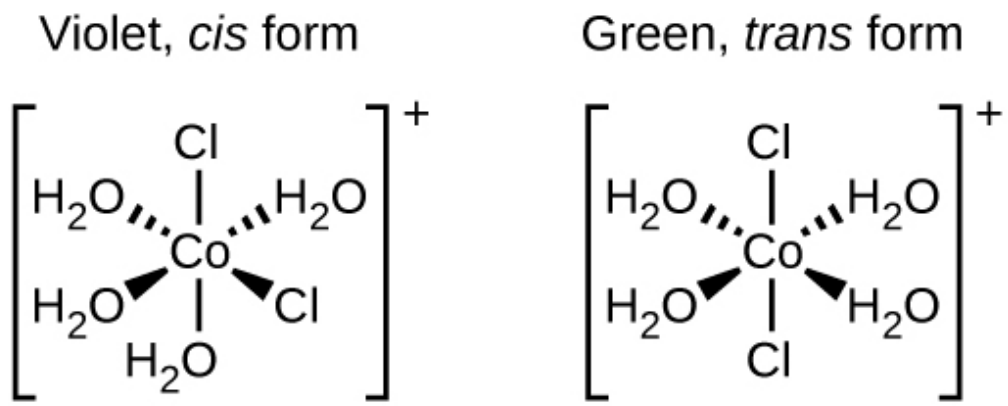
By the end of this section, you will be able to:

- Explain and provide examples of geometric and optical isomerism
- Identify several natural and technological occurrences of coordination compounds

Isomers are different chemical species that have the same chemical formula. Transition metal complexes often exist as **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral $[Co(NH_3)_4Cl_2]^+$ ion has two isomers. In the *cis* configuration, the two chloride ligands are adjacent to each other (Figure 34.1). The other isomer, the *trans* configuration, has the two chloride ligands directly across from one another.

Figure 34.1

The cis and trans isomers of $[Co(H_2O)_4Cl_2]^+$ contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.



Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[Co(NH_3)_4Cl_2]NO_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two $[Co(NH_3)_4Cl_2]NO_3$ isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

EXAMPLE 34.1.1

Geometric Isomers

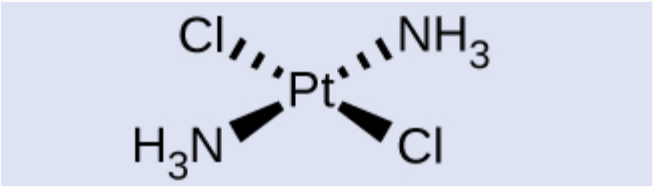
Identify which geometric isomer of $[Pt(NH_3)_2Cl_2]$ is shown in Figure 34.3. Draw the other geometric isomer and give its full name.

Solution

In the Figure 34.3, the two chlorine ligands occupy *cis* positions. The other form is shown in Figure 34.2. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diamminedichloroplatinum(II).

Figure 34.2

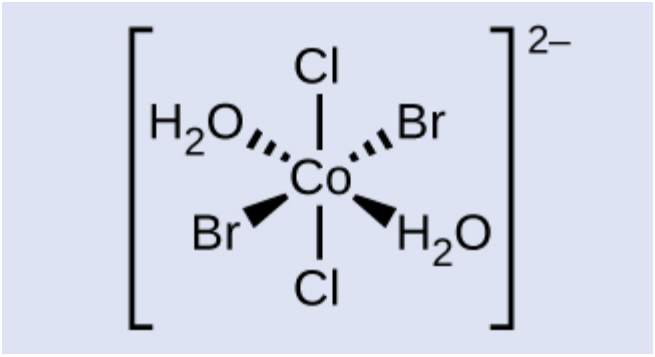
The trans isomer of $[Pt(NH_3)_2Cl_2]$ has each ligand directly across from an adjacent ligand.



Check Your Learning

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

Answer

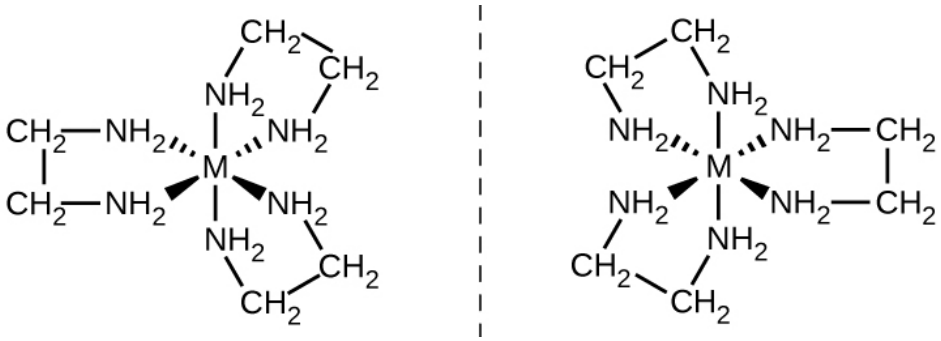


Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in Figure 34.3. These two isomers will react differently with other optical isomers. For example, DNA helices are

optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

Figure 34.3

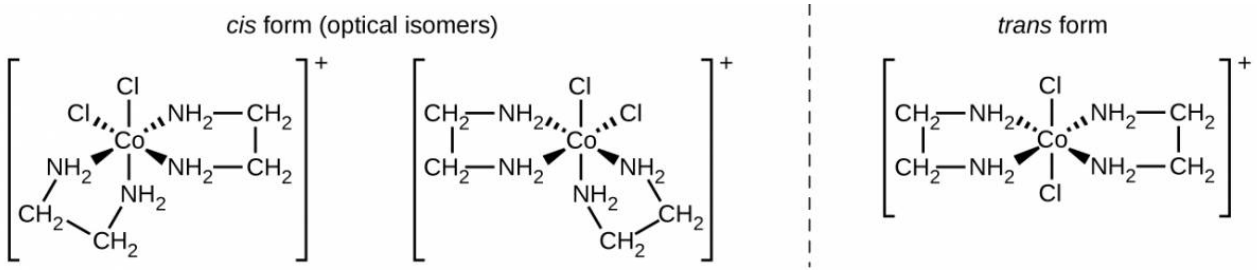
The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.



The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis*/*trans*), and its *cis* isomer exists as a pair of optical isomers (Figure 34.4).

Figure 34.4

Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The trans isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the cis isomers. The mirror images of the cis isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.



Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly, SCN^- can be bound through the sulfur or nitrogen atom, affording two distinct compounds ($[Co(NH_3)_5SCN]^{2+}$ or $[Co(NH_3)_5NCS]^{2+}$).

Ionization isomers (or coordination isomers) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are $[CoCl_6][Br]$ and $[CoCl_5Br][Cl]$.

34.1.2 Isomers of Coordination Compounds

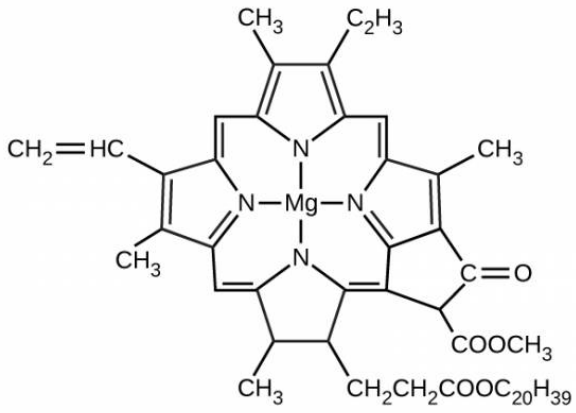
Watch on YouTube

34.1.3 Coordination Complexes in Nature and Technology

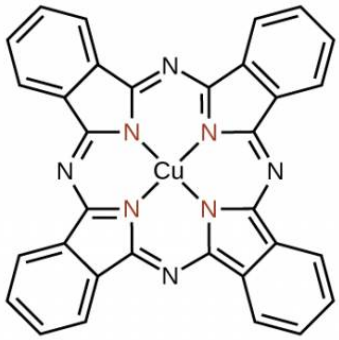
Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 34.5). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

Figure 34.5

(a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.



(a)



(b)

34.1.4 CHEMISTRY IN EVERYDAY LIFE

Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see Figure 34.6). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

Figure 34.6

(a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)

(a)

(b)

(c)

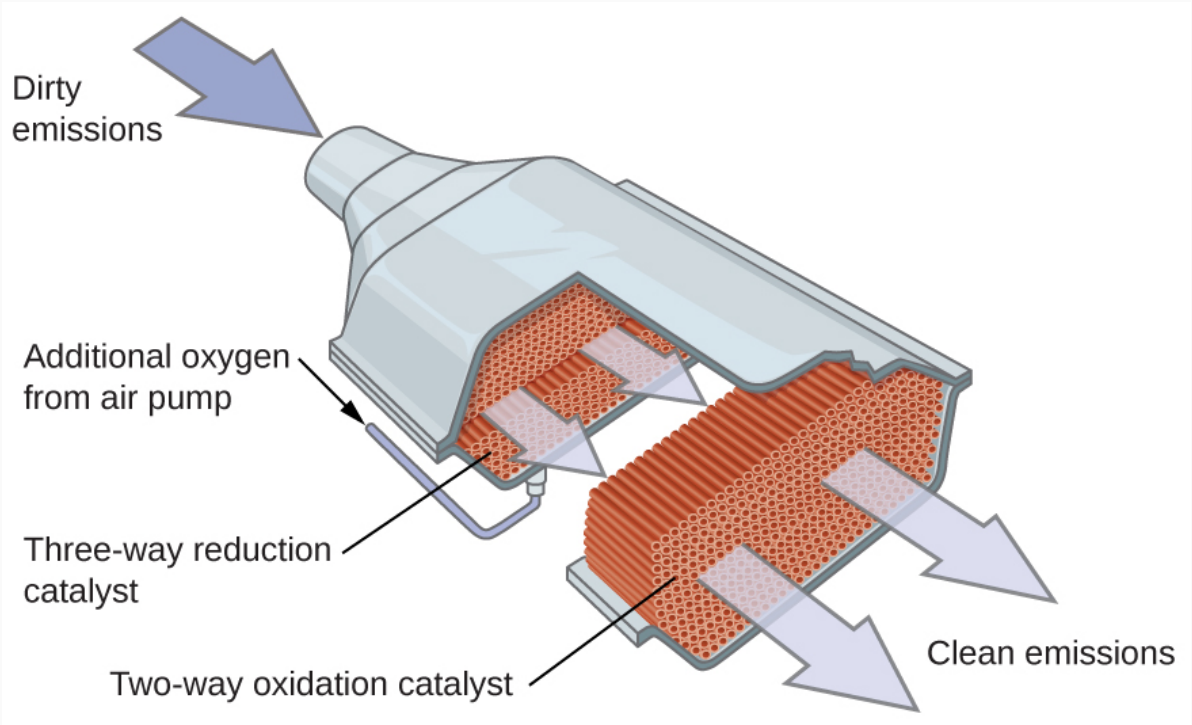
34.1.5 PORTRAIT OF A CHEMIST

Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see Figure 34.7).

Figure 34.7

Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.



Another project involves the development of porous, sponge-like materials that are "photoactive." The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this video to learn more about this research and listen to Dr. D'Alessandro (shown in Figure 34.8) describe what it is like being a research chemist.

Figure 34.8

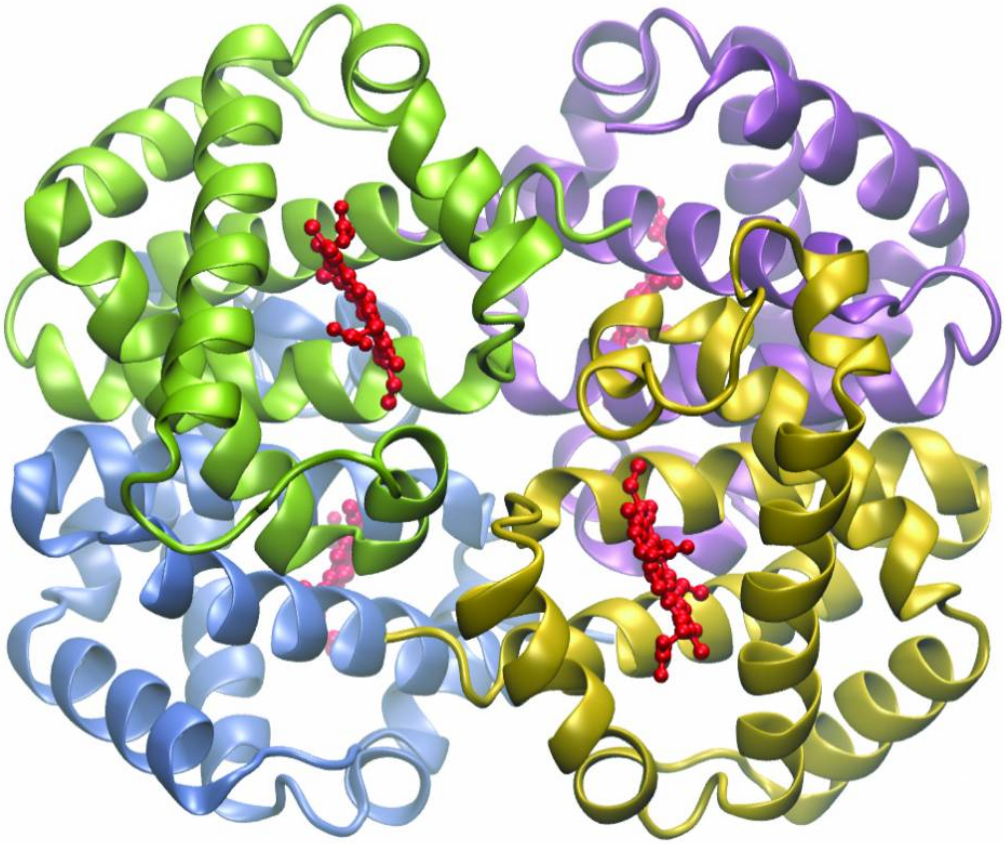
Dr. Deanna D'Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 34.5) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (Figure 34.9), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.

Figure 34.9

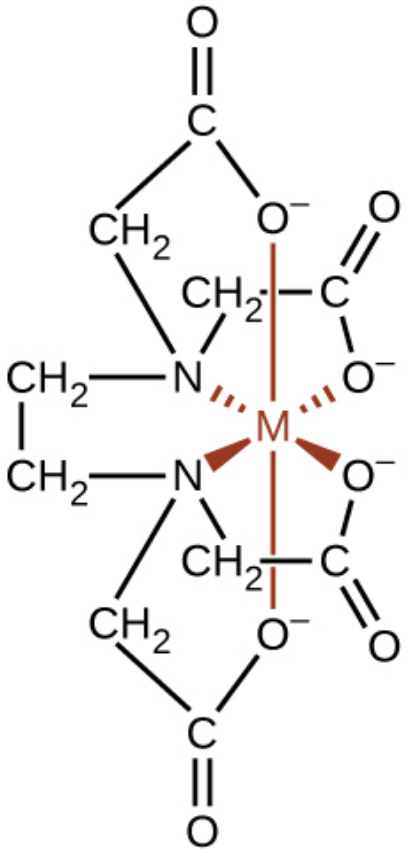
Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.



Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (Figure 34.10). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

Figure 34.10

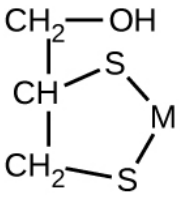
The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.



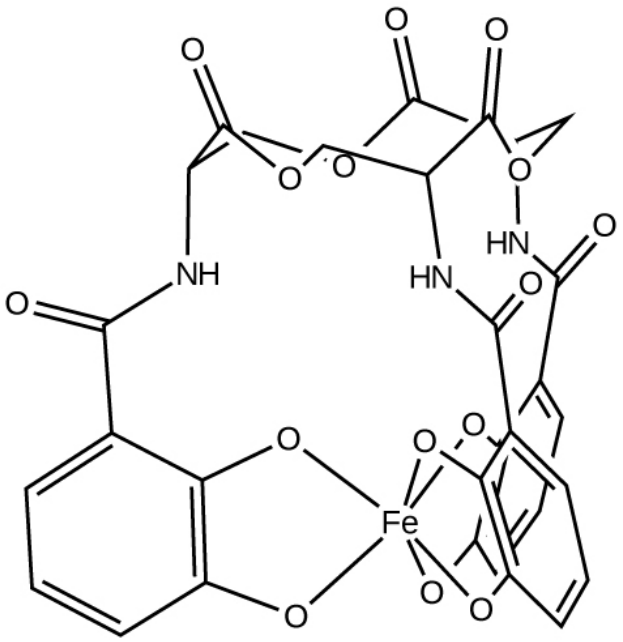
Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (Figure 34.11). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

Figure 34.11

Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.



(a)



(b)

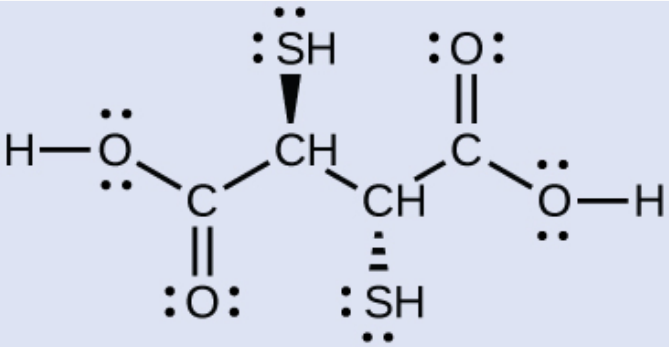
EXAMPLE 34.1.6

Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in Figure 34.12. Identify which atoms in this molecule could act as donor atoms.

Figure 34.12

Dimercaptosuccinic acid is used to treat heavy metal poisoning.



Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

Check Your Learning

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.[1] Identify at least two biologically important metals that could be disrupted by chelation therapy.

Answer

Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$,

and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Footnotes

- 1National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

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Unit 7

Electrochemistry and Solids

Redox, Electrochemical Cells
Cell Potentials
Nernst Equation
Batteries and Fuel Cells
Metals, Alloys and Semiconductors
Covalent Network Solids, Salts, Polymers

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35

Redox, Electrochemical Cells

Redox reactions are defined by changes in reactant oxidation numbers, and those most relevant to electrochemistry involve actual transfer of electrons. Aqueous phase redox processes often involve water or its characteristic ions, H+ and OH−, as reactants in addition to the oxidant and reductant, and equations representing these reactions can be challenging to balance. The half-reaction method is a systematic approach to balancing such equations that involves separate treatment of the oxidation and reduction half-reactions. Galvanic cells are devices in which a spontaneous redox reaction occurs indirectly, with the oxidant and reductant redox couples contained in separate half-cells. Electrons are transferred from the reductant (in the anode half-cell) to the oxidant (in the cathode half-cell) through an external circuit, and inert solution phase ions are transferred between half-cells, through a salt bridge, to maintain charge neutrality.

35.1 Review of Redox Chemistry

Learning Objectives

By the end of this section, you will be able to:

- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reactio stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

35.1.1 Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of th elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equa to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sur of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na^+ cations and Cl^- anions, and so oxidation numbers for sodium and chlorine are, +1 and −1, respectively. Calcium fluoride, CaF_2, is comprised of Ca^{2+} cations and F^- anions, and so oxidation numbers for calcium and fluorine are, +2 and −1, respectively.

Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O–H bonds. The shared electrons comprising an O–H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O–H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2-} anions and H^+ cations. And so, the oxidations numbers for oxygen and hydrogen in water are −2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl_4, yields oxidation numbers of +4 for carbon and −1 for chlorine. In the nitrate ion,

$$NO_3^-$$

, the oxidation number for nitrogen is +5 and that for oxygen is −2, summing to equal the 1− charge on the molecule:

$$(1\text{N atom})(\frac{+5}{\text{N atom}}) + (3\text{ O atoms})(\frac{-2}{\text{O atom}}) = +5 + -6 = -1$$

35.1.2 Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\text{NaCl}(l) \longrightarrow \text{Na}(l) + \text{Cl}_2(g) \qquad \textit{unbalanced}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\text{NaCl}(l) \longrightarrow 2\text{Na}(l) + \text{Cl}_2(g) \qquad \textit{balanced}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful. This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ io (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

EXAMPLE 35.1.3

Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

1. *Write skeletal equations for the oxidation and reduction half-reactions.*
   oxidation: $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq)$
   reduction: $\mathrm{HNO_3}(aq) \longrightarrow \mathrm{NO}(g)$
2. *Balance each half-reaction for all elements except H and O.*
   oxidation: $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq)$
   reduction: $\mathrm{HNO_3}(aq) \longrightarrow \mathrm{NO}(g)$
3. *Balance each half-reaction for O by adding H_2O.*
   oxidation: $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq)$
   reduction: $\mathrm{HNO_3}(aq) \longrightarrow \mathrm{NO}(g) + 2\mathrm{H_2O}(l)$
4. *Balance each half-reaction for H by adding H^+.*
   oxidation: $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq)$
   reduction: $3\mathrm{H}^+(\mathrm{aq}) + \mathrm{HNO_3}(aq) \longrightarrow \mathrm{NO}(g) + 2\mathrm{H_2O}(l)$
5. *Balance each half-reaction for charge by adding electrons.*
   oxidation: $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^-$
   reduction: $3\mathrm{e}^- + 3\mathrm{H}^+(aq) + \mathrm{HNO_3}(aq) \longrightarrow \mathrm{NO}(g) + 2\mathrm{H_2O}(l)$
6. *If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.*
   oxidation (×3): $3\mathrm{Cu}(s) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + 62\mathrm{e}^-$
   reduction (×2): $63\mathrm{e}^- + 63\mathrm{H}^+(aq) + 2\mathrm{HNO_3}(aq) \longrightarrow 2\mathrm{NO}(g) + 42\mathrm{H_2O}(l)$
7. *Add the two half-reactions and simplify.*
   $3\mathrm{Cu}(s) + 6\mathrm{e}^- + 6\mathrm{H}^+(aq) + 2\mathrm{HNO_3}(aq) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + 6\mathrm{e}^- + 2\mathrm{NO}(g) + 4\mathrm{H_2O}(l)$
   $3\mathrm{Cu}(s) + 6\mathrm{H}^+(aq) + 2\mathrm{HNO_3}(aq) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + 2\mathrm{NO}(g) + 4\mathrm{H_2O}(l)$
8. *If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.*
   This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$3\mathrm{Cu}(s) + 6\mathrm{H}^+(aq) + 2\mathrm{HNO_3}(aq) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + 2\mathrm{NO}(g) + 4\mathrm{H_2O}(l)$$

Check Your Learning

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer

$$\mathrm{Cu}(s) + 2\mathrm{H}^{+}(aq) + 2\mathrm{HNO}_3(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{NO}_2(g) + 2\mathrm{H}_2\mathrm{O}(l)$$

EXAMPLE 35.1.4

Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion,

$$MnO_4^-$$

, and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion,

$$CrO_4^{2-}$$

The reaction takes place in a basic solution.

Solution

Following the steps of the half-reaction method:

1. *Write skeletal equations for the oxidation and reduction half-reactions.*

   oxidation: $Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$

   reduction: $MnO_4^-(aq) \longrightarrow MnO_2(s)$

2. *Balance each half-reaction for all elements except H and O.*

   oxidation: $Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$

   reduction: $MnO_4^-(aq) \longrightarrow MnO_2(s)$

3. *Balance each half-reaction for O by adding H_2O.*

   oxidation: $H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$

   reduction: $MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$

4. *Balance each half-reaction for H by adding H^+.*

   oxidation: $H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 5H^+(aq)$

   reduction: $4H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$

5. *Balance each half-reaction for charge by adding electrons.*

   oxidation: $H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 5H^+(aq) + 3e^-$

   reduction: $3e^- + 4H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$

6. *If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.*

   This step is not necessary since the number of electrons is already in balance.

7. *Add the two half-reactions and simplify.*

$$H_2O(l) + Cr(OH)_3(s) + 3e^- + 4H^+(aq) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + 5H^+(aq) + 3e^- + MnO_2(s) + 2H_2O(l)$$

$$Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + H^+(aq) + MnO_2(s) + H_2O(l)$$

8. *If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.*

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + H^+(aq) + OH^-(aq) + MnO_2(s)$$

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2H_2O(l)$$

Check Your Learning

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^-. Write the balanced equation for this reaction occurring in a basic medium.

Answer

$$H_2O(l) + 2MnO_4^-(aq) + Br^-(aq) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

35.2 Galvanic Cells

Learning Objectives

By the end of this section, you will be able to:

- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

As demonstration of spontaneous chemical change, Figure 35.1 shows the result of immersing a coiled wire of coppe into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initial colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gra solid.

Figure 35.1
A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue $Cu^{2+}(aq)$ and gray Ag(s) (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, $Cu^{2+}(aq)$, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:

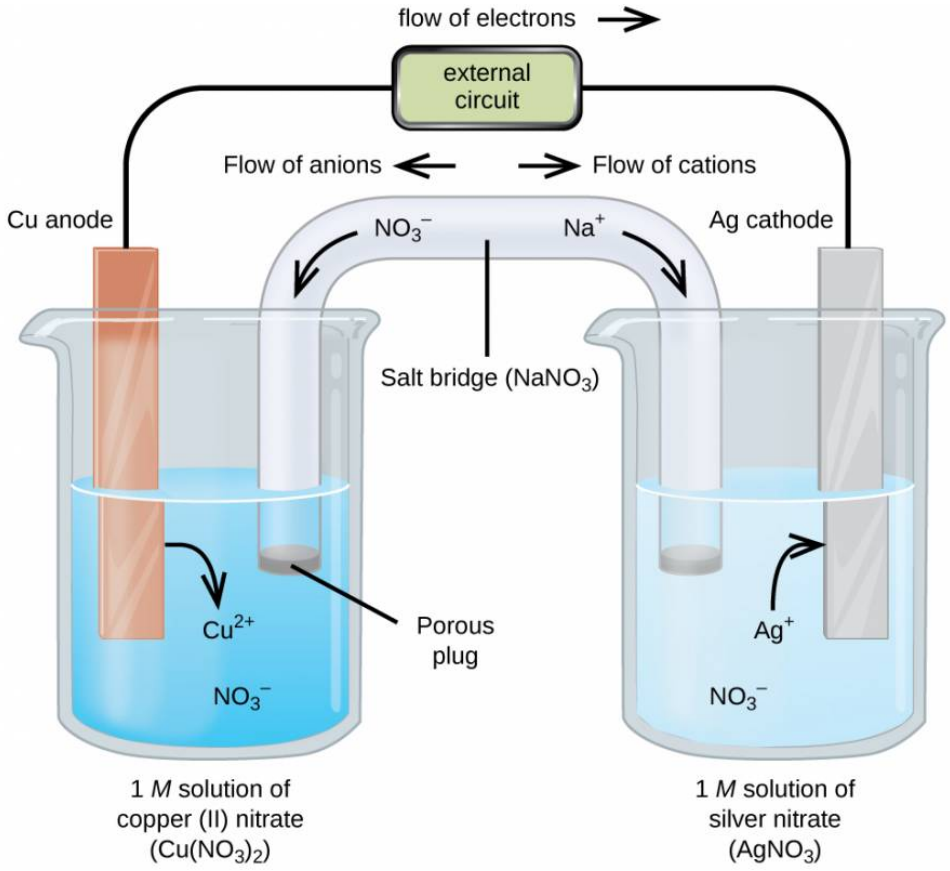
overall reaction:	$\mathrm{Cu}(s) + 2\mathrm{Ag}^{+}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{Ag}(s)$
oxidation half-reaction:	$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^{-}$
reduction half-reaction:	$2\mathrm{Ag}^{+}(aq) + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{Ag}(s)$

Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort ar generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called galvanic cells (or voltaic cells).

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in Figure 35.2. The cell is comprised of two half-cells, each containing the redox conjugate pair ("couple") of a single reactant. The half-cell shov at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution. An externa circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the anode of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the cathode is the electrode where reduction occurs (the Ag foil). The redox reactions in a galvanic cell occur only at th interface between each half-cell's reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a salt bridge. The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^{+} ions in th cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of NO_3^{-} from the salt bridge, while a flow of Na^{+} into the cathode half-cell compensates for the decreasing Ag^{+} concentration.

Figure 35.2

A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.



Cell Notation

Abbreviated symbolism is commonly used to represent a galvanic cell by providing essential information on its composition and structure. These symbolic representations are called cell notations or cell schematics, and they are written following a few guidelines:

- The relevant components of each half-cell are represented by their chemical formulas or element symbols
- All interfaces between component phases are represented by vertical parallel lines; if two or more components ar present in the same phase, their formulas are separated by commas
- By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

A verbal description of the cell as viewed from anode-to-cathode is often a useful first-step in writing its schematic. Fo example, the galvanic cell shown in Figure 35.2 consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a soli silver cathode. Converting this statement to symbolism following the above guidelines results in the cell schematic:

$$\mathrm{Cu}(s) \mid 1\,M\,\mathrm{Cu(NO_3)_2}\,(aq) \parallel 1\,M\,\mathrm{AgNO_3}\,(aq) \mid \mathrm{Ag}(s)$$

Consider a different galvanic cell (see Figure 35.3) based on the spontaneous reaction between solid magnesium and aqueous iron(III) ions:

$$\begin{aligned}
\text{net cell reaction:} &\quad \mathrm{Mg}(s) + 2\mathrm{Fe}^{3+}(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\mathrm{Fe}^{2+}(aq) \\
\text{oxidation half-reaction:} &\quad \mathrm{Mg}(s) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\mathrm{e}^{-} \\
\text{reduction half-reaction:} &\quad 2\mathrm{Fe}^{3+}(aq) + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{Fe}^{2+}(aq)
\end{aligned}$$

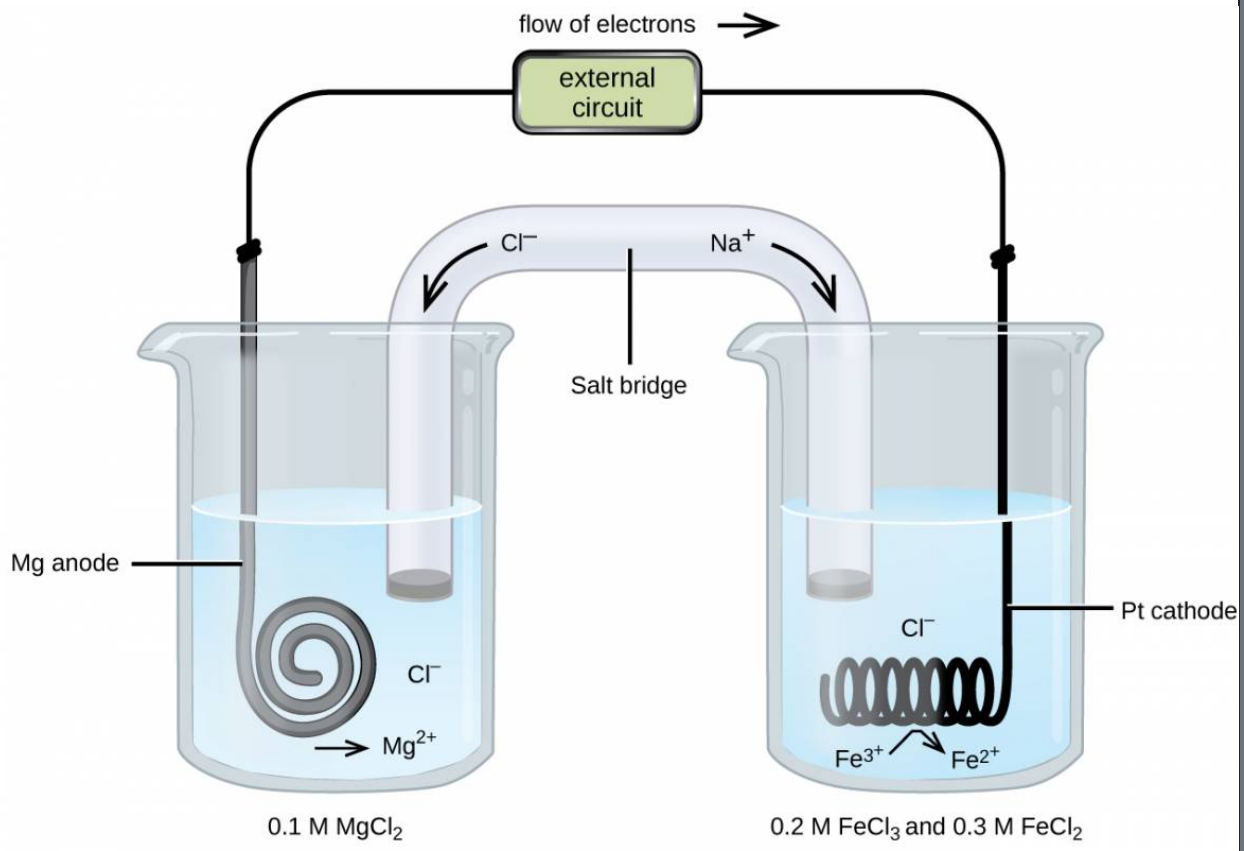
In this cell, a solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode. The cell schematic is then written as

$$\mathrm{Mg}(s) \mid 0.1\,M\,\mathrm{MgCl}_2(aq) \parallel 0.2\,M\,\mathrm{FeCl}_3(aq), 0.3\,M\,\mathrm{FeCl}_2(aq) \mid \mathrm{Pt}(s)$$

Notice the cathode half-cell is different from the others considered thus far in that its electrode is comprised of a substance (Pt) that is neither a reactant nor a product of the cell reaction. This is required when neither member of the half-cell's redox couple can reasonably function as an electrode, which must be electrically conductive and in a phase separate from the half-cell solution. In this case, both members of the redox couple are solute species, and so Pt is used as an inert electrode that can simply provide or accept electrons to redox species in solution. Electrodes constructed from a member of the redox couple, such as the Mg anode in this cell, are called active electrodes.

Figure 35.3

A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.



EXAMPLE 35.2.1

Writing Galvanic Cell Schematics

A galvanic cell is fabricated by connecting two half-cells with a salt bridge, one in which a chromium wire is immersed in a 1 M $CrCl_3$ solution and another in which a copper wire is immersed in 1 M $CuCl_2$. Assuming the chromium wire functions as an anode, write the schematic for this cell along with equations for the anode half-reaction, the cathode half-reaction, and the overall cell reaction.

Solution

Since the chromium wire is stipulated to be the anode, the schematic begins with it and proceeds left-to-right, symbolizing the other cell components until ending with the copper wire cathode:

$$\mathrm{Cr}(s) \mid 1\,M\,\mathrm{CrCl_3}\,(aq) \parallel 1\,M\,\mathrm{CuCl_2}\,(aq) \mid \mathrm{Cu}(s)$$

The half-reactions for this cell are

$$\begin{aligned} &\text{anode (oxidation):} && \mathrm{Cr}(s) \longrightarrow \mathrm{Cr^{3+}}\,(aq) + 3\mathrm{e^-} \\ &\text{cathode (reduction):} && \mathrm{Cu^{2+}}\,(aq) + 2\mathrm{e^-} \longrightarrow \mathrm{Cu}(s) \end{aligned}$$

Multiplying to make the number of electrons lost by Cr and gained by Cu^{2+} equal yields

$$\begin{aligned} &\text{anode (oxidation):} && 2\mathrm{Cr}(s) \longrightarrow 2\mathrm{Cr^{3+}}\,(aq) + 6\mathrm{e^-} \\ &\text{cathode (reduction):} && 3\mathrm{Cu^{2+}}\,(aq) + 6\mathrm{e^-} \longrightarrow 3\mathrm{Cu}(s) \end{aligned}$$

Adding the half-reaction equations and simplifying yields an equation for the cell reaction:

$$2\mathrm{Cr}(s) + 3\mathrm{Cu^{2+}}\,(aq) \longrightarrow 2\mathrm{Cr^{3+}}\,(aq) + 3\mathrm{Cu}(s)$$

Check Your Learning

Omitting solute concentrations and spectator ion identities, write the schematic for a galvanic cell whose net cell reaction is shown below.

$$\mathrm{Sn^{4+}}\,(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Sn^{2+}}\,(aq) + \mathrm{Zn^{2+}}\,(aq)$$

Answer

$$\mathrm{Zn}(s) \mid \mathrm{Zn^{2+}}\,(aq) \parallel \mathrm{Sn^{4+}}\,(aq), \mathrm{Sn^{2+}}\,(aq) \mid \mathrm{Pt}(s)$$

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Cell Potentials

The property of potential, E, is the energy associated with the separation/transfer of charge. In electrochemistry, the potentials of cells and half-cells are thermodynamic quantities that reflect the driving force or the spontaneity of their redox processes. The cell potential of an electrochemical cell is the difference in between its cathode and anode. To permit easy sharing of half-cell potential data, the standard hydrogen electrode (SHE) is assigned a potential of exactly 0 V and used to define a single electrode potential for any given half-cell. The electrode potential of a half-cell, EX, is the cell potential of said half-cell acting as a cathode when connected to a SHE acting as an anode. When the half-cell is operating under standard state conditions, its potential is the standard electrode potential, E°X. Standard electrode potentials reflect the relative oxidizing strength of the half-reaction's reactant, with stronger oxidants exhibiting larger (more positive) E°X values. Tabulations of standard electrode potentials may be used to compute standard cell potentials, E°cell, for many redox reactions. The arithmetic sign of a cell potential indicates the spontaneity of the cell reaction, with positive values for spontaneous reactions and negative values for nonspontaneous reactions (spontaneous in the reverse direction).

36.1 Electrode and Cell Potentials

Learning Objectives

By the end of this section, you will be able to:

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described in section 17.2, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $Ag^+(aq)$ and $Pb^{2+}(aq)$, thus show a distinct difference in their redox activity towards copper: the silver ion spontaneously oxidized copper, but the lead ion did not. Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, *potential*. This property is more commonly called *voltage* when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge. Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, V = J/C.

When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants. Considering the nature of potential in this

context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called cell potentials, E_{cell}, defined as

$$E_{cell} = E_{cathode} - E_{anode}$$

where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. As for other thermodynamic quantities, the standard cell potential, $E°_{cell}$, is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

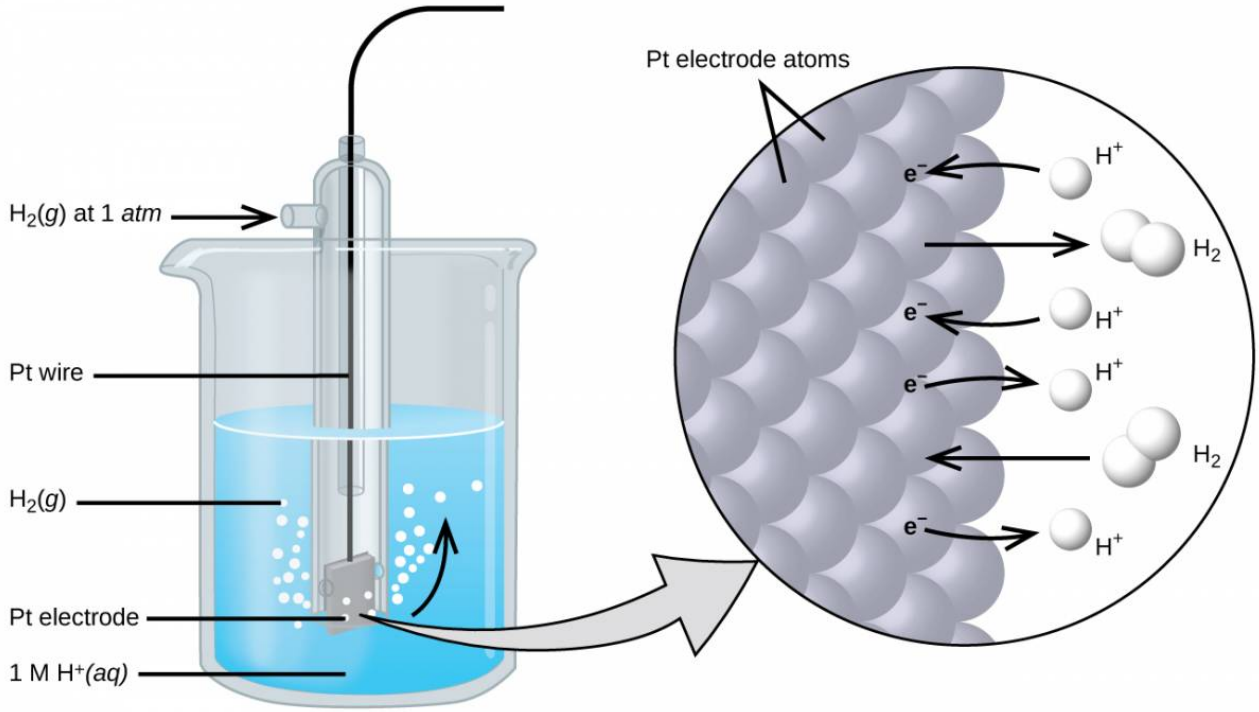
To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the standard hydrogen electrode (SHE) and it is based on half-reaction below:

$$2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$$

A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see Figure 36.1).

Figure 36.1

A standard hydrogen electrode (SHE).



The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The electrode potential (E_X) for a half-cell *X* is defined as *the potential measured for a cell comprised of X acting as cathode*

and the SHE acting as anode:

$$E_{cell} = E_X - E_{SHE}$$
$$E_{SHE} = 0\ V\ (defined)$$
$$E_{cell} = E_X$$

When the half-cell *X* is under standard-state conditions, its potential is the standard electrode potential, $E°_X$. Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials*.

This approach to measuring electrode potentials is illustrated in Figure 36.2, which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E^\circ_{cell} = E^\circ_{Cu} = +0.337\ V$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

Figure 36.2
A cell permitting experimental measurement of the standard electrode potential for the half-reaction $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

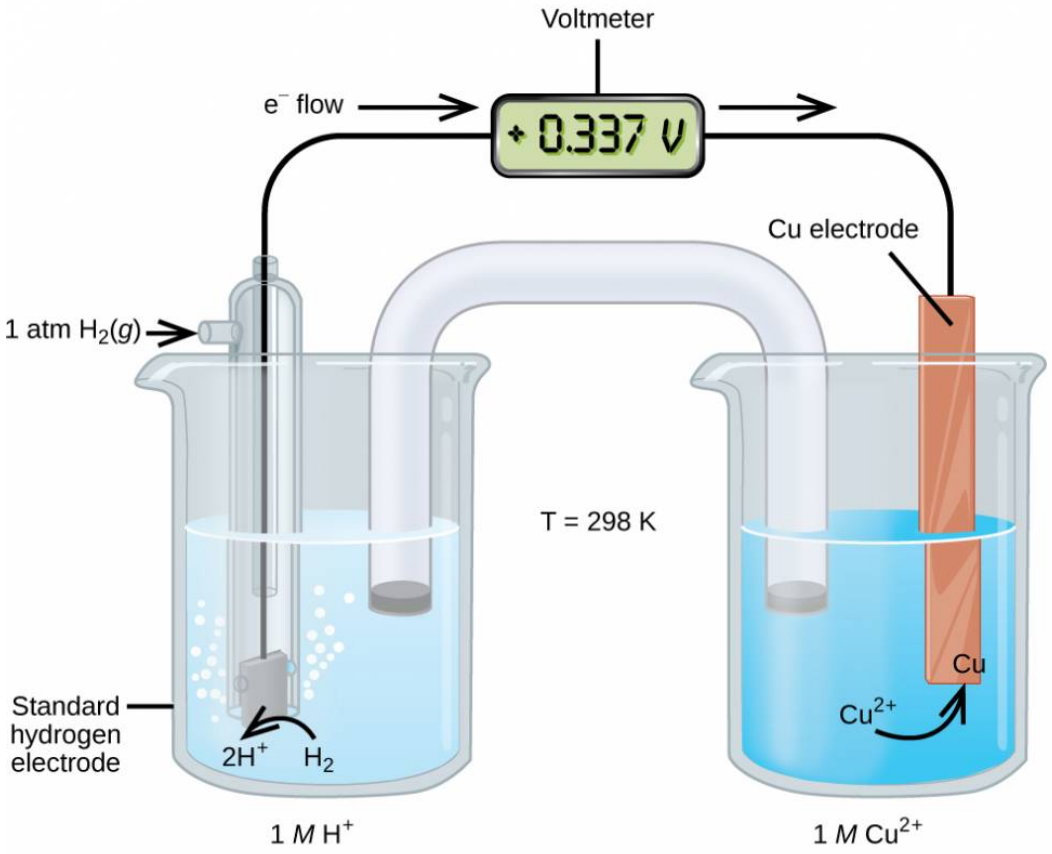


Table 36.1 provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in Appendix L.

Table 36.3

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558

Half-Reaction	E° (V)
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.1375
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.185
$Zn(OH)_2(s) + 2e^- \rightarrow Zn(s) + 2OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.662
$Mg^{2}(aq) + 2e^- \rightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \rightarrow K(s)$	−2.931
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

EXAMPLE 36.1.1

Calculating Standard Cell Potentials

What is the standard potential of the galvanic cell shown in Figure 37.3?

Solution

The cell in Figure 37.3 is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:

$$\begin{aligned} &\text{cell reaction:} && \mathrm{Cu}(s) + 2\mathrm{Ag}^{+}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{Ag}(s) \\ &\text{anode half-reaction:} && \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^{-} \\ &\text{cathode half-reaction:} && 2\mathrm{Ag}^{+}(aq) + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{Ag}(s) \end{aligned}$$

The standard cell potential computed as

$$\begin{aligned} \mathrm{E}^{\circ}_{\text{cell}} &= \mathrm{E}^{\circ}_{\text{cathode}} - \mathrm{E}^{\circ}_{\text{anode}} \\ &= \mathrm{E}^{\circ}_{\text{Ag}} - \mathrm{E}^{\circ}_{\text{Cu}} \\ &= 0.7996\ \text{V} - 0.34\ \text{V} \\ &= +0.46\ \text{V} \end{aligned}$$

Check Your Learning

What is the standard cell potential expected if the silver cathode half-cell in Figure 36.3 is replaced with a lead half-cell:

$$\mathrm{Pb}^{2+}(aq) + 2\mathrm{e}^{-} \longrightarrow \mathrm{Pb}(s)$$

?

Answer

−0. 47 V

36.1.2 Interpreting Electrode and Cell Potentials

Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions. Results of the calculations in Example 36.1 have just shown *the spontaneous process is described by a positive cell potential* while *the nonspontaneous process exhibits a negative cell potential.* And so, with regard to the relative effectiveness ("strength") with which aqueous Ag^{+} and Pb^{2+} ions oxidize Cu under standard conditions, *the stronger oxidant is the one exhibiting the greater standard electrode potential, E°*. Since by convention electrode potentials are for reduction processes, an increased value of *E°* corresponds to an increased driving force behind the reduction of the species (hence increased

effectiveness of its action as an *oxidizing agent* on some other species). Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in Table 36.1 shows this listing to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive $E°$) to weakest oxidant (most negative $E°$). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, $E°_{cell}$ is positive when $E°_{cathode} > E°_{anode}$, and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in Example 36.1 provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^+ is predicted to be spontaneous ($E°_{cathode} > E°_{anode}$ and so $E°_{cell} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E°_{cathode} < E°_{anode}$ and so $E°_{cell} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,

$$\mathrm{Cu}(s) + \mathrm{Pb}^{2+}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{Pb}(s) E^{\circ}_{forward} = -0.47\ \mathrm{V}\ (\text{negative, non-spontaneous})$$

and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:

$$\mathrm{Pb}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Pb}^{2+}(aq) + \mathrm{Cu}(s) E^{\circ}_{forward} = +0.47\ \mathrm{V}\ (\text{positive, spontaneous})$$

Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of −0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be +0.47 V.

EXAMPLE 36.1.3

Predicting Redox Spontaneity

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in Table 36.1.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:

$$\mathrm{Cr}(s) + \mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Cr}^{3+}(aq) + \mathrm{Fe}(s)$$

The entry for the putative oxidant, Fe^{2+}, appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

$$\begin{aligned} \mathrm{E}^{\circ}_{\text{cell}} &= \mathrm{E}^{\circ}_{\text{cathode}} - \mathrm{E}^{\circ}_{\text{anode}} \\ &= \mathrm{E}^{\circ}_{\text{Fe(II)}} - \mathrm{E}^{\circ}_{\text{Cr}} \\ &= -0.447\ \text{V} - -0.744\ \text{V} = +0.297\ \text{V} \end{aligned}$$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

Check Your Learning

Use the data in Table 36.1 to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the reaction. Repeat for the oxidation of iodide ion by molecular bromine.

Answer

$$\mathrm{I}_2(s) + 2\mathrm{Br}^-(aq) \longrightarrow 2\mathrm{I}^-(aq) + \mathrm{Br}_2(l) \qquad E^{\circ}_{\text{cell}} = -0.5518\ \text{V (nonspontaneous)}$$

$$\mathrm{Br}_2(s) + 2\mathrm{I}^-(aq) \longrightarrow 2\mathrm{Br}^-(aq) + \mathrm{I}_2(l) \qquad E^{\circ}_{\text{cell}} = +0.5518\ \text{V (spontaneous)}$$

36.2 Potential, Free Energy, and Equilibrium

Learning Objectives

By the end of this section, you will be able to:

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction (see chapter on thermodynamics). The interpretation of potentials as measures of oxidant *strength* was presented, bringing to mind similar measures of acid-base strength as reflected in equilibrium constants (see the chapter on acid-base equilibria). This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K.

36.2.1 E° and ΔG°

The standard free energy change of a process, $\Delta G°$, was defined in a previous chapter as the maximum work that could be performed by a system, w_{max}. In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec}:

$$\Delta G° = w_{max} = w_{elec}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\begin{aligned} \Delta G° = w_{elec} &= -nFE^{\circ}_{cell} \\ \Delta G° &= -nFE^{\circ}_{cell} \end{aligned}$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and E°_{cell} is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

36.2.2 E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and E°_{cell} yields the following:

$$\begin{aligned} \Delta G° &= -RT \ln K = -nFE^{\circ}_{cell} \\ E^{\circ}_{cell} &= \left(\frac{RT}{nF}\right) \ln K \end{aligned}$$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the

relations between $E°$, $\Delta G°$ and K is depicted in Figure 36.3, and a table correlating reaction spontaneity to values of these properties is provided in Table 36.1.

Figure 36.4

Graphic depicting the relation between three important thermodynamic properties.

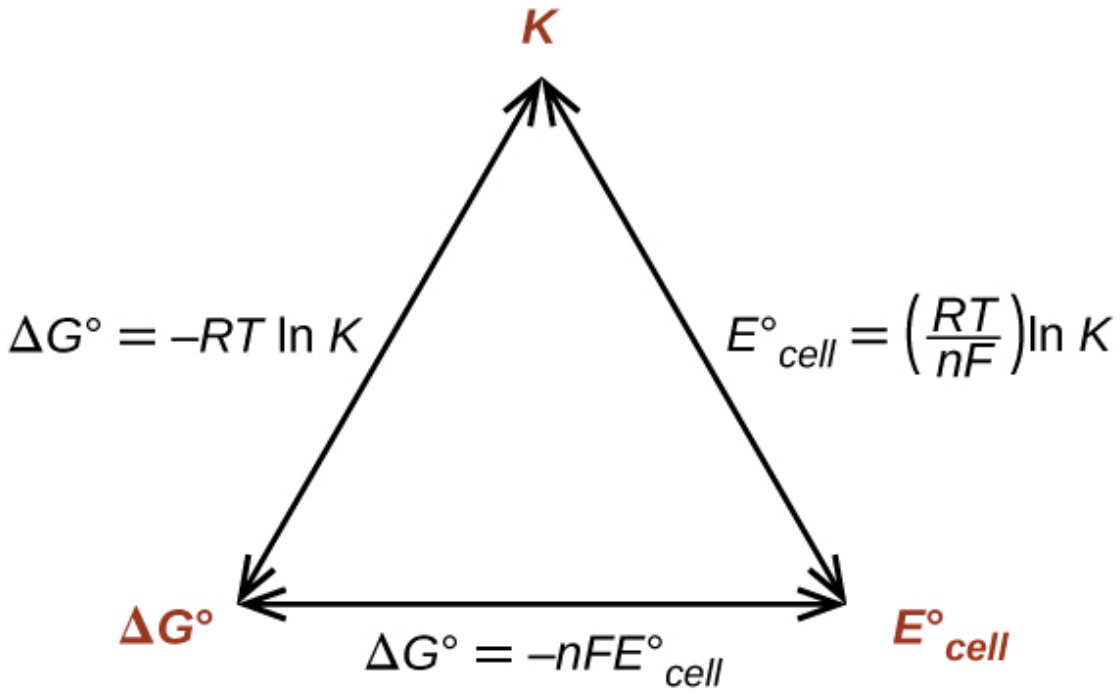


Table 36.5

K	$\Delta G°$	$E°_{cell}$	
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
= 1	= 0	= 0	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

EXAMPLE 36.2.3

Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

Use data from Appendix L to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products.

$$2\text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Appendix L.

$$\begin{aligned}
&\text{anode (oxidation):} && \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\text{e}^- && E^\circ_{\text{Fe}^{2+}/\text{Fe}} &= -0.447\ \text{V}\\
&\text{cathode (reduction):} && 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) && E^\circ_{\text{Ag}^+/\text{Ag}} &= 0.7996\ \text{V}\\
& && E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = && E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} &= +1.247\ \text{V}
\end{aligned}$$

With $n = 2$, the equilibrium constant is then

$$\begin{aligned}
E^\circ_{\text{cell}} &= \frac{0.0592\ \text{V}}{n} \log K\\
K &= 10^{n \times E^\circ_{\text{cell}}/0.0592\ \text{V}}\\
K &= 10^{2 \times 1.247\ \text{V}/0.0592\ \text{V}}\\
K &= 10^{42.128}\\
K &= 1.3 \times 10^{42}
\end{aligned}$$

The standard free energy is then

$$\begin{aligned}
\Delta G^\circ &= -nFE^\circ_{\text{cell}}\\
\Delta G^\circ &= -2 \times 96{,}485\ \frac{\text{C}}{\text{mol}} \times 1.247\ \frac{\text{J}}{\text{C}} = -240.6\ \frac{\text{kJ}}{\text{mol}}
\end{aligned}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The K value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

Check Your Learning

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\text{Cu}^+(aq)$$

Answer

Spontaneous; $n = 2$;

$E^\circ_{\text{cell}} = +0.291\ \text{V}$;

$\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$;

$K = 6.8$

$\times$

10^9

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37

Nernst Equation

Potential is a thermodynamic quantity reflecting the intrinsic driving force of a redox process, and it is directly related to the free energy change and equilibrium constant for the process. For redox processes taking place in electrochemical cells, the maximum (electrical) work done by the system is easily computed from the cell potential and the reaction stoichiometry and is equal to the free energy change for the process. The equilibrium constant for a redox reaction is logarithmically related to the reaction's cell potential, with larger (more positive) potentials indicating reactions with greater driving force that equilibrate when the reaction has proceeded far towards completion (large value of K). Finally, the potential of a redox process varies with the composition of the reaction mixture, being related to the reactions standard potential and the value of its reaction quotient, Q, as described by the Nernst equation.

37.1 Potential, Free Energy, and Equilibrium

Learning Objectives

By the end of this section, you will be able to:

- Use the Nernst equation to determine cell potentials under nonstandard conditions

37.1.1 Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Notice the reaction quotient, *Q*, appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the Nernst equation:

$$-nFE_{\text{cell}} = -nFE^{\circ}_{\text{cell}} + RT \ln Q$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, *n*, the temperature, *T*, and the reaction mixture composition as reflected in *Q*. A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and standard temperature (298) K), along with a factor converting from natural to base-10 logarithms, have been included:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\text{V}}{n} \log Q$$

EXAMPLE 37.1.2

Predicting Redox Spontaneity Under Nonstandard Conditions

Use the Nernst equation to predict the spontaneity of the redox reaction shown below.

$$\mathrm{Co}(s) + \mathrm{Fe}^{2+}(aq,\ 1.94\ M) \longrightarrow \mathrm{Co}^{2+}(aq,\ 0.15\ M) + \mathrm{Fe}(s)$$

Solution

Collecting information from Appendix L and the problem,

$$\begin{aligned}
&\text{Anode (oxidation):} && \mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2\mathrm{e}^- && E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}} &= -0.28\ \mathrm{V}\\
&\text{Cathode (reduction):} && \mathrm{Fe}^{2+}(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{Fe}(s) && E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} &= -0.447\ \mathrm{V}\\
& && E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} = && -0.447\ \mathrm{V} - (-0.28\ \mathrm{V}) &= -0.17\ \mathrm{V}
\end{aligned}$$

Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions yields:

$$\begin{aligned}
Q &= \frac{[\mathrm{Co}^{2+}]}{[\mathrm{Fe}^{2+}]} = \frac{0.15\ M}{1.94\ M} = 0.077\\
E_{\mathrm{cell}} &= E^\circ_{\mathrm{cell}} - \frac{0.0592\ \mathrm{V}}{n}\log Q\\
E_{\mathrm{cell}} &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log 0.077\\
E_{\mathrm{cell}} &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} = -0.14\ \mathrm{V}
\end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Check Your Learning

For the cell schematic below, identify values for n and Q, and calculate the cell potential, E_{cell}.

$$\mathrm{Al}(s) \mid \mathrm{Al}^{3+}(aq,\ 0.15\ M) \parallel \mathrm{Cu}^{2+}(aq,\ 0.025\ M) \mid \mathrm{Cu}(s)$$

Answer

n = 6; Q = 1440; E_{cell} = +1.97 V, spontaneous.

A concentration cell is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration

cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

EXAMPLE 37.1.3

Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(aq, 0.10\ M) \parallel \mathrm{Zn}^{2+}(aq, 0.50\ M) \mid \mathrm{Zn}(s)$$

Solution

From the information given:

$$\begin{array}{lll} \text{Anode:} & \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq, 0.10\ M) + 2\mathrm{e}^- & E^\circ_{\text{anode}} = -0.7618\ \text{V} \\ \text{Cathode:} & \mathrm{Zn}^{2+}(aq, 0.50\ M) + 2\mathrm{e}^- \longrightarrow \mathrm{Zn}(s) & E^\circ_{\text{cathode}} = -0.7618\ \text{V} \\ \text{Overall:} & \mathrm{Zn}^{2+}(aq, 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq, 0.10\ M) & E^\circ_{\text{cell}} = 0.000\ \text{V} \end{array}$$

Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000\ \text{V} - \frac{0.0592\ \text{V}}{2} \log \frac{0.10}{0.50} = +0.021\ \text{V}$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{\text{cathode}} > E_{\text{anode}}$).

Check Your Learning

The concentration cell above was allowed to operate until the cell reaction reached equilibrium. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now?

Answer

$E_{\text{cell}} = 0.000$ V; $[\mathrm{Zn}^{2+}]_{\text{cathode}} = [\mathrm{Zn}^{2+}]_{\text{anode}} = 0.30\ M$

Files

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38

Batteries and Fuel Cells

Galvanic cells designed specifically to function as electrical power supplies are called batteries. A variety of both single-use batteries (primary cells) and rechargeable batteries (secondary cells) are commercially available to serve a variety of applications, with important specifications including voltage, size, and lifetime. Fuel cells, sometimes called flow batteries, are devices that harness the energy of spontaneous redox reactions normally associated with combustion processes. Like batteries, fuel cells enable the reaction's electron transfer via an external circuit, but they require continuous input of the redox reactants (fuel and oxidant) from an external reservoir. Fuel cells are typically much more efficient in converting the energy released by the reaction to useful work in comparison to internal combustion engines. Spontaneous oxidation of metals by natural electrochemical processes is called corrosion, familiar examples including the rusting of iron and the tarnishing of silver. Corrosion process involve the creation of a galvanic cell in which different sites on the metal object function as anode and cathode, with the corrosion taking place at the anodic site. Approaches to preventing corrosion of metals include use of a protective coating of zinc (galvanization) and the use of sacrificial anodes connected to the metal object (cathodic protection). Nonspontaneous redox processes may be forced to occur in electrochemical cells by the application of an appropriate potential using an external power source—a process known as electrolysis. Electrolysis is the basis for certain ore refining processes, the industrial production of many chemical commodities, and the electroplating of metal coatings on various products. Measurement of the current flow during electrolysis permits stoichiometric calculations.

38.1 Batteries and Fuel Cells

Learning Objectives

By the end of this section, you will be able to:

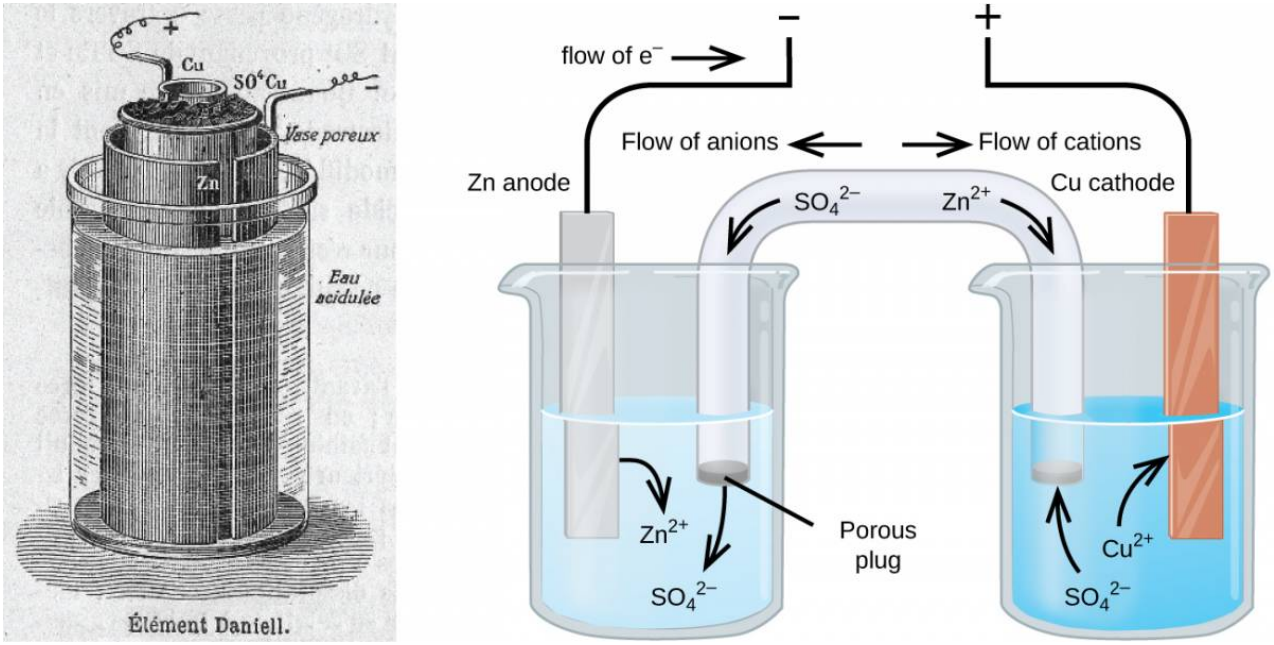
- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A battery is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (Figure 38.1):

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

Figure 38.1

Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the other half-cell.



Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (primary cells), while others are based on conveniently reversible cell reactions that allow recharging by an external power source (secondary cells). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

LINK TO LEARNING

Visit this site to learn more about batteries.

38.2 Single-Use Batteries

A common primary battery is the dry cell, which uses a zinc can as both container and anode ("–" terminal) and a graphite rod as the cathode ("+" terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc:

$$\text{anode reaction: } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\mathrm{e}^{-}$$

and the reduction of manganese(IV)

$$\text{reduction reaction: } 2\text{MnO}_2\,(s) + 2\text{NH}_4\,\text{Cl}(aq) + 2\,\text{e}^- \longrightarrow \text{Mn}_2\,\text{O}_3\,(s) + 2\text{NH}_3\,(aq) + \text{H}_2\,\text{O}(l) + 2\text{Cl}^-$$

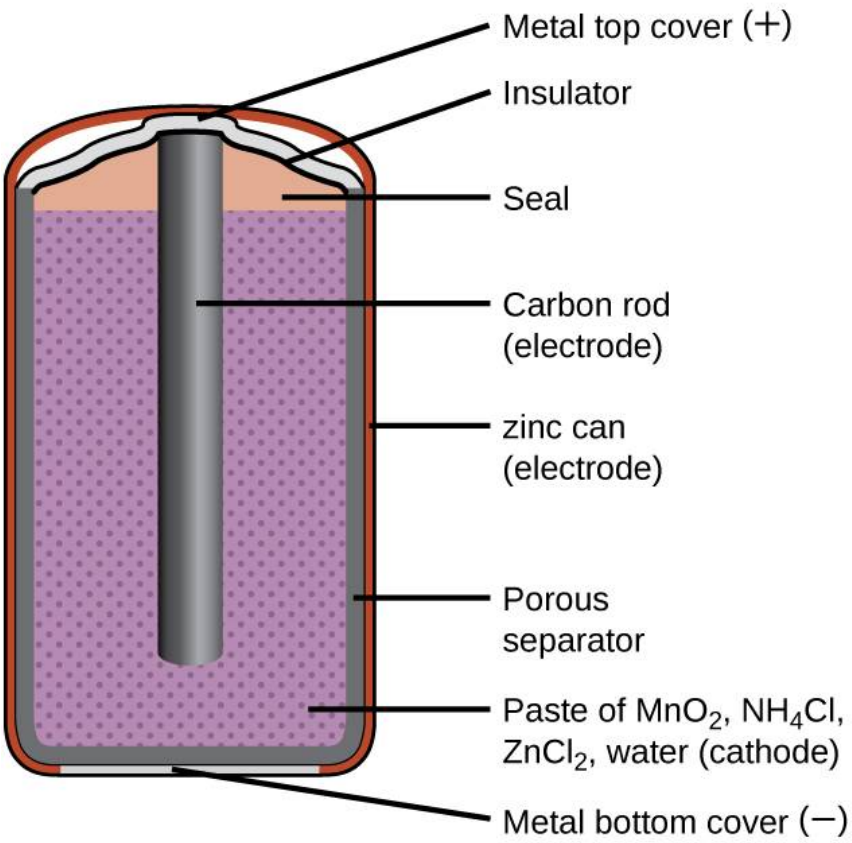
which together yield the cell reaction:

$$\text{cell reaction: } 2\text{MnO}_2\,(s) + 2\text{NH}_4\,\text{Cl}(aq) + \text{Zn}(s) \longrightarrow \text{Zn}^{2+}\,(aq) + \text{Mn}_2\,\text{O}_3\,(s) + 2\text{NH}_3\,(aq) + \text{H}_2\,\text{O}(l) +$$

The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

Figure 38.2

A schematic diagram shows a typical dry cell.



LINK TO LEARNING

Visit this site to learn more about zinc-carbon batteries.

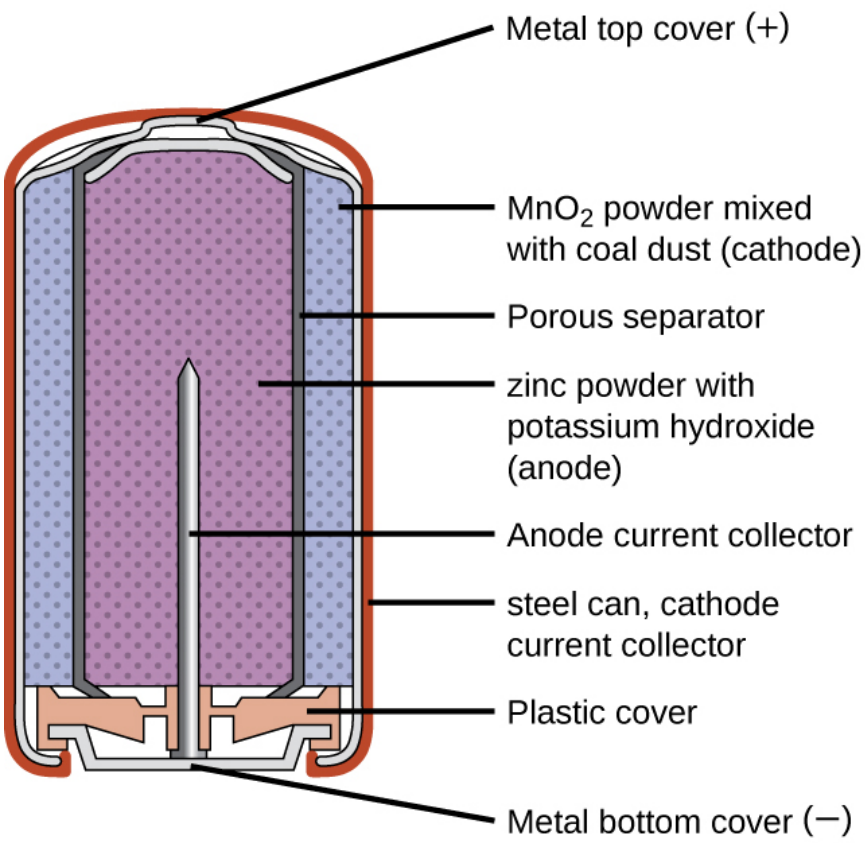
Alkaline batteries (Figure 38.3) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\text{anode:} \quad \text{Zn}(s) + 2\text{OH}^-(aq) \longrightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2\text{e}^-$$
$$\text{cathode:} \quad 2\text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2\text{e}^- \longrightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^-(aq)$$
$$\text{cell:} \quad \text{Zn}(s) + 2\text{MnO}_2(s) \longrightarrow \text{ZnO}(s) + \text{Mn}_2\text{O}_3(s) \qquad E_{\text{cell}} = +1.43\ \text{V}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so they should be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

Figure 38.3

Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.



LINK TO LEARNING

Visit this site to learn more about alkaline batteries.

38.3 Rechargeable (Secondary) Batteries

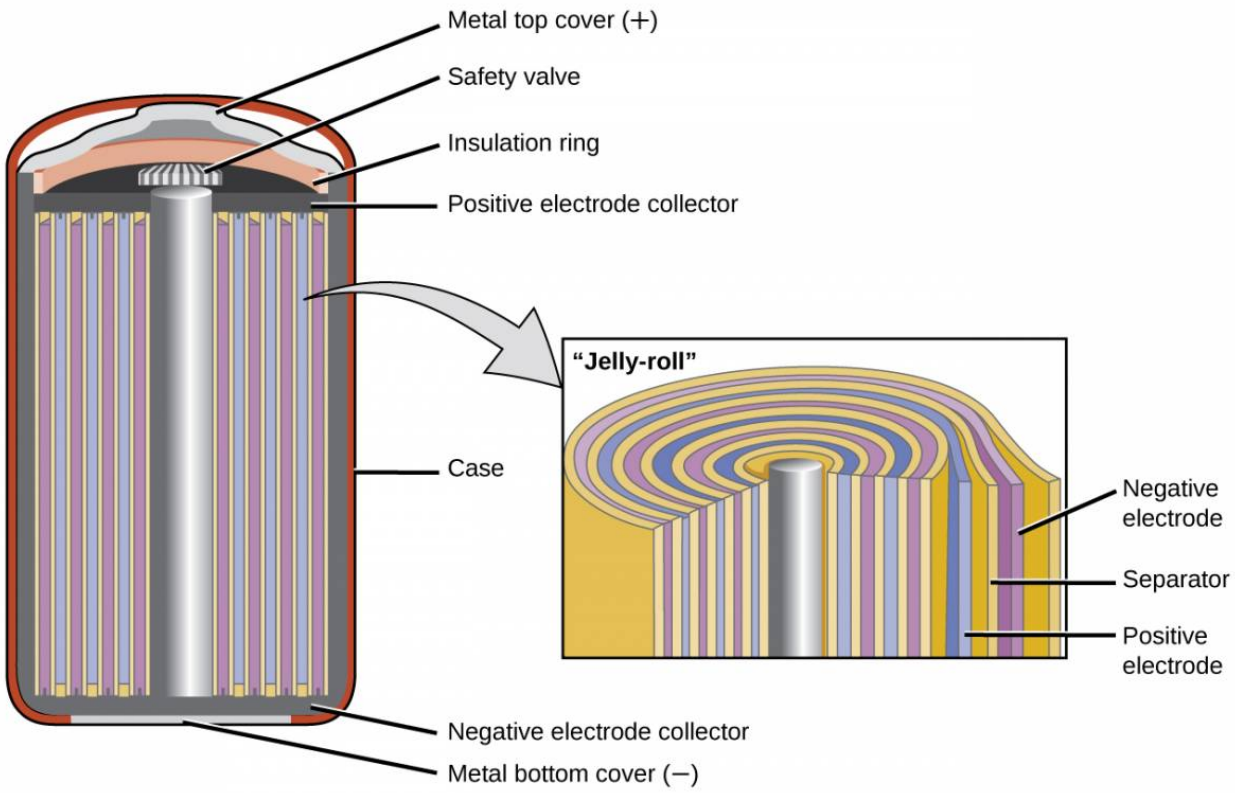
Nickel-cadmium, or NiCd, batteries (Figure 38.4) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{aligned}
&\text{anode:} && \mathrm{Cd}(s) + 2\mathrm{OH}^-(aq) \longrightarrow \mathrm{Cd(OH)_2}(s) + 2\mathrm{e}^- \\
&\text{cathode:} && \mathrm{NiO_2}(s) + 2\mathrm{H_2O}(l) + 2\mathrm{e}^- \longrightarrow \mathrm{Ni(OH)_2}(s) + 2\mathrm{OH}^-(aq) \\
&\text{cell:} && \mathrm{Cd}(s) + \mathrm{NiO_2}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Cd(OH)_2}(s) + \mathrm{Ni(OH)_2}(s) \qquad E_{\text{cell}} \sim 1.2\ \text{V}
\end{aligned}$$

When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

Figure 38.4

NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.



LINK TO LEARNING

Visit this site for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 38.5) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\text{anode:} \quad \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\,\mathrm{Li^+} + x\,\mathrm{e^-}$$

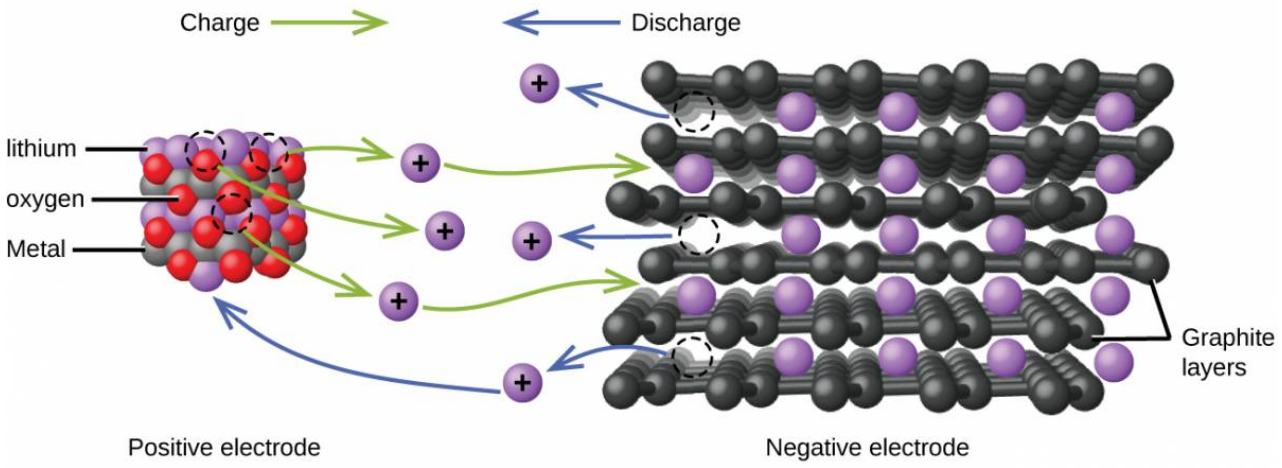
$$\text{cathode:} \quad x\,\mathrm{Li^+} + x\,\mathrm{e^-} + x\,\mathrm{C_6} \rightleftharpoons x\,\mathrm{LiC_6}$$

$$\text{cell:} \quad \mathrm{LiCoO_2} + x\,\mathrm{C_6} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\,\mathrm{LiC_6} \qquad E_{\text{cell}} \sim 3.7\ \text{V}$$

The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, x is usually no more than 0.5 and the cell voltage is approximately 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

Figure 38.5

In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.



LINK TO LEARNING

Visit this site for more information about lithium ion batteries.

The lead acid battery (Figure 38.6) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\text{anode:} \quad \text{Pb}(s) + \text{HSO}_4^-(aq) \longrightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2\text{e}^-$$

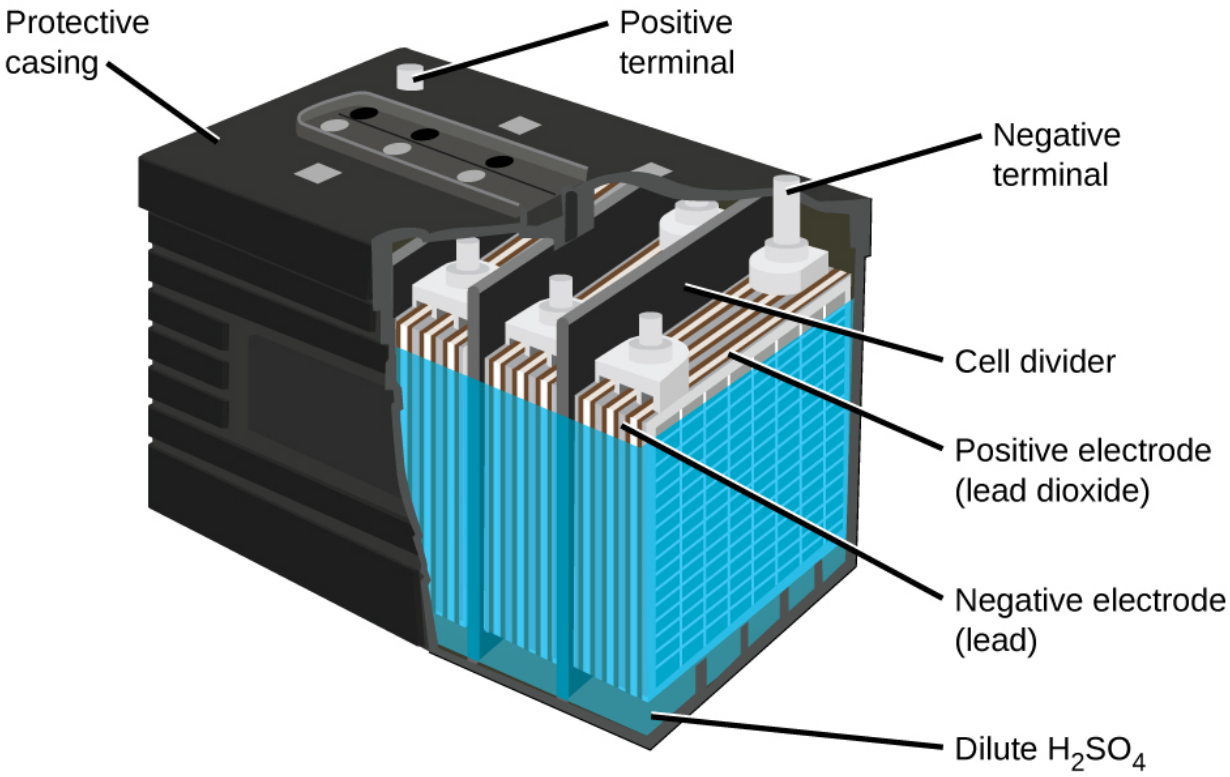
$$\text{cathode:} \quad \text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3\text{H}^+(aq) + 2\text{e}^- \longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$$

$$\text{cell:} \quad \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_2\text{SO}_4(aq) \longrightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \qquad E_{\text{cell}} \sim 2\ \text{V}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, $H_2SO_4(aq)$, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

Figure 38.6

The lead acid battery in your automobile consists of six cells connected in series to give 12 V.



LINK TO LEARNING

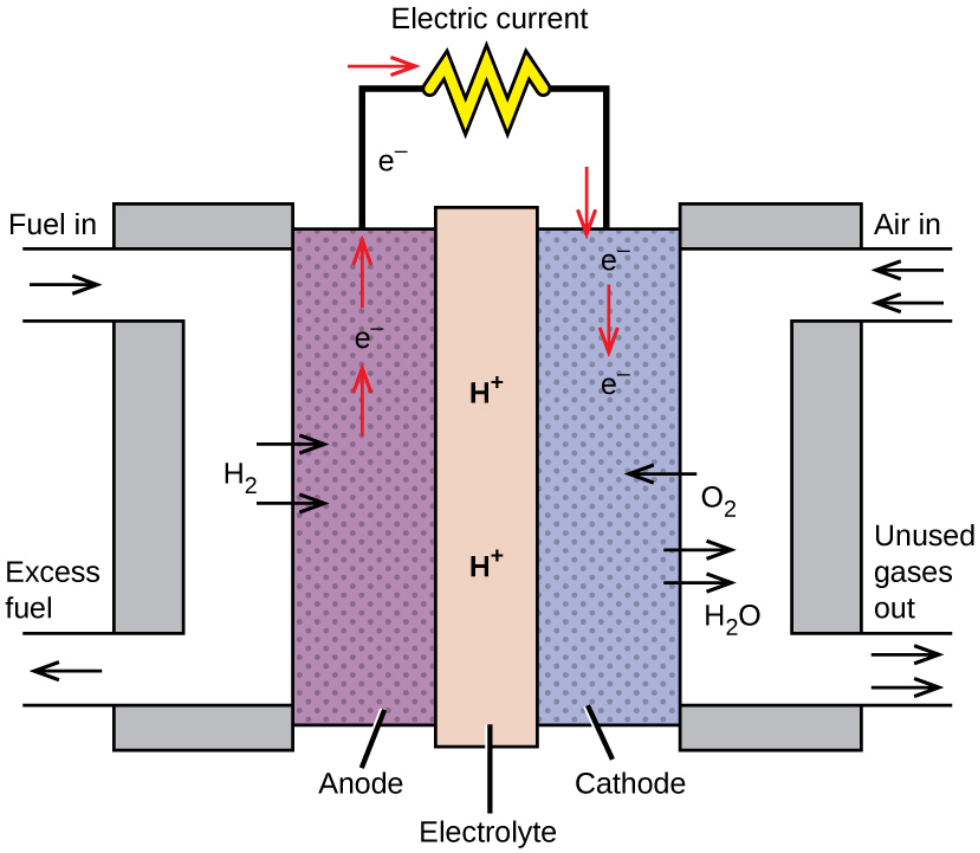
Visit this site for more information about lead acid batteries.

38.4 Fuel Cells

A fuel cell is a galvanic cell that uses traditional combustive fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

Figure 38.7

In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.



$$\text{Anode:} \qquad 2H_2\,(g) \longrightarrow 4H^+\,(aq) + 4e^-$$

$$\text{Cathode:}\ O_2\,(g) + 4H^+\,(aq) + 4e^- \longrightarrow 2H_2O(g)$$

$$\text{Cell:} \qquad 2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O(g) \qquad E_{\text{cell}} \sim 1.2\ \text{V}$$

These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

LINK TO LEARNING

Check out this link to learn more about fuel cells.

38.5 Corrosion

Learning Objectives

By the end of this section, you will be able to:

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals by a naturally occurring electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion remediation in the United States is significant, with estimates in excess of half a trillion dollars a year.

38.5.1 CHEMISTRY IN EVERYDAY LIFE

Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color (Figure 38.8). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2\text{Cu}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{Cu}_2\text{O}(s) \qquad \text{(red)}$$

$$\text{Cu}_2\text{O}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow 2\text{CuO}(s) \qquad \text{(black)}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the CuO

$$2\text{CuO}(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{Cu}_2\text{CO}_3(\text{OH})_2(s) \qquad \text{(green)}$$

$$3\text{CuO}(s) + 2\text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{Cu}_2(\text{CO}_3)_2(\text{OH})_2(s) \qquad \text{(blue)}$$

$$4\text{CuO}(s) + \text{SO}_3(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{Cu}_4\text{SO}_4(\text{OH})_6(s) \qquad \text{(green)}$$

These three compounds are responsible for the characteristic blue-green patina seen on the Statue of Liberty (and other outdoor copper structures). Fortunately, formation of patina creates a protective layer on the copper surface, preventing further corrosion of the underlying copper. The formation of the protective layer is called *passivation*, a phenomenon discussed further in another chapter of this text.

Figure 38.8

(a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

(a) (b)

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. Rust formation involves the creation of a galvanic cell at an iron surface, as illustrated in Figure 38.8. The relevant redox reactions are described by the following equations:

$$\begin{array}{lcll} \text{anode:} & \mathrm{Fe}(s) \longrightarrow \mathrm{Fe}^{2+}(aq) + 2\mathrm{e}^- & E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} & = -0.44\ \mathrm{V} \\ \text{cathode:} & \mathrm{O_2}(g) + 4\mathrm{H}^+(aq) + 4\mathrm{e}^- \longrightarrow 2\mathrm{H_2O}(l) & E^\circ_{\mathrm{O_2}/\mathrm{O}^2} & = +1.23\ \mathrm{V} \\ \text{overall:} & 2\mathrm{Fe}(s) + \mathrm{O_2}(g) + 4\mathrm{H}^+(aq) \longrightarrow 2\mathrm{Fe}^{2+}(aq) + 2\mathrm{H_2O}(l) & E^\circ_{\text{cell}} & = +1.67\ \mathrm{V} \end{array}$$

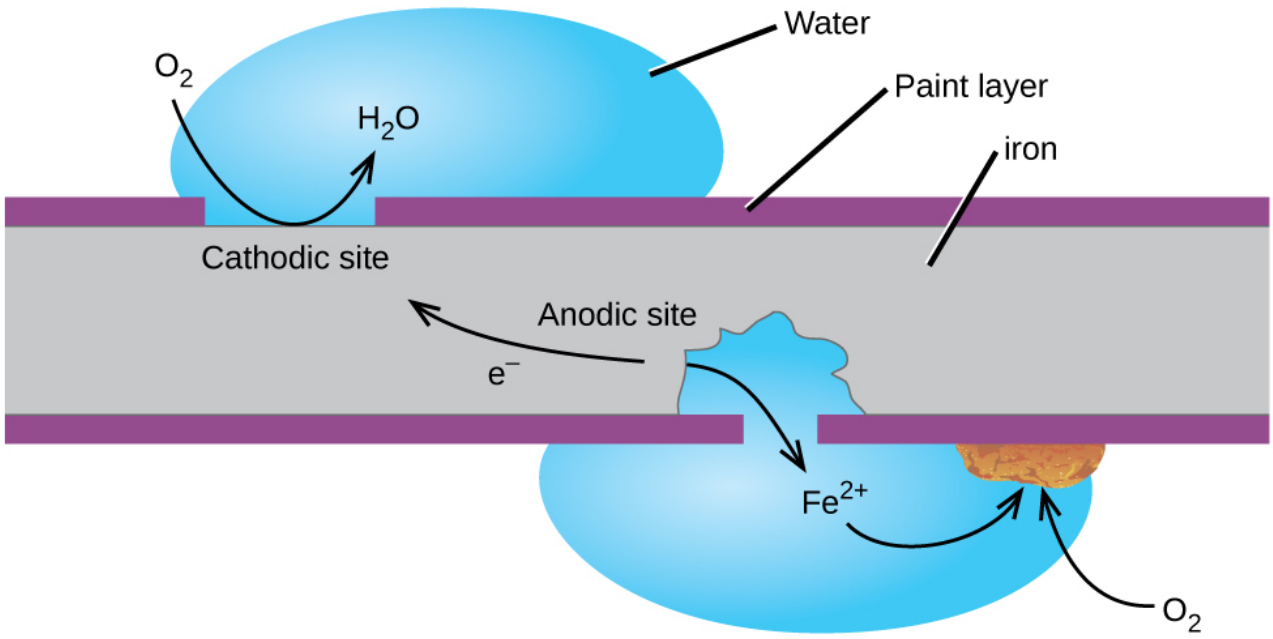
Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:

$$4\mathrm{Fe}^{2+}(aq) + \mathrm{O_2}(g) + (4+2x)\,\mathrm{H_2O}(l) \longrightarrow 2\mathrm{Fe_2O_3}\cdot x\mathrm{H_2O}(s) + 8\mathrm{H}^+(aq)$$

The stoichiometry of the hydrate varies, as indicated by the use of *x* in the compound formula. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

Figure 38.9

Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic Fe(s) | Fe^{2+}(aq) ||O_2(aq), H_2O(l) | Fe(s).



One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

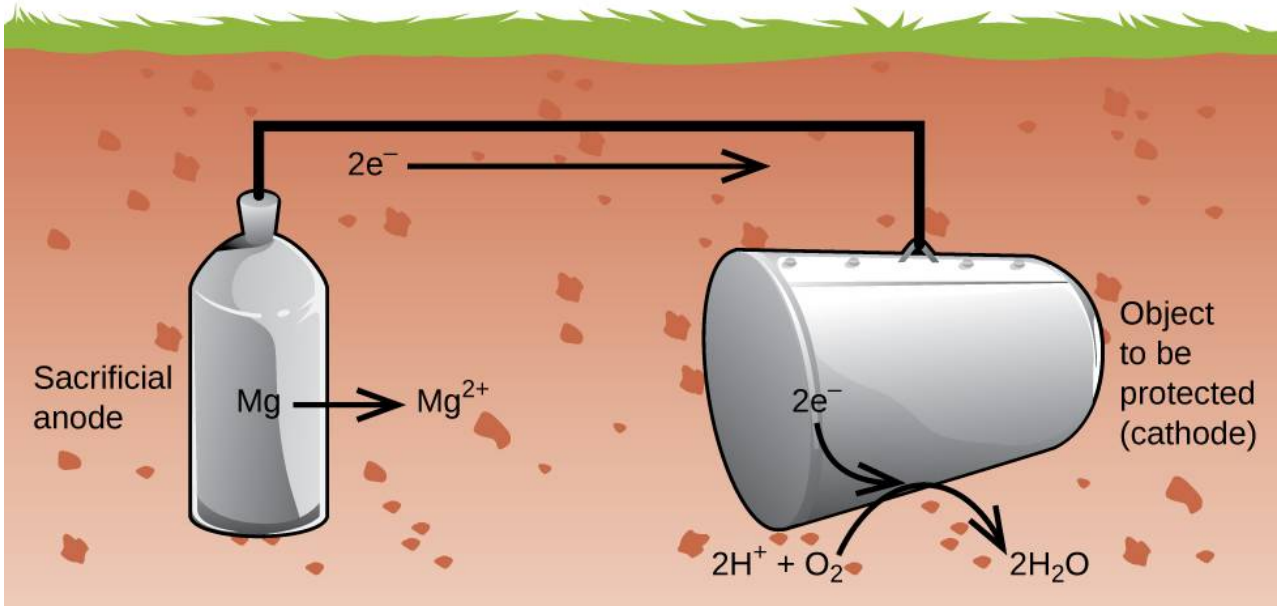
Other strategies include alloying the iron with other metals. For example, stainless steel is an alloy of iron containing a small amount of chromium. The chromium tends to collect near the surface, where it corrodes and forms a passivating an oxide layer that protects the iron.

Iron and other metals may also be protected from corrosion by galvanization, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc. When the zinc layer is intact, it prevents air from contacting the underlying iron and thus prevents corrosion. If the zinc layer is breached by either corrosion or mechanical abrasion, the iron may still be protected from corrosion by a *cathodic protection* process, which is described in the next paragraph.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is cathodic protection and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (Figure 38.10). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called sacrificial anodes because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode for the reduction of oxygen in air, and so it simply serves to conduct (not react with) the electrons being transferred. When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

Figure 38.10

Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.



38.6 Electrolysis

Learning Objectives

By the end of this section, you will be able to:

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as electrolysis. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

38.7 The Electrolysis of Molten Sodium Chloride

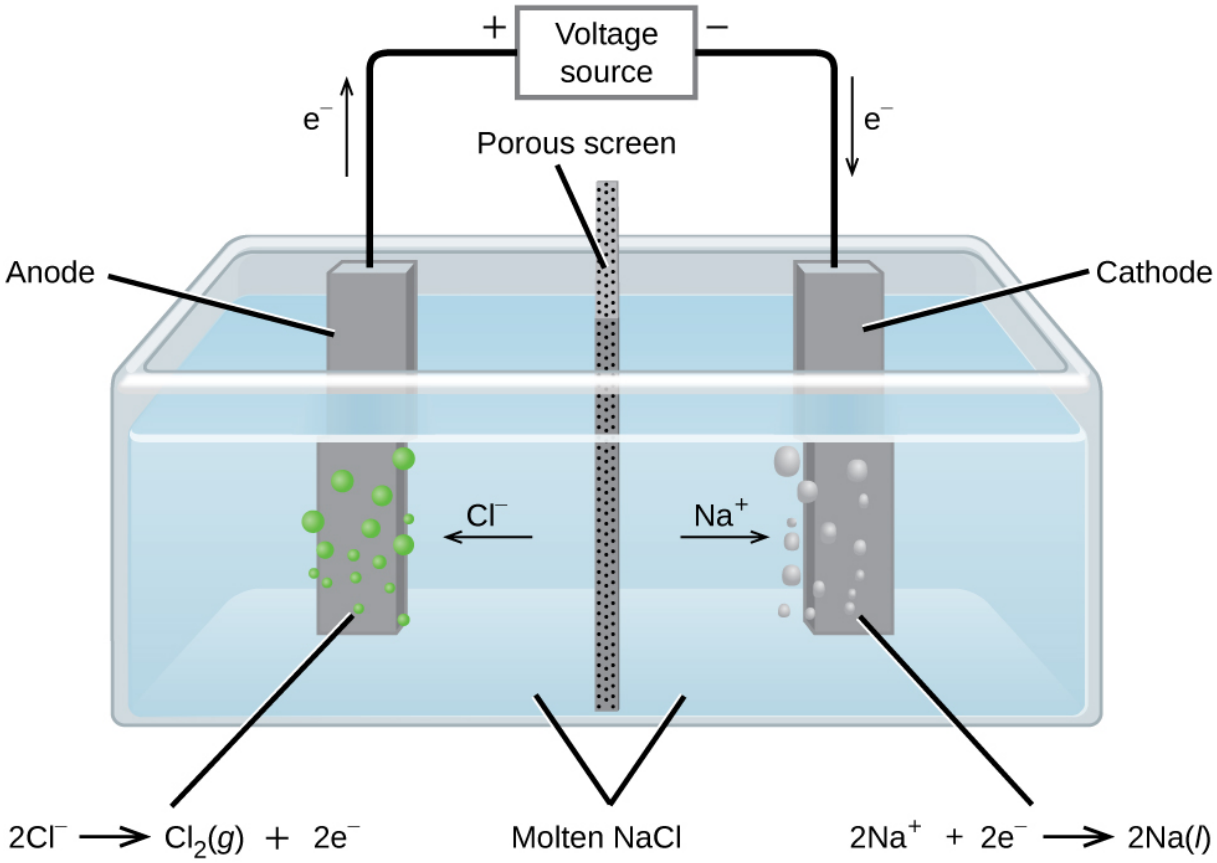
Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl(*l*). The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in Figure 38.11. The reactions associated with this process are:

$$\text{anode:} \quad 2Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$$
$$\text{cathode:} \quad Na^+(l) + e^- \longrightarrow Na(l)$$
$$\text{cell:} \quad 2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(l) + Cl_2(g)$$

The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, *a positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

Figure 38.11

Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the Downs process for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.



38.8 The Electrolysis of Water

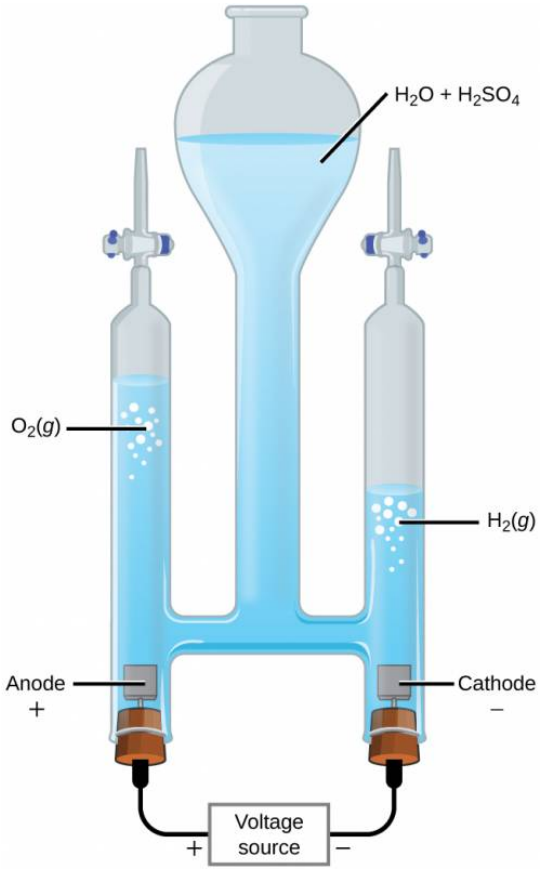
Water may be electrolytically decomposed in a cell similar to the one illustrated in Figure 38.12. To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are

$$\begin{aligned}
&\text{anode:} && 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- && E^\circ_{\text{anode}} &= +1.229\ \text{V}\\
&\text{cathode:} && 2H^+(aq) + 2e^- \longrightarrow H_2(g) && E^\circ_{\text{cathode}} &= 0\ \text{V}\\
&\text{cell:} && 2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) && E^\circ_{\text{cell}} &= -1.229\ \text{V}
\end{aligned}$$

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

Figure 38.12

The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.



38.9 The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O, H^+, OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

$$\begin{aligned}
&\text{(i)}\ 2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- && E^\circ_{\text{anode}} &= +1.35827\ \text{V}\\
&\text{(ii)}\ 2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- && E^\circ_{\text{anode}} &= +1.229\ \text{V}
\end{aligned}$$

The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (−1.229 V) than chloride ion (−1.358 V). Thermodynamics thus predicts that water would be more readily oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:

$$\begin{aligned} \text{(iii)}\ 2\mathrm{H^+}(aq) + 2\mathrm{e^-} &\longrightarrow \mathrm{H_2}(g) & E^\circ_{\text{cathode}} &= 0\ \text{V} \\ \text{(iv)}\ 2\mathrm{H_2O}(l) + 2\mathrm{e^-} &\longrightarrow \mathrm{H_2}(g) + 2\mathrm{OH^-}(aq) & E^\circ_{\text{cathode}} &= -0.8277\ \text{V} \\ \text{(v)}\ \mathrm{Na^+}(aq) + \mathrm{e^-} &\longrightarrow \mathrm{Na}(s) & E^\circ_{\text{cathode}} &= -2.71\ \text{V} \end{aligned}$$

Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1 *M* (approximately 10^{-7} *M*), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then

$$\text{cell:}\ 2\mathrm{H_2O}(l) + 2\mathrm{Cl^-}(aq) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) + 2\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cell}} = -2.186\ \text{V}$$

This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

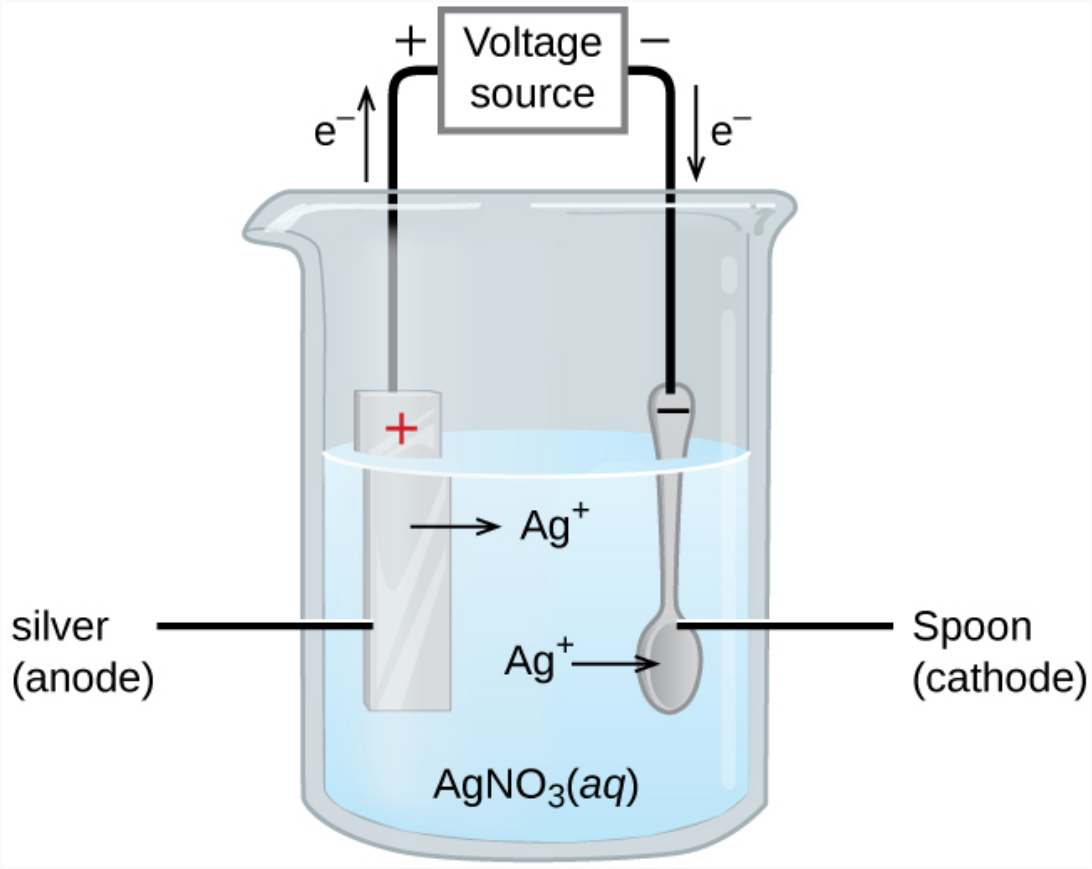
38.9.1 CHEMISTRY IN EVERYDAY LIFE

Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. The silver plating of eating utensils is used here to illustrate the process. (Figure 38.13).

Figure 38.13

This schematic shows an electrolytic cell for silver plating eating utensils.



In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. Applying a sufficient potential results in the oxidation of the silver anode

$$\text{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^{+}(aq) + \mathrm{e}^{-}$$

and reduction of silver ion at the (spoon) cathode:

$$\text{cathode: } \mathrm{Ag}^{+}(aq) + \mathrm{e}^{-} \longrightarrow \mathrm{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

38.10 Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow for any charged species. Most relevant to this discussion is the flow of electrons. Current is measured in a composite unit called an ampere, defined as one coulomb per second (A = 1 C/s). The charge transferred, *Q*, by passage of a constant current, *I*, over a specified time interval, *t*, is then given by the simple mathematical product

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved. For example, the generic reduction process

$$\mathrm{M}^{\mathrm{n}+}(aq) + \mathrm{ne}^{-} \longrightarrow \mathrm{M}(s)$$

involves the transfer of *n* mole of electrons. The charge transferred is, therefore,

$$Q = nF$$

where *F* is Faraday's constant, the charge in coulombs for one mole of electrons. If the reaction takes place in an electrochemical cell, the current flow is conveniently measured, and it may be used to assist in stoichiometric calculations related to the cell reaction.

EXAMPLE 38.10.1

Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\ \text{C}}{\text{s}} \times 1\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{60\ \text{s}}{\text{min}}}{96{,}485\ \text{C/mol e}^-} = \frac{36{,}830\ \text{C}}{96{,}485\ \text{C/mol e}^-} = 0.3817\ \text{mol e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } Ag^+(aq) + e^- \longrightarrow Ag(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817\ \text{mol e}^- \times \frac{1\ \text{mol Ag}}{1\ \text{mol e}^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 41.19\ \text{g Ag}$$

Check Your Learning

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer

$Al^{3+}(aq) + 3\ e^- \longrightarrow Al(s);$

0.0777 mol Al = 2.10 g Al.

EXAMPLE 38.10.2

Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution

First, compute the volume of chromium that must be produced (equal to the product of surface area and thickness):

$$\text{volume} = (0.010\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}}) \times (3.3\ \text{m}^2 \times (\frac{10{,}000\ \text{cm}^2}{1\ \text{m}^2})) = 33\ \text{cm}^3$$

Use the computed volume and the provided density to calculate the molar amount of chromium required:

$$\text{mass} = \text{volume} \times \text{density} = 33\ \text{cm}^3 \times \frac{7.19\ \text{g}}{\text{cm}^3} = 237\ \text{g Cr}$$

$$\text{mol Cr} = 237\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} = 4.56\ \text{mol Cr}$$

The stoichiometry of the chromium(III) reduction process requires three moles of electrons for each mole of chromium(0) produced, and so the total charge required is:

$$Q = 4.56\ \text{mol Cr} \times \frac{3\ \text{mol e}^-}{1\ \text{mol Cr}} \times \frac{96485\ \text{C}}{\text{mol e}^-} = 1.32 \times 10^6\ \text{C}$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\ \text{C}}{33.46\ \text{C/s}} = 3.95 \times 10^4\ \text{s} = 11.0\ \text{hr}$$

Check Your Learning

What mass of zinc is required to galvanize the top of a 3.00 m

×

5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

11.8 kg Zn requires 382 hours.

Files

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Flowers, P., et al. (2019). Chemistry: Atoms First 2e. https://openstax.org/details/books/chemistry-atoms-first-2e (16.5-16.7)

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39

Metals, Alloys and Semiconductors

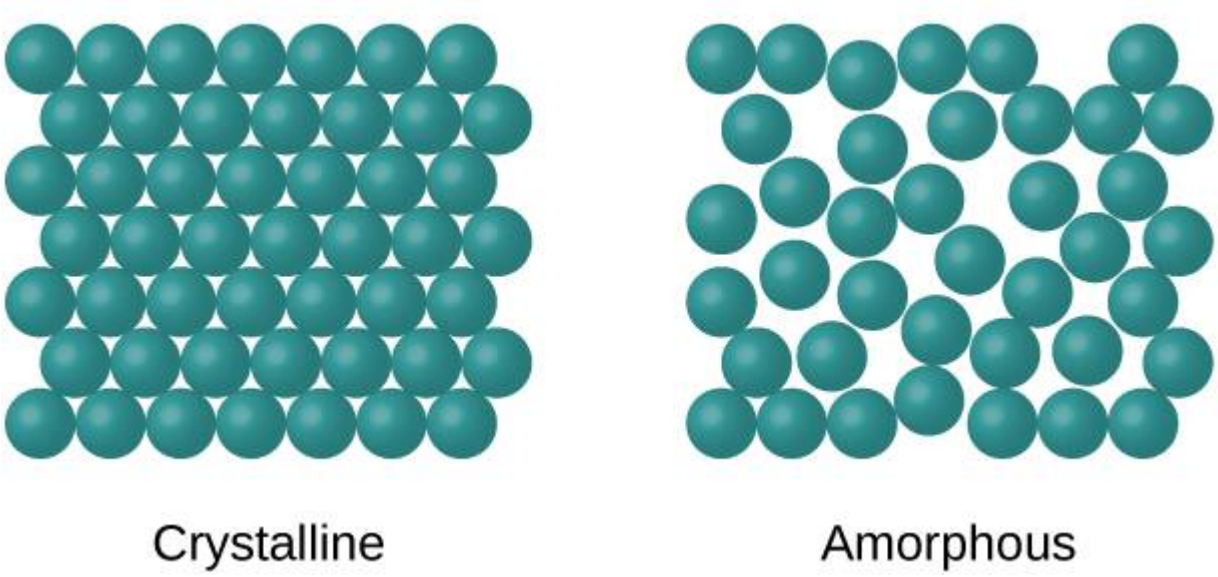
Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips. The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures. The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell. The type of structure and dimensions of the unit cell can be determined by X-ray diffraction measurements.

39.1 The Solid State of Matter

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure 39.1).

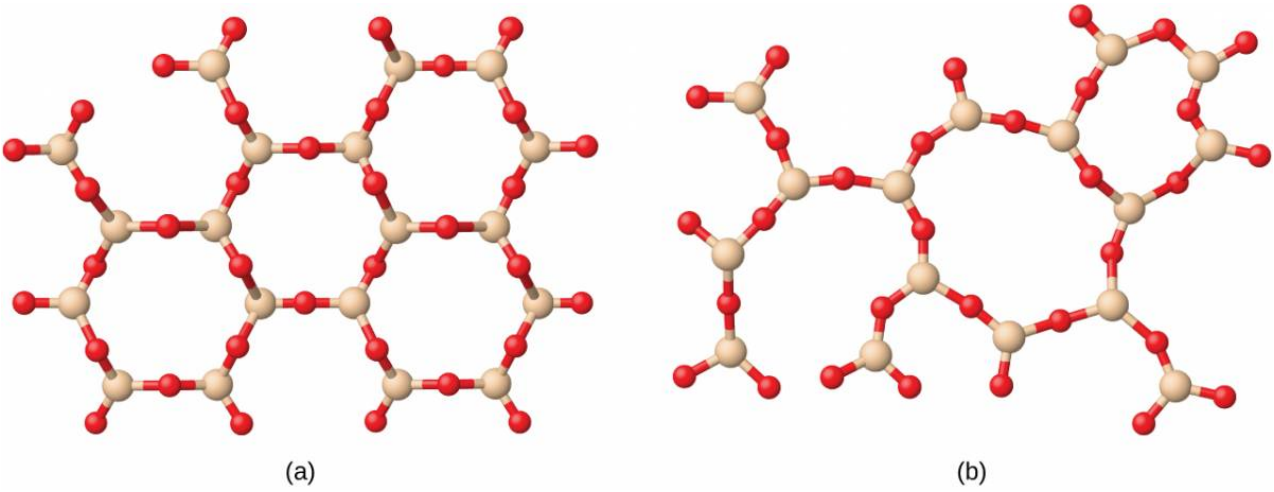
Figure 39.1

The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).



Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as silicon dioxide (shown in Figure 39.2), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

Figure 39.2
(a) Silicon dioxide, SiO_2, is abundant in nature as one of several crystalline forms of the mineral quartz. (b) Rapid cooling of molten SiO_2 yields an amorphous solid known as "fused silica".



Crystalline solids are generally classified according to the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

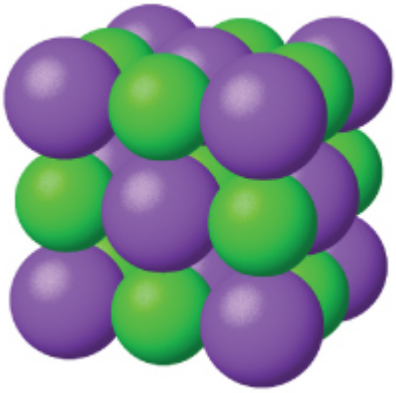
39.1.1 Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure 39.3). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they

shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

Figure 39.3

Sodium chloride is an ionic solid.

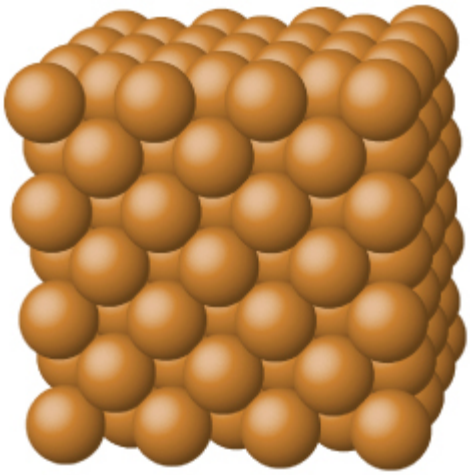


39.1.2 Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 39.4. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

Figure 39.4

Copper is a metallic solid.

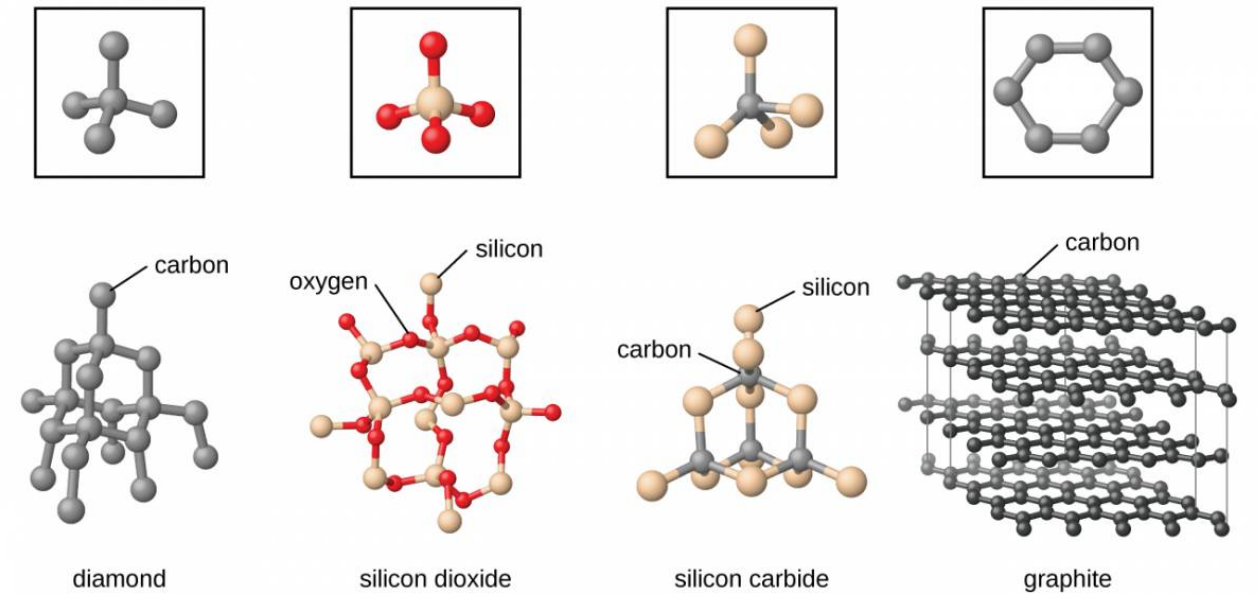


39.1.3 Covalent Network Solid

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure 39.5. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

Figure 39.5

A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

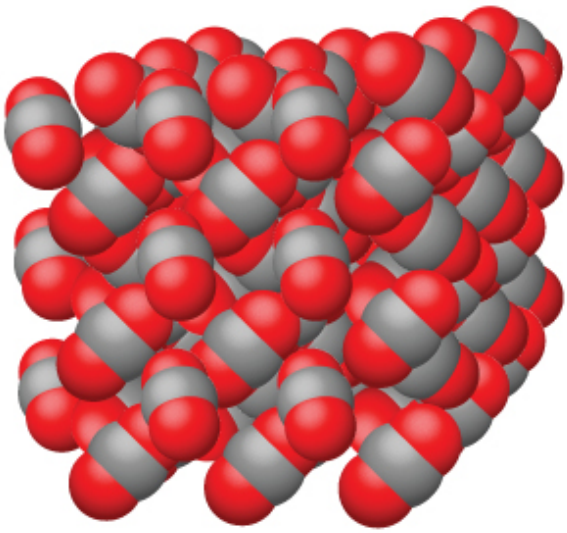


39.1.4 Molecular Solid

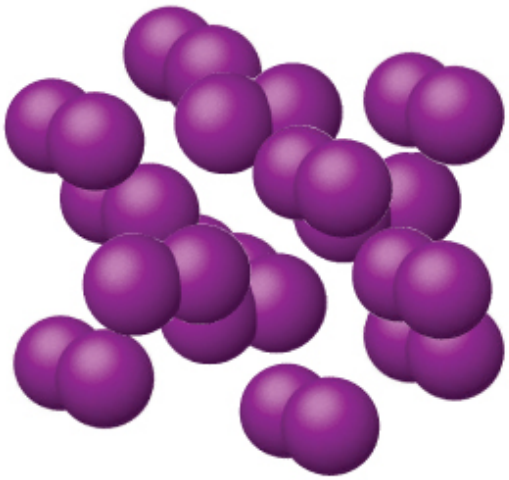
Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 39.6, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

Figure 39.6

Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.



carbon dioxide



iodine

39.1.5 Properties of Solids

A crystalline solid, like those listed in Table 39.1, has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table 39.7

Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

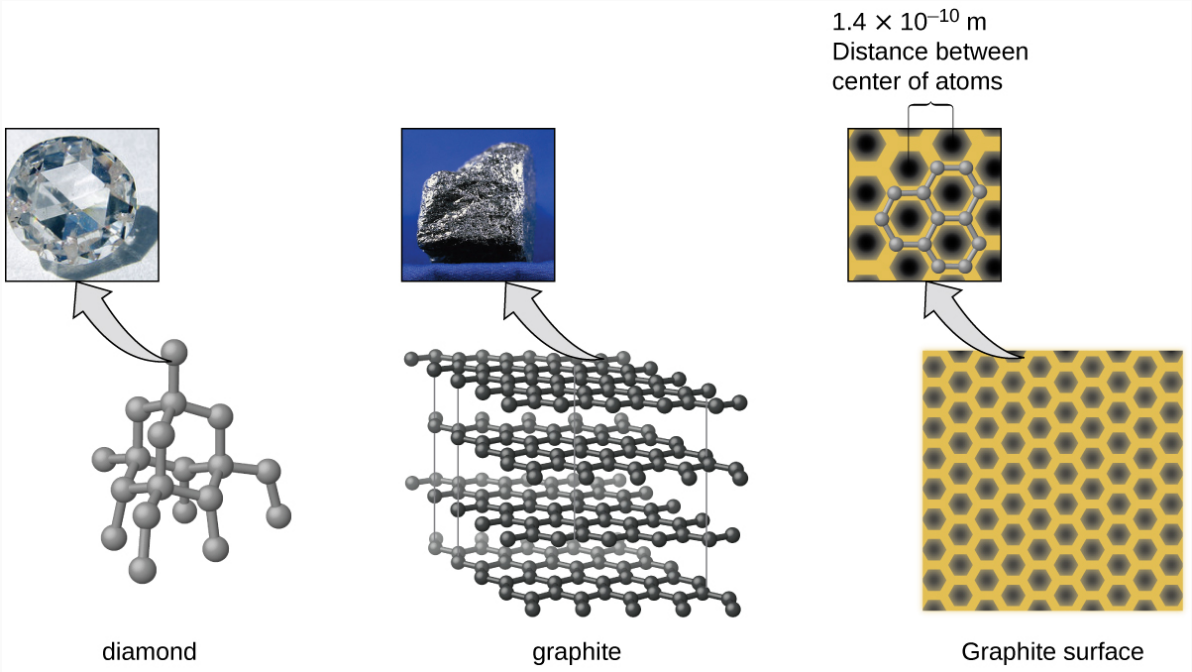
39.1.6 HOW SCIENCES INTERCONNECT

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 39.7. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

Figure 39.8

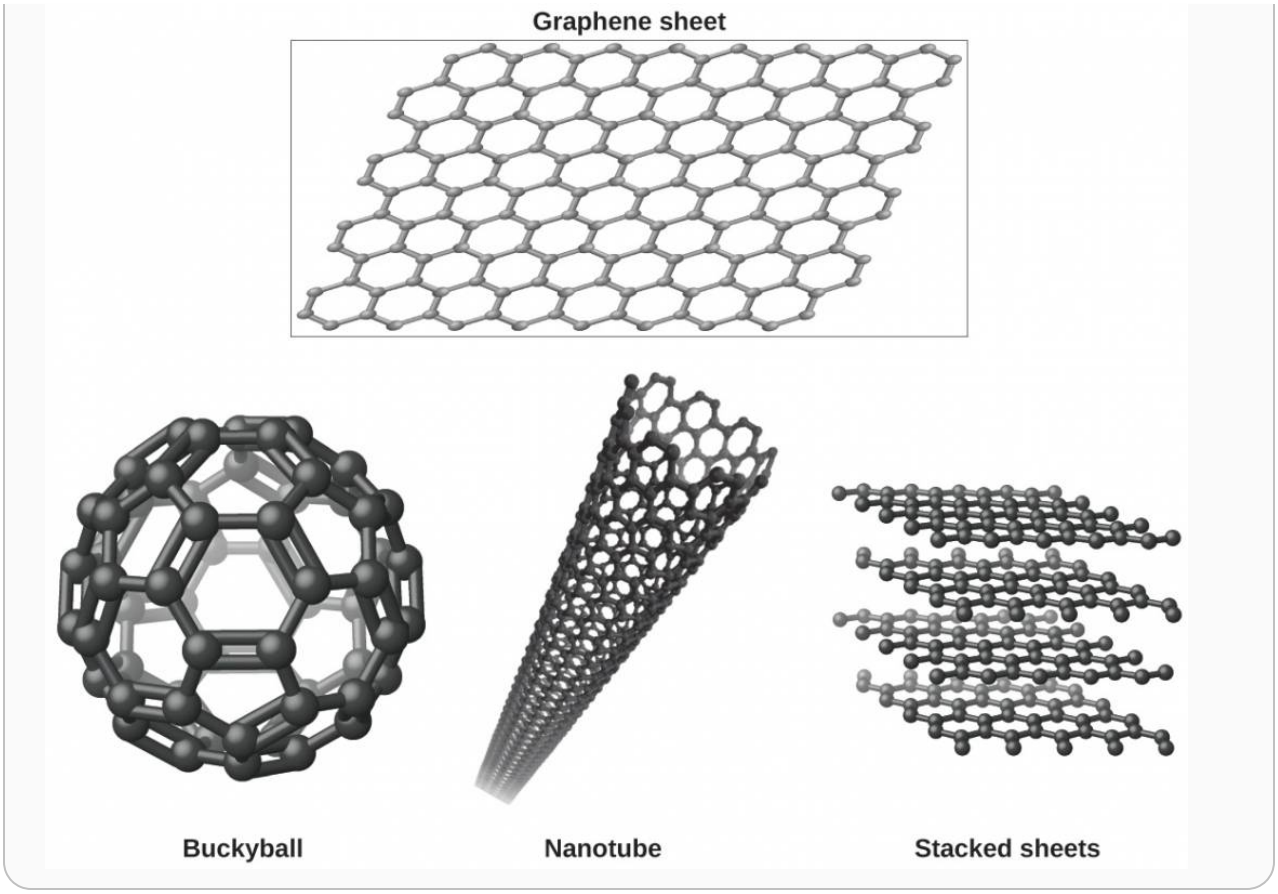
Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)



You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure 39.8, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

Figure 39.9

Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

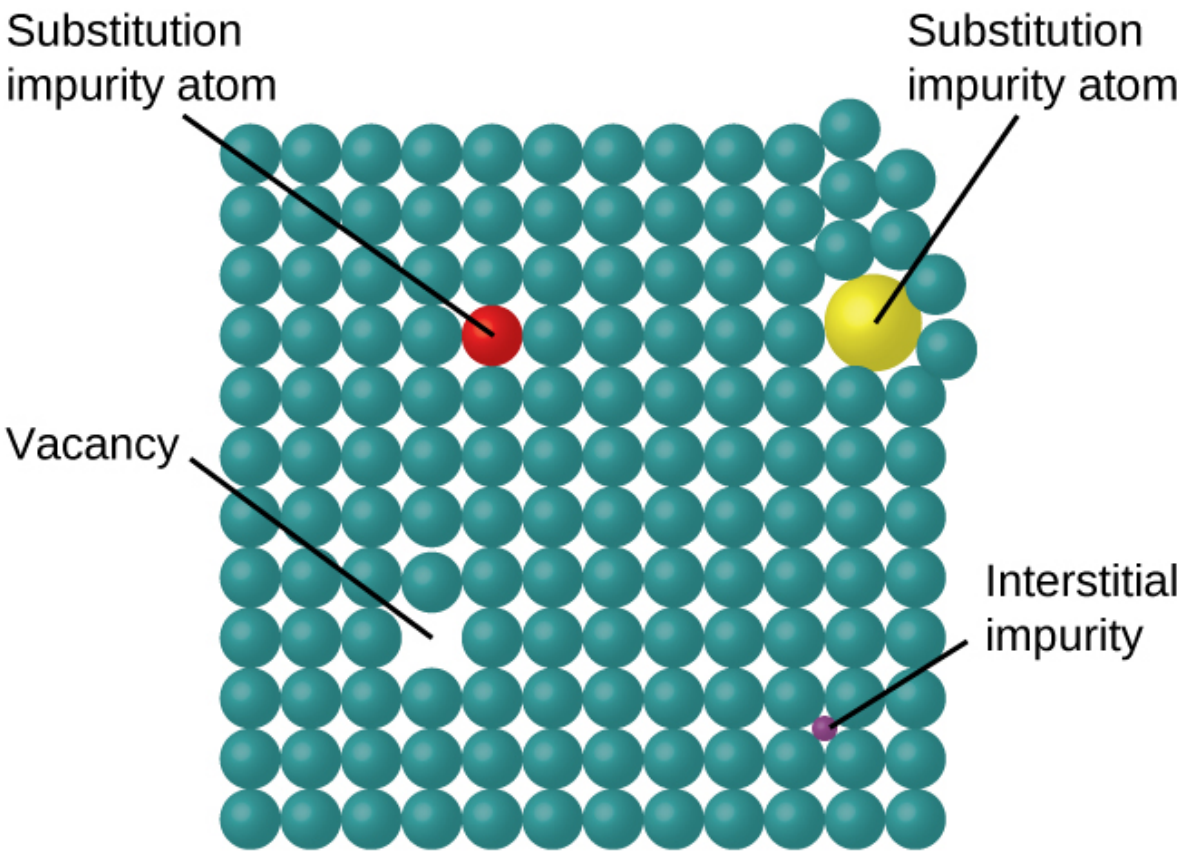


39.1.7 Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure 39.9. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

Figure 39.10

Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.



39.2 Lattice Structures in Crystalline Solids

Learning Objectives

By the end of this section, you will be able to:

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

39.2.1 The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially

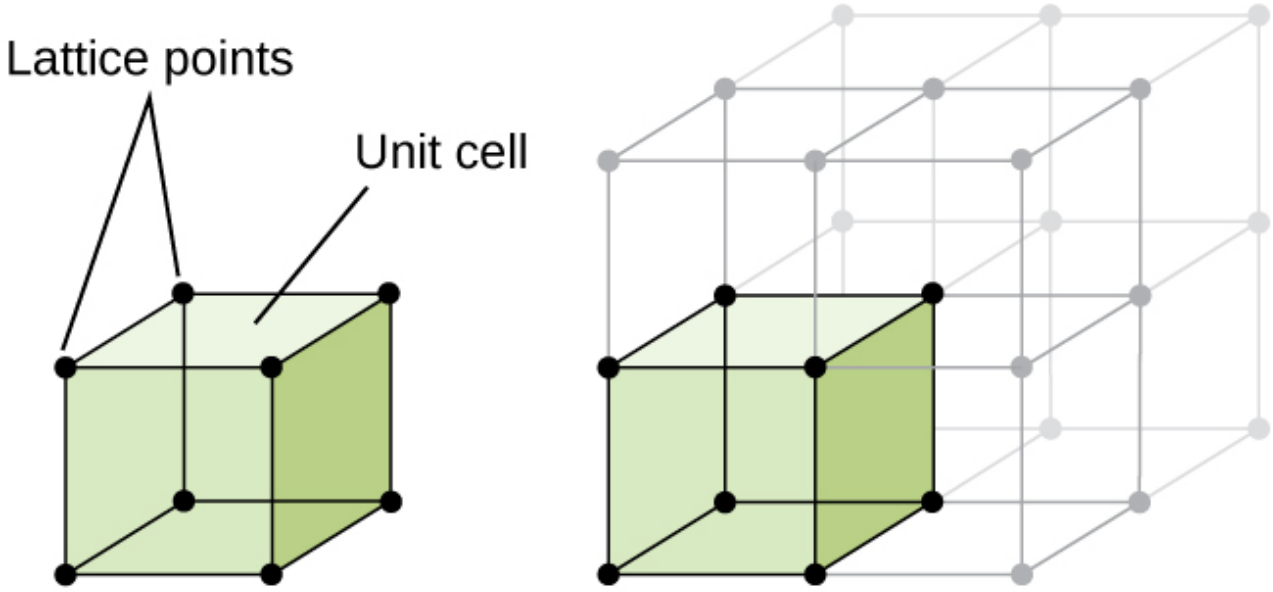
depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

39.2.2 Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its unit cell. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in Figure 39.10.

Figure 39.11

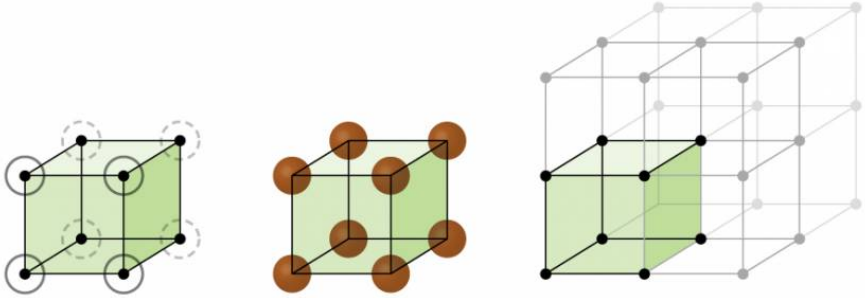
A unit cell shows the locations of lattice points repeating in all directions.



Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in Figure 39.11. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

Figure 39.12

When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

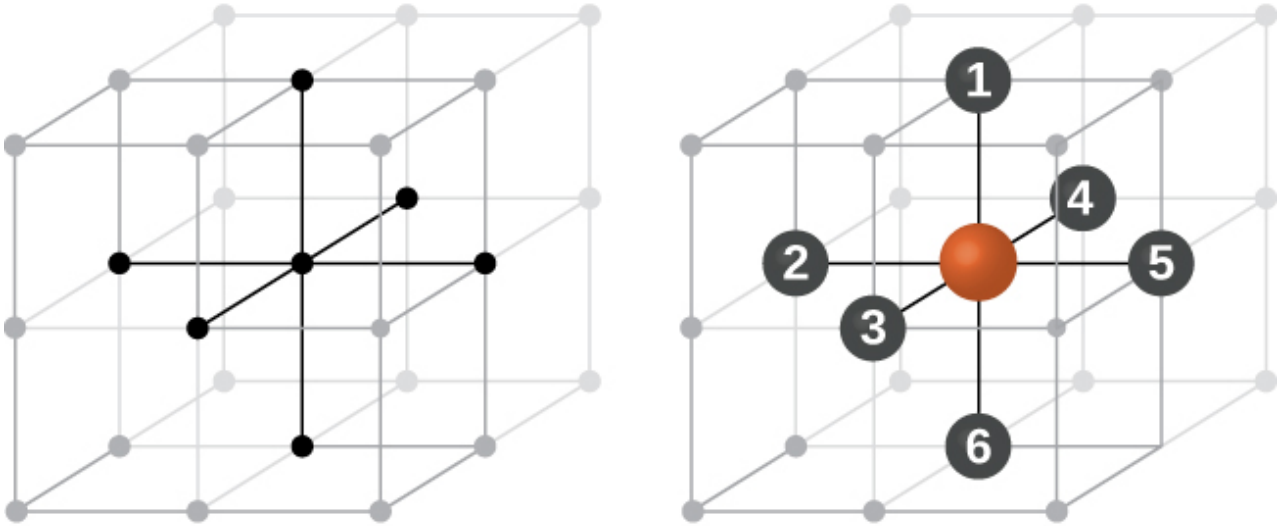


In a simple cubic structure, the spheres are not packed as closely as they could be, and they only “fill” about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a

simple cubic structure. As shown in Figure 39.12, a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its coordination number. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

Figure 39.13

An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.



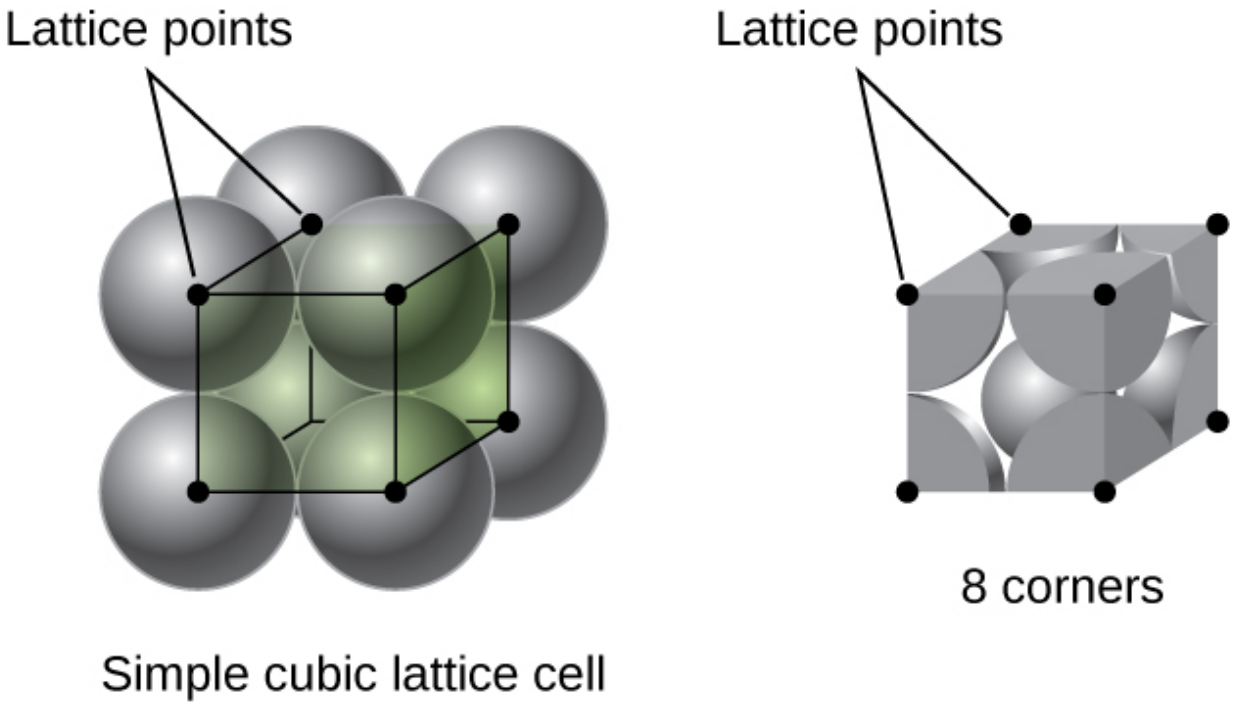
In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in Figure 39.13. Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight "corners," there is

$$8 \times \frac{1}{8} = 1$$

atom within one simple cubic unit cell.

Figure 39.14

A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.



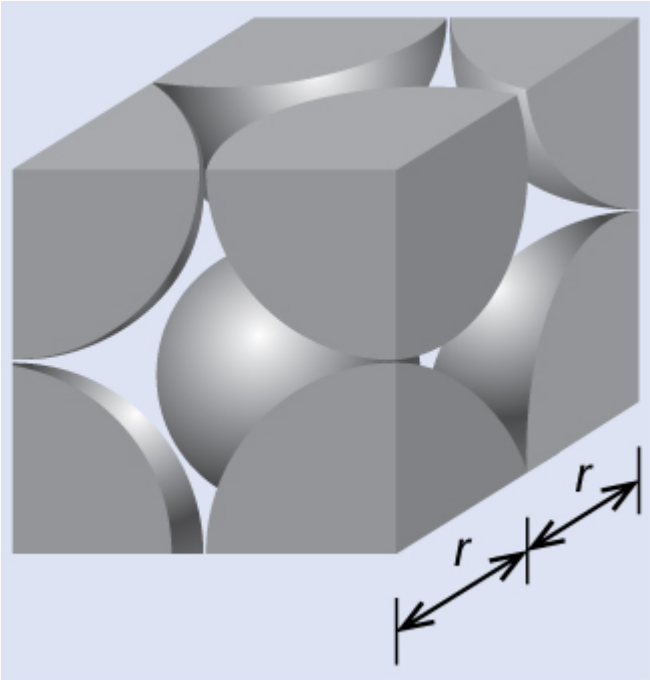
Simple cubic lattice cell

EXAMPLE 39.2.3

Calculation of Atomic Radius and Density for Metals, Part 39.2.3.1

The edge length of the unit cell of alpha polonium is 336 pm.
(a) Determine the radius of a polonium atom.

(b) Determine the density of alpha polonium.



Solution

Alpha polonium crystallizes in a simple cubic unit cell:
(a) Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is

$$r = \frac{l}{2} = \frac{336\ \text{pm}}{2} = 168\ \text{pm}.$$

(b) Density is given by

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

The density of polonium can be found by determining the density of its unit cell (the mass contained within a unit cell divided by the volume of the unit cell). Since a Po unit cell contains one-eighth of a Po atom at each of its eight corners, a unit cell contains one Po atom.

The mass of a Po unit cell can be found by:

$$1 \text{ Po unit cell} \times \frac{1 \text{ Po atom}}{1 \text{ Po unit cell}} \times \frac{1 \text{ mol Po}}{6.022 \times 10^{23} \text{ Po atoms}} \times \frac{208.998 \text{ g}}{1 \text{ mol Po}} = 3.47 \times 10^{-22} \text{ g}$$

The volume of a Po unit cell can be found by:

$$V = l^3 = (336 \times 10^{-10} \text{ cm})^3 = 3.79 \times 10^{-23} \text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Therefore, the density of

$$\text{Po} = \frac{3.471 \times 10^{-22} \text{ g}}{3.79 \times 10^{-23} \text{ cm}^3} = 9.16 \text{ g/cm}^3$$

Check Your Learning

The edge length of the unit cell for nickel is 0.3524 nm. The density of Ni is 8.90 g/cm^3. Does nickel crystallize in a simple cubic structure? Explain.

Answer

No. If Ni was simple cubic, its density would be given by:

$$1 \text{ Ni atom} \times \frac{1 \text{ mol Ni}}{6.022 \times 10^{23} \text{ Ni atoms}} \times \frac{58.693 \text{ g}}{1 \text{ mol Ni}} = 9.746 \times 10^{-23} \text{ g}$$

$$V = l^3 = (3.524 \times 10^{-8} \text{ cm})^3 = 4.376 \times 10^{-23} \text{ cm}^3$$

Then the density of Ni would be

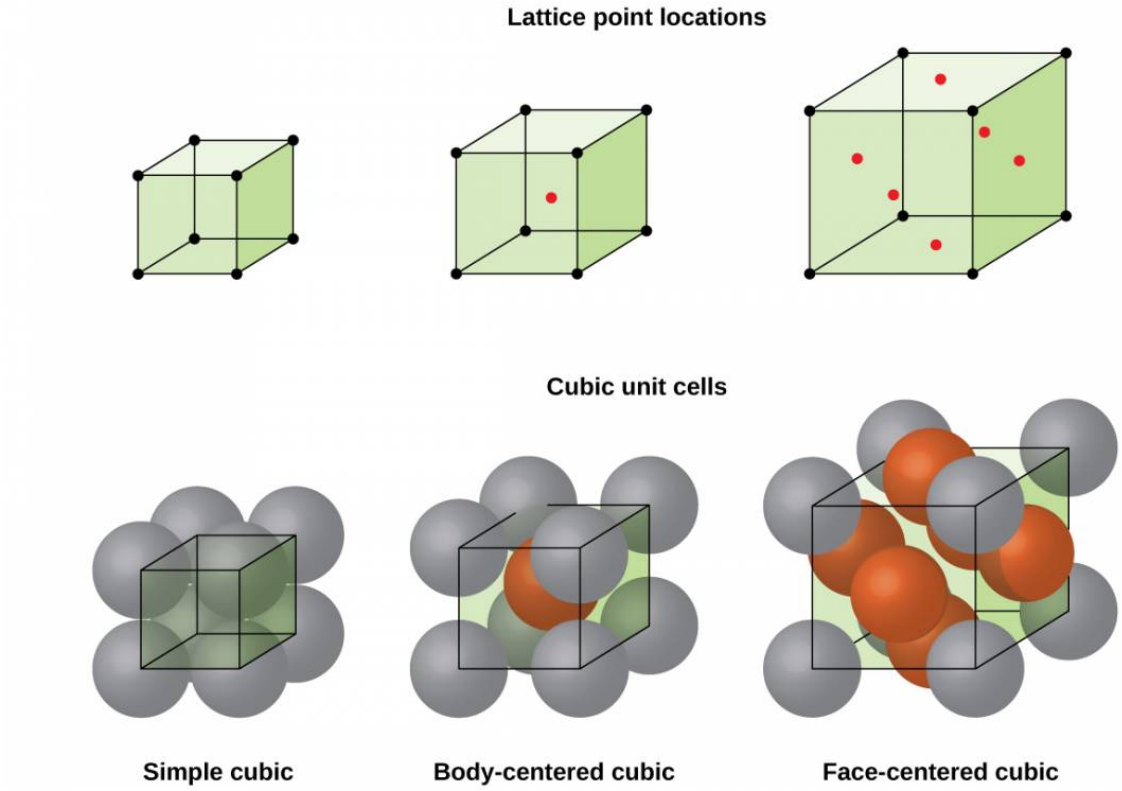
$$= \frac{9.746 \times 10^{-23} \text{ g}}{4.376 \times 10^{-23} \text{ cm}^3} = 2.23 \text{ g/cm}^3$$

Since the actual density of Ni is not close to this, Ni does not form a simple cubic structure.

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic (which we have already seen), body-centered cubic unit cell, and face-centered cubic unit cell—all of which are illustrated in Figure 39.14. (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. We leave the more complicated geometries for later in this module.)

Figure 39.15

Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.



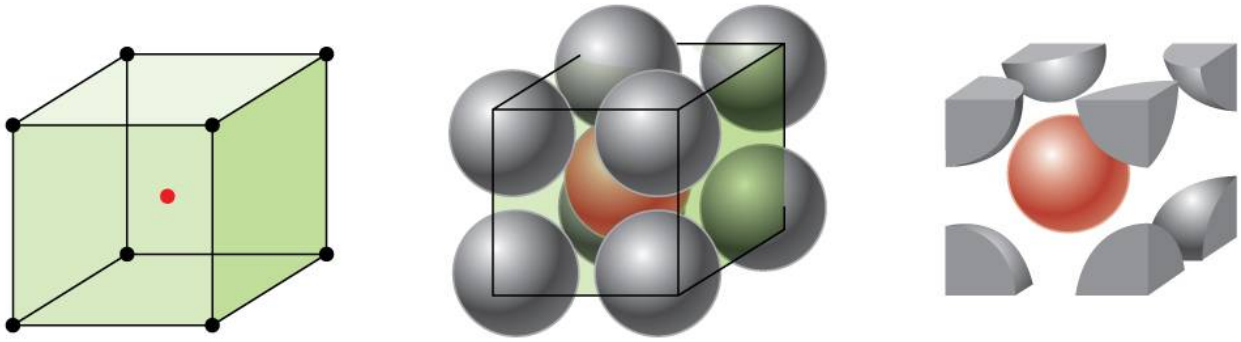
Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in Figure 39.15. This is called a body-centered cubic (BCC) solid. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners

$$(8 \times \tfrac{1}{8} = 1$$

atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.

Figure 39.16

In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.



Body-centered cubic structure

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be isomorphous.)

Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in Figure 39.16. This arrangement is called a face-centered cubic (FCC) solid. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners

$$(8 \times \tfrac{1}{8} = 1$$

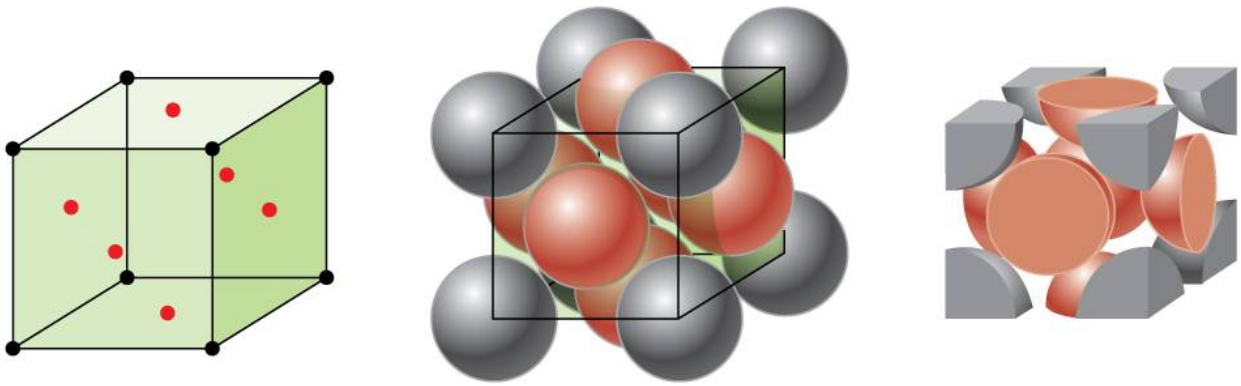
atom from the corners) and one-half of an atom on each of the six faces

$$(6 \times \tfrac{1}{2} = 3$$

atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.

Figure 39.17

A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.



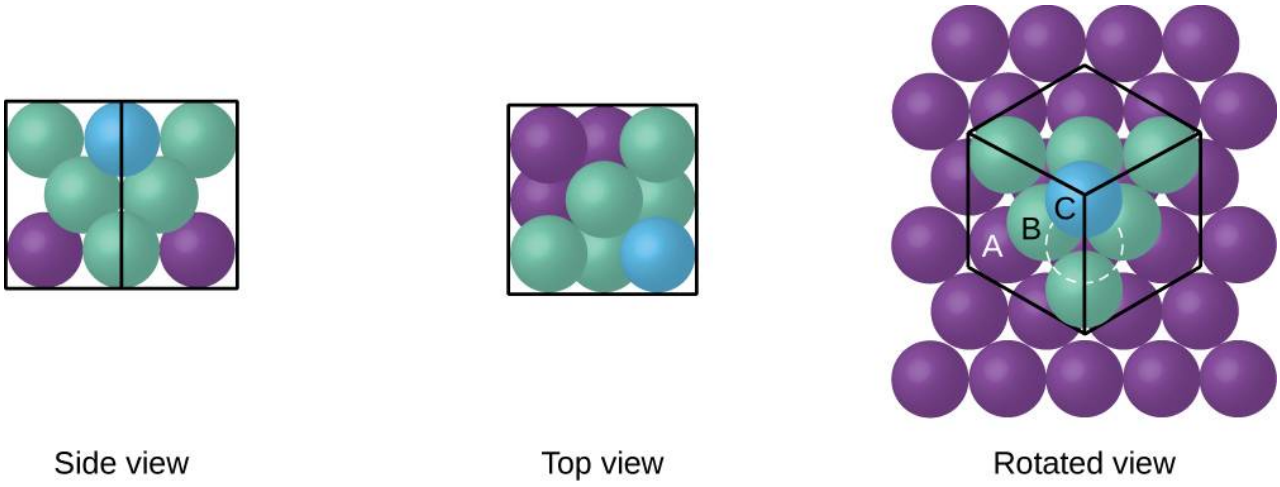
Face-centered cubic structure

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called cubic closest packing (CCP). In CCP, there are three repeating layers of hexagonally

arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in Figure 39.17.

Figure 39.18

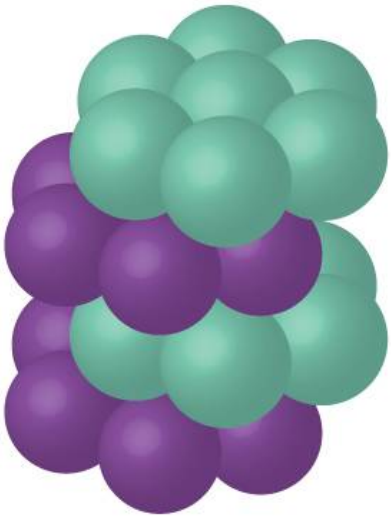
A CCP arrangement consists of three repeating layers (ABCABC…) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.



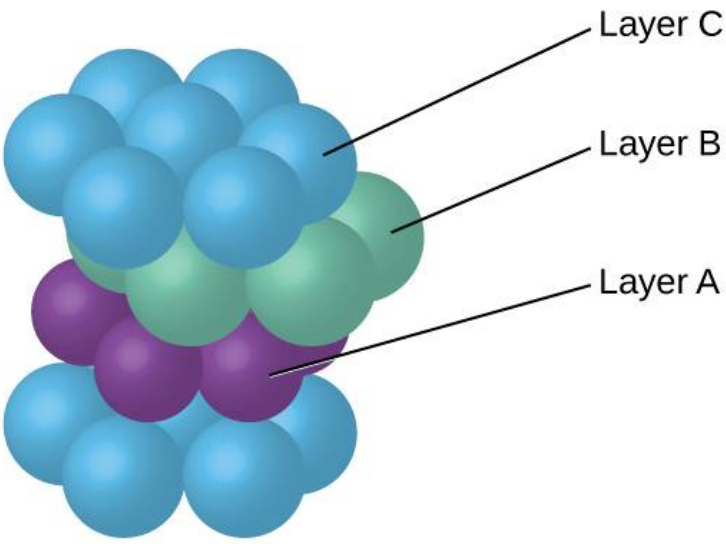
Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and hexagonal closest packing (HCP) shown in Figure 39.18. Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB⋯). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC⋯). About two–thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.

Figure 39.19

In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB…). Cubic closest packing consists of three alternating layers (ABCABCABC…).



Hexagonal closest packed



Cubic closest packed

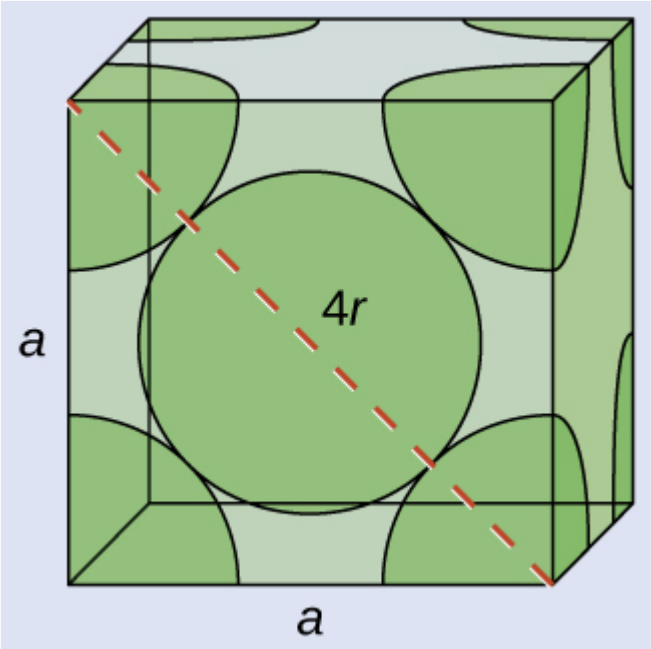
EXAMPLE 39.2.4

Calculation of Atomic Radius and Density for Metals, Part 39.2.4.1

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm.
(a) What is the atomic radius of Ca in this structure?

(b) Calculate the density of Ca.

Solution



(a) In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii (d = 4*r*). Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

$$a^2 + a^2 = d^2 \longrightarrow (558.8\text{ pm})^2 + (558.5\text{ pm})^2 = (4r)^2$$

Solving this gives

$$r = \frac{\sqrt{(558.8\text{ pm})^2 + (558.5\text{ pm})^2}}{16} = 197.6\text{ pm for a Ca radius}.$$

(b) Density is given by

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

The density of calcium can be found by determining the density of its unit cell: for example, the mass contained within a unit cell divided by the volume of the unit cell. A face-centered Ca unit cell has one-eighth of an atom at each of the eight corners

$(8 \times \frac{1}{8} = 1$

atom) and one-half of an atom on each of the six faces

$6 \times \frac{1}{2} = 3$

atoms), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

$$1 \text{ Ca unit cell} \times \frac{4 \text{ Ca atoms}}{1 \text{ Ca unit cell}} \times \frac{1 \text{ mol Ca}}{6.022 \times 10^{23} \text{ Ca atoms}} \times \frac{40.078 \text{ g}}{1 \text{ mol Ca}} = 2.662 \times 10^{-22} \text{ g}$$

The volume of a Ca unit cell can be found by:

$$V = a^3 = (558.8 \times 10^{-10} \text{ cm})^3 = 1.745 \times 10^{-22} \text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of

$$\text{Ca} = \frac{2.662 \times 10^{-22} \text{ g}}{1.745 \times 10^{-22} \text{ cm}^3} = 1.53 \text{ g/cm}^3$$

Check Your Learning

Silver crystallizes in an FCC structure. The edge length of its unit cell is 409 pm.
(a) What is the atomic radius of Ag in this structure?

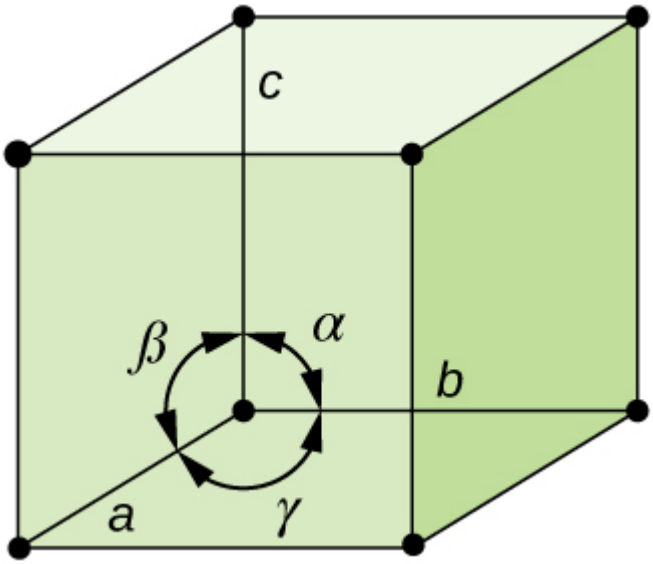
(b) Calculate the density of Ag.

Answer

(a) 144 pm; (b) 10.5 g/cm^3

In general, a unit cell is defined by the lengths of three axes (*a*, *b*, and *c*) and the angles (*α*, *β*, and *γ*) between them, as illustrated in Figure 3919. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

Figure 39.20
A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.



There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in Figure 39.20.

Figure 39.21

There are seven different lattice systems and 14 different unit cells.

System/Axes/Angles	Unit Cells
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Face-centered, Body-centered
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Body-centered
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Simple, Body-centered, Base-centered, Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Simple, Base-centered
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	

39.2.5 The Structures of Ionic Crystals

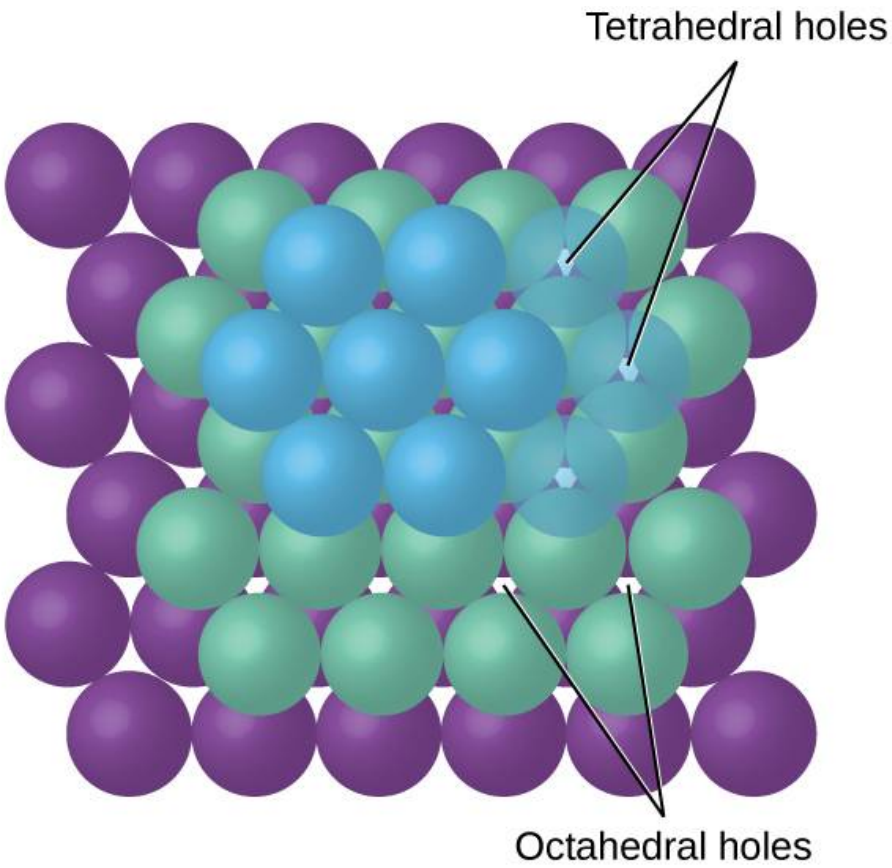
Ionic crystals consist of two or more different kinds of ions that usually have different sizes. The packing of these ions into a crystal structure is more complex than the packing of metal atoms that are the same size.

Most monatomic ions behave as charged spheres, and their attraction for ions of opposite charge is the same in every direction. Consequently, stable structures for ionic compounds result (1) when ions of one charge are surrounded by as many ions as possible of the opposite charge and (2) when the cations and anions are in contact with each other. Structures are determined by two principal factors: the relative sizes of the ions and the ratio of the numbers of positive and negative ions in the compound.

In simple ionic structures, we usually find the anions, which are normally larger than the cations, arranged in a closest-packed array. (As seen previously, additional electrons attracted to the same nucleus make anions larger and fewer electrons attracted to the same nucleus make cations smaller when compared to the atoms from which they are formed.) The smaller cations commonly occupy one of two types of holes (or interstices) remaining between the anions. The smaller of the holes is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this hole are arranged at the corners of a tetrahedron, so the hole is called a tetrahedral hole. The larger type of hole is found at the center of six anions (three in one layer and three in an adjacent layer) located at the corners of an octahedron; this is called an octahedral hole. Figure 39.21 illustrates both of these types of holes.

Figure 39.22

Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

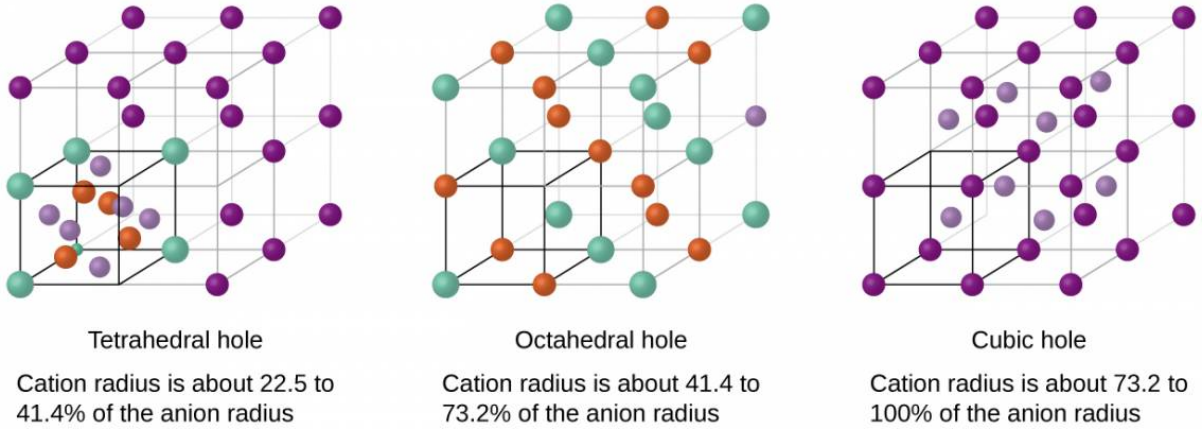


Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes, as illustrated in Figure 39.22. Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes. If the cations are too large to fit into the octahedral holes, the anions may adopt a more open

structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.

Figure 39.23

A cation's size and the shape of the hole occupied by the compound are directly related.



There are two tetrahedral holes for each anion in either an HCP or CCP array of anions. A compound that crystallizes in a closest-packed array of anions with cations in the tetrahedral holes can have a maximum cation:anion ratio of 2:1; all of the tetrahedral holes are filled at this ratio. Examples include Li_2O, Na_2O, Li_2S, and Na_2S. Compounds with a ratio of less than 2:1 may also crystallize in a closest-packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit. In these compounds, however, some of the tetrahedral holes remain vacant.

EXAMPLE 39.2.6

Occupancy of Tetrahedral Holes

Zinc sulfide is an important industrial source of zinc and is also used as a white pigment in paint. Zinc sulfide crystallizes with zinc ions occupying one-half of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of zinc sulfide?

Solution

Because there are two tetrahedral holes per anion (sulfide ion) and one-half of these holes are occupied by zinc ions, there must be

$$\frac{1}{2} \times 2,$$

or 1, zinc ion per sulfide ion. Thus, the formula is ZnS.

Check Your Learning

Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What it the formula of lithium selenide?

Answer

Li_2Se

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

EXAMPLE 39.2.7

Stoichiometry of Ionic Compounds

Sapphire is aluminum oxide. Aluminum oxide crystallizes with aluminum ions in two-thirds of the octahedral holes in a closest-packed array of oxide ions. What is the formula of aluminum oxide?

Solution

Because there is one octahedral hole per anion (oxide ion) and only two-thirds of these holes are occupied, the ratio of aluminum to oxygen must be

$\frac{2}{3}$

:1, which would give

$\mathrm{Al}_{2/3}\,\mathrm{O}$.

The simplest whole number ratio is 2:3, so the formula is Al_2O_3.

Check Your Learning

The white pigment titanium oxide crystallizes with titanium ions in one-half of the octahedral holes in a closest-packed array of oxide ions. What is the formula of titanium oxide?

Answer

TiO_2

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2, UO_2, $SrCl_2$, and CaF_2.

Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

39.2.8 Unit Cells of Ionic Compounds

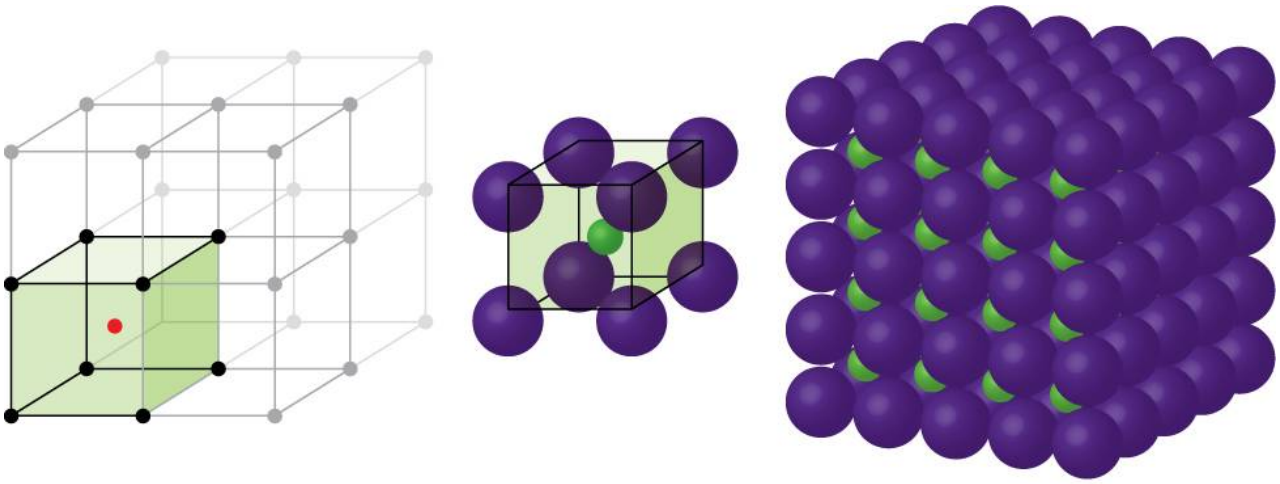
Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic structures.

When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (illustrated in Figure 39.23) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit cells. One cesium ion and one chloride ion are present per unit cell, giving the l:l stoichiometry

required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.

Figure 39.24

Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.



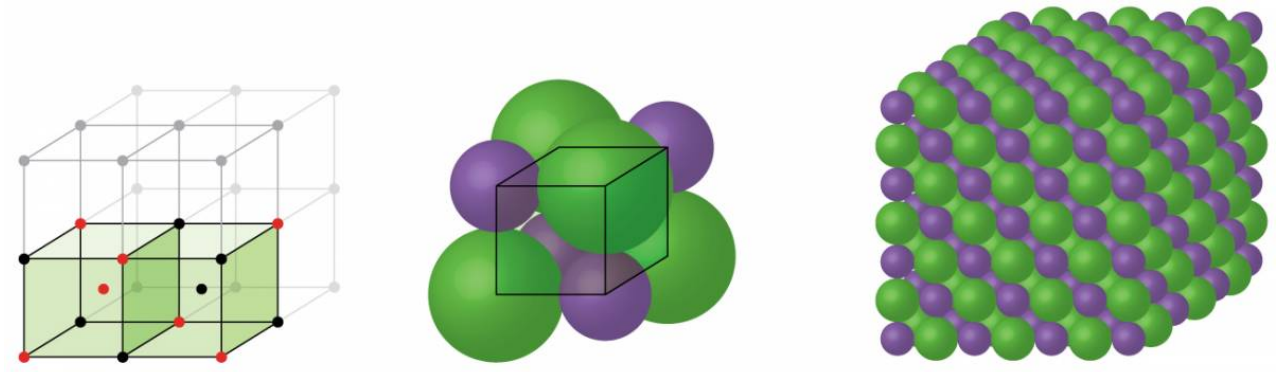
Simple cubic structure

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in Figure 39.24. Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.

Figure 39.25

Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes.

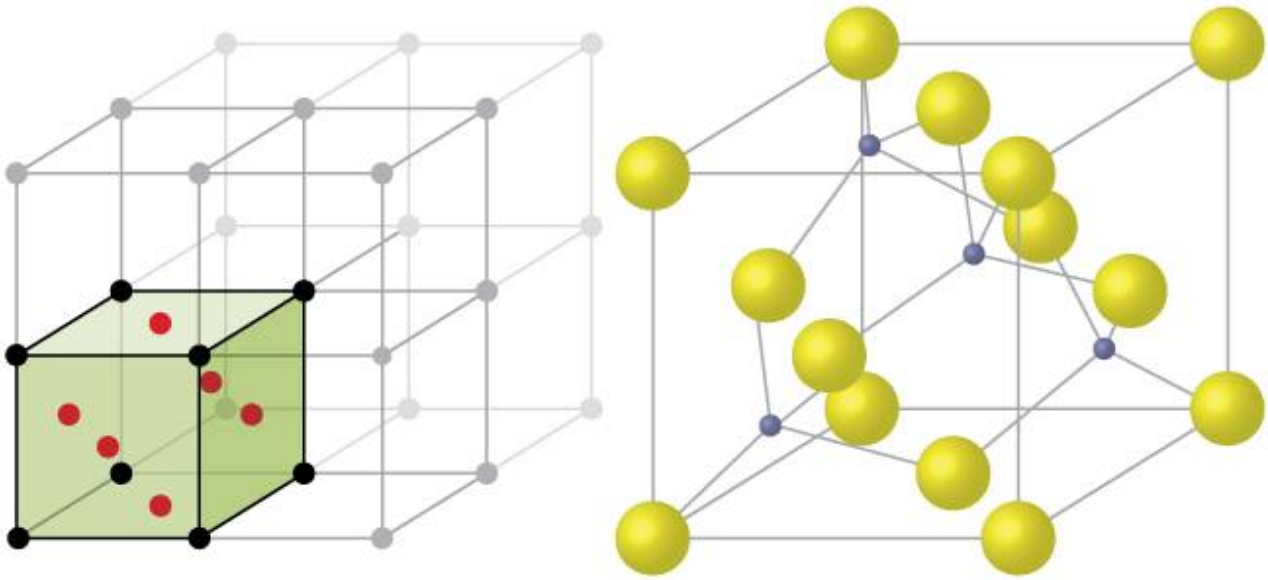


Face-centered simple cubic structure

The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure 39.25. This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.

Figure 39.26

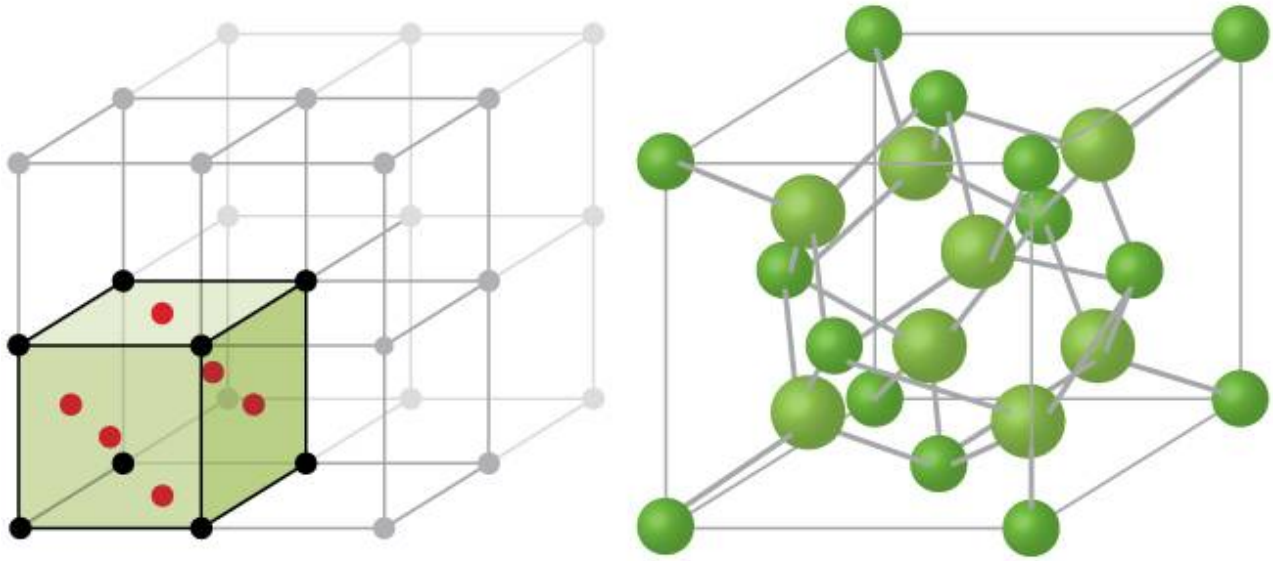
ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.



A calcium fluoride unit cell, like that shown in Figure 39.26, is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2. Close examination of Figure 39.26 will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a space lattice of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.

Figure 39.27

Calcium fluoride, CaF_2, forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.



CaF_2 face-centered unit cell

39.2.9 Calculation of Ionic Radii

If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

EXAMPLE 39.2.10

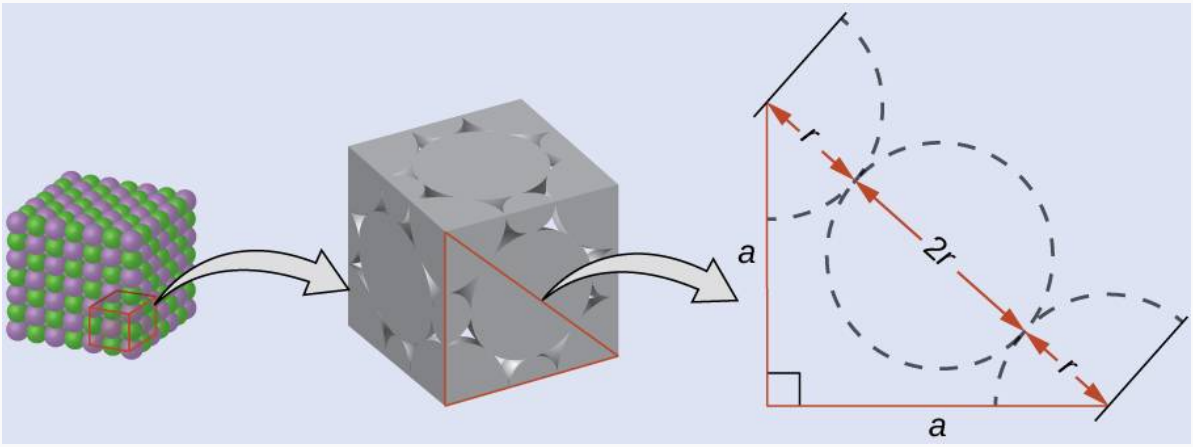
Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, as in Figure 39.24, calculate the ionic radius for the chloride ion.

Note: The length unit angstrom, Å, is often used to represent atomic-scale dimensions and is equivalent to 10^{-10} m.

Solution

On the face of a LiCl unit cell, chloride ions contact each other across the diagonal of the face:



Drawing a right triangle on the face of the unit cell, we see that the length of the diagonal is equal to four chloride radii (one radius from each corner chloride and one diameter—which equals two radii—from the chloride ion in the center of the face), so $d = 4r$. From the Pythagorean theorem, we have:

$$a^2 + a^2 = d^2$$

which yields:

$$(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2 = (4r)^2 = 16r^2$$

Solving this gives:

$$r = \frac{\sqrt{(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2}}{16} = 0.182\ \text{nm}\ (1.82\ \text{Å})\ \text{for a}\ \text{Cl}^-\ \text{radius}.$$

Check Your Learning

The edge length of the unit cell of KCl (NaCl-like structure, FCC) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the potassium ion. The radius of the chloride ion is 1.82 Å.

Answer

The radius of the potassium ion is 1.33 Å.

It is important to realize that values for ionic radii calculated from the edge lengths of unit cells depend on numerous assumptions, such as a perfect spherical shape for ions, which are approximations at best. Hence, such calculated values are themselves approximate and comparisons cannot be pushed too far. Nevertheless, this method has proved useful for calculating ionic radii from experimental measurements such as X-ray crystallographic determinations.

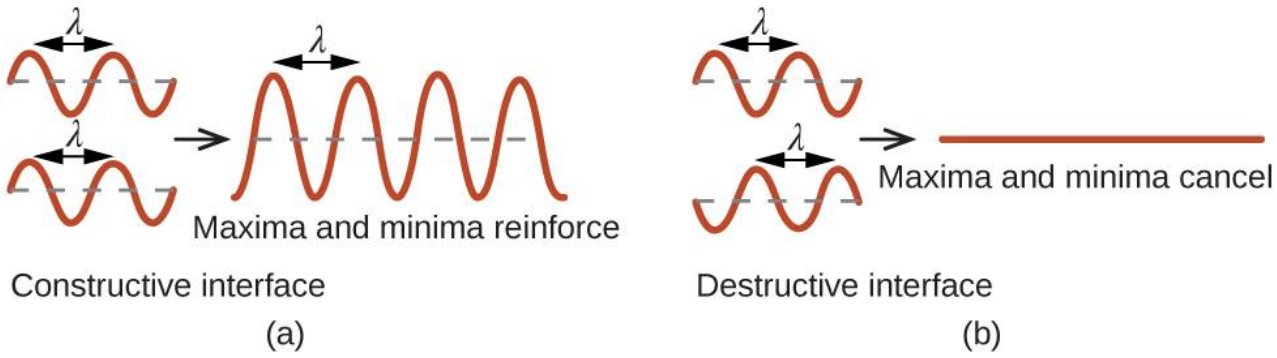
39.2.11 X-Ray Crystallography

The size of the unit cell and the arrangement of atoms in a crystal may be determined from measurements of the *diffraction* of X-rays by the crystal, termed X-ray crystallography. Diffraction is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light. X-rays are electromagnetic radiation with wavelengths about as long as the distance between neighboring atoms in crystals (on the order of a few Å).

When a beam of monochromatic X-rays strikes a crystal, its rays are scattered in all directions by the atoms within the crystal. When scattered waves traveling in the same direction encounter one another, they undergo *interference*, a process by which the waves combine to yield either an increase or a decrease in amplitude (intensity) depending upon the extent to which the combining waves' maxima are separated (see Figure 39.27).

Figure 39.28

Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.



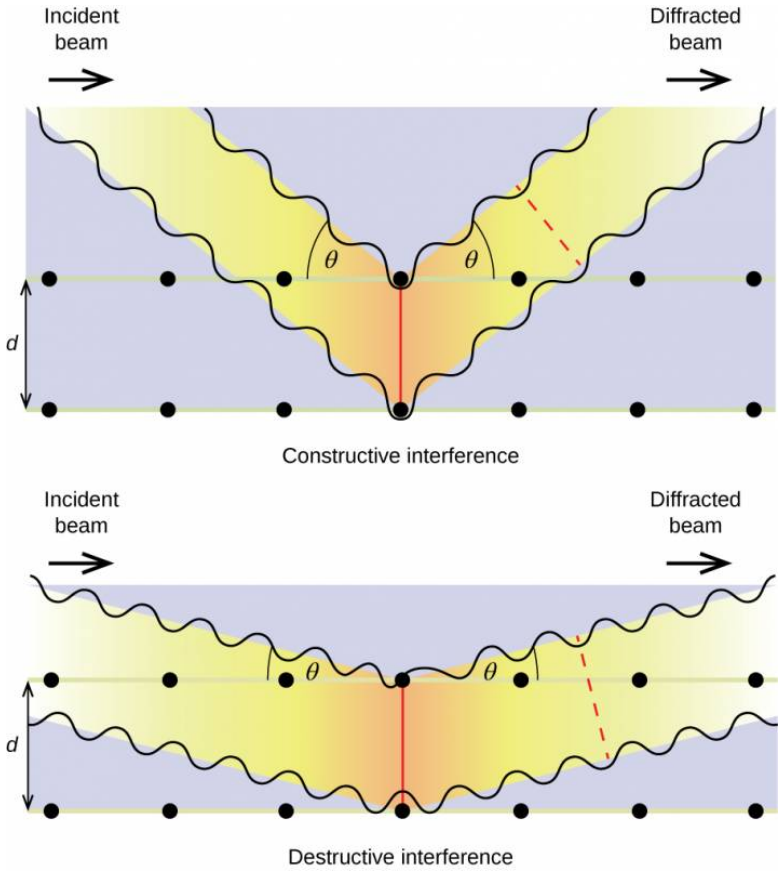
When X-rays of a certain wavelength, λ, are scattered by atoms in adjacent crystal planes separated by a distance, d, they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n, of the wavelength. This condition is satisfied when the angle of the diffracted beam, θ, is related to the wavelength and interatomic distance by the equation:

$$n\lambda = 2d \sin \theta$$

This relation is known as the Bragg equation in honor of W. H. Bragg, the English physicist who first explained this phenomenon. Figure 39.28 illustrates two examples of diffracted waves from the same two crystal planes. The figure on the left depicts waves diffracted at the Bragg angle, resulting in constructive interference, while that on the right shows diffraction and a different angle that does not satisfy the Bragg condition, resulting in destructive interference.

Figure 39.29

The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.



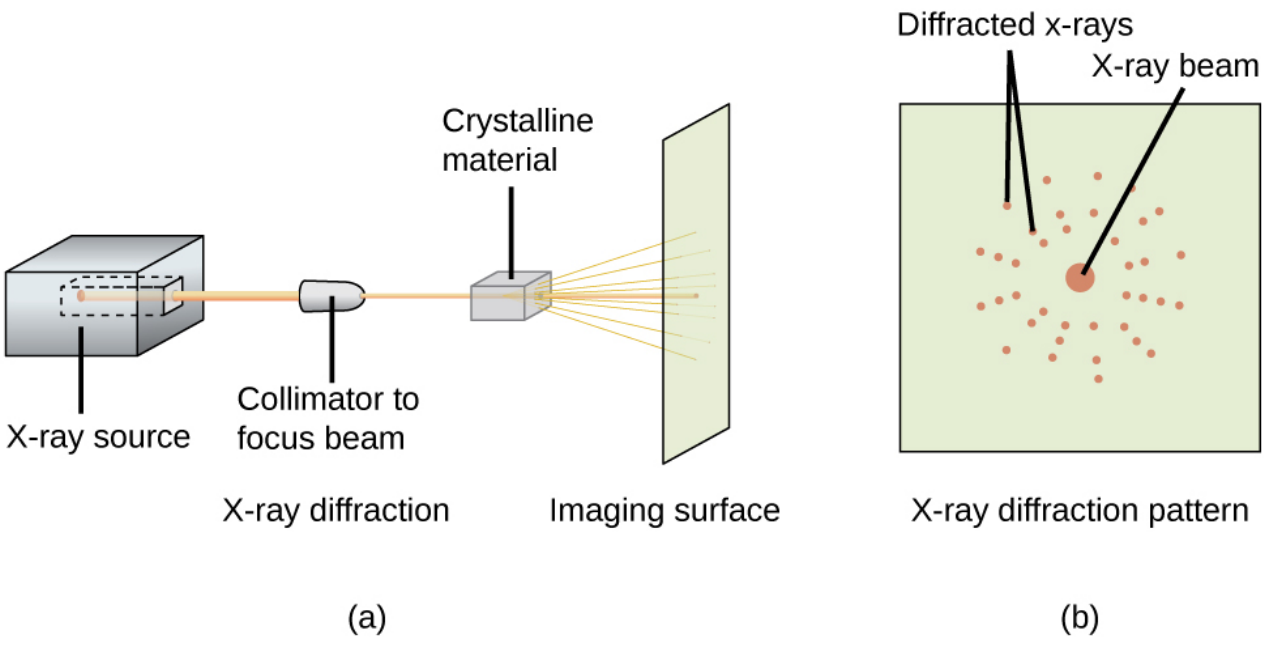
LINK TO LEARNING

Visit this site for more details on the Bragg equation and a simulator that allows you to explore the effect of each variable on the intensity of the diffracted wave.

An X-ray diffractometer, such as the one illustrated in Figure 39.29, may be used to measure the angles at which X-rays are diffracted when interacting with a crystal as described earlier. From such measurements, the Bragg equation may be used to compute distances between atoms as demonstrated in the following example exercise.

Figure 39.30

(a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.



EXAMPLE 39.2.12

Using the Bragg Equation

In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction ($n = 1$) occurred at an angle $\theta = 25.25°$. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation, $n\lambda = 2d \sin \theta$, for d.
This gives:

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{1(0.1315 \text{ nm})}{2 \sin (25.25°)} = 0.154 \text{ nm}$$

Check Your Learning

A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

Answer

10.8°

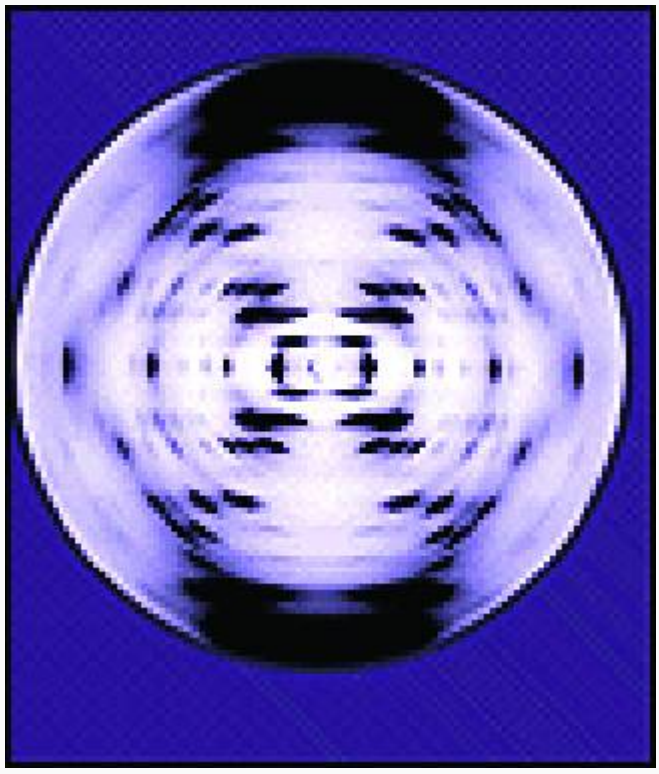
39.2.13 PORTRAIT OF A CHEMIST

X-ray Crystallographer Rosalind Franklin

The discovery of the structure of DNA in 1953 by Francis Crick and James Watson is one of the great achievements in the history of science. They were awarded the 1962 Nobel Prize in Physiology or Medicine, along with Maurice Wilkins, who provided experimental proof of DNA's structure. British chemist Rosalind Franklin made invaluable contributions to this monumental achievement through her work in measuring X-ray diffraction images of DNA. Early in her career, Franklin's research on the structure of coals proved helpful to the British war effort. After shifting her focus to biological systems in the early 1950s, Franklin and doctoral student Raymond Gosling discovered that DNA consists of two forms: a long, thin fiber formed when wet (type "B") and a short, wide fiber formed when dried (type "A"). Her X-ray diffraction images of DNA (Figure 39.30) provided the crucial information that allowed Watson and Crick to confirm that DNA forms a double helix, and to determine details of its size and structure. Franklin also conducted pioneering research on viruses and the RNA that contains their genetic information, uncovering new information that radically changed the body of knowledge in the field. After developing ovarian cancer, Franklin continued to work until her death in 1958 at age 37. Among many posthumous recognitions of her work, the Chicago Medical School of Finch University of Health Sciences changed its name to the Rosalind Franklin University of Medicine and Science in 2004, and adopted an image of her famous X-ray diffraction image of DNA as its official university logo.

Figure 39.31

This illustration shows an X-ray diffraction image similar to the one Franklin found in her research. (credit: National Institutes of Health)



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40

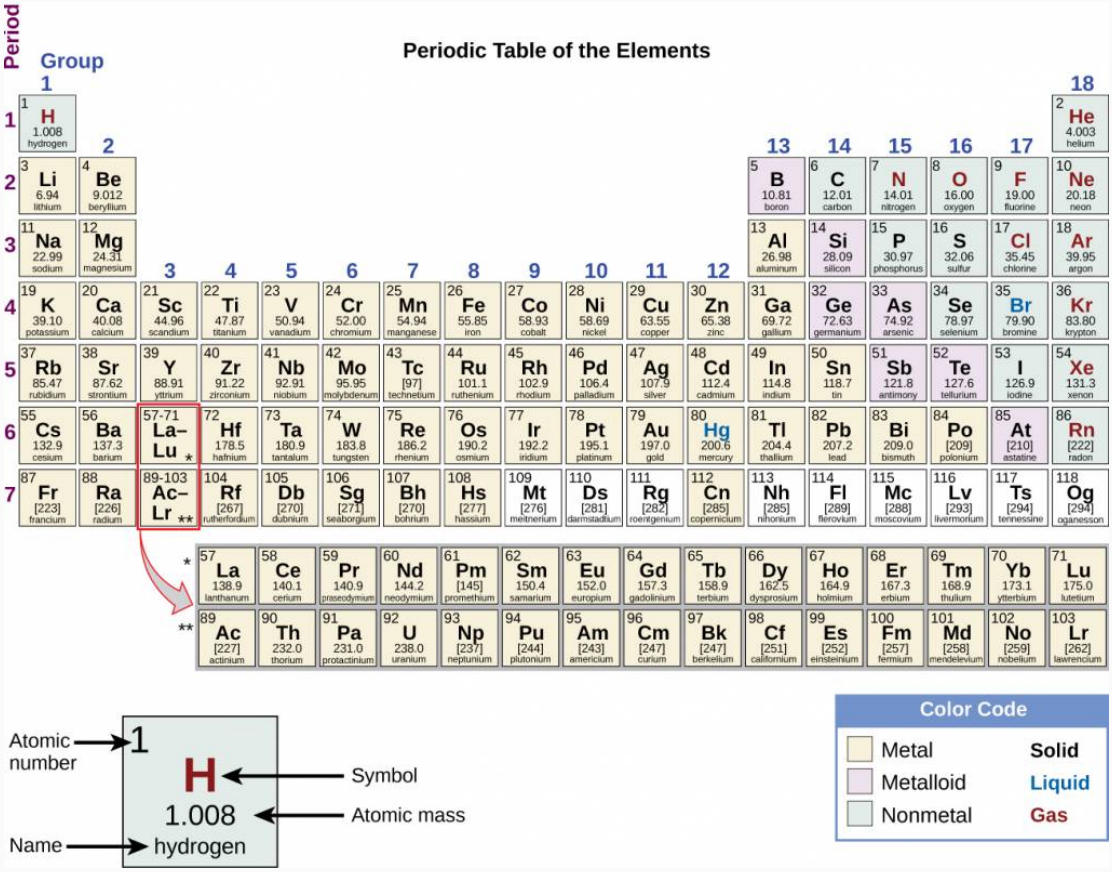
Covalent Network Solids, Salts, Polymers

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. The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. The common geometries found in complexes are tetrahedral and square planar (both with a coordination number of four) and octahedral (with a coordination number of six). Cis and trans configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use. Crystal field theory treats interactions between the electrons on the metal and the ligands as a simple electrostatic effect. The presence of the ligands near the metal ion changes the energies of the metal d orbitals relative to their energies in the free ion. Both the color and the magnetic properties of a complex can be attributed to this crystal field splitting. The magnitude of the splitting (Δoct) depends on the nature of the ligands bonded to the metal. Strong-field ligands produce large splitting and favor low-spin complexes, in which the t2g orbitals are completely filled before any electrons occupy the eg orbitals. Weak-field ligands favor formation of high-spin complexes. The t2g and the eg orbitals are singly occupied before any are doubly occupied.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure 40.2, 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 40.1

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 *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.

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 40.0.1

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) $Pb^{2+}[Xe]6s^{2}5d^{10}4f^{14}$; 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

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+}.

40.0.2 CHEMISTRY IN EVERYDAY LIFE

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

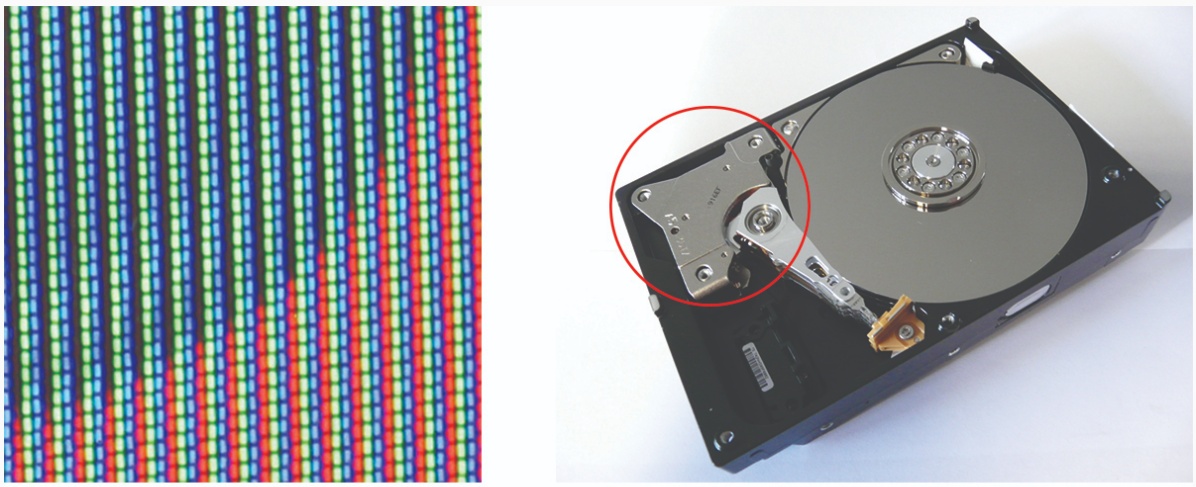
MoO_4^{2-}

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 40.3). 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 40.2

(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)



(a) (b)

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.

40.1 Properties of the Transition Elements

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (see Appendix H), 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

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad +1.33\ V$$

and

$$TiO_2 + 4H^+ + 2e^- \longrightarrow Ti^{2+} + 2H_2O \qquad -0.50\ V$$

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 40.4. 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+).

Figure 40.3

Transition metals of the first transition series can form compounds with varying oxidation states.

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+					

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 40.1.1

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 (in Appendix L) for each oxide in the specified oxidation state:

$$CO_2\,(g) + C(s) \longrightarrow 2CO(g)$$

$$CaCO_3\,(s) + SiO_2\,(s) \longrightarrow CaSiO_3\,(l) + CO_2\,(g)$$

$$2Cu_2S(l) + 3O_2\,(g) \longrightarrow 2Cu_2O(l) + 2SO_2\,(g)$$

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.

Check Your Learning

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 Appendix L.

Answer

$[Ag(CN)_2]^-$,

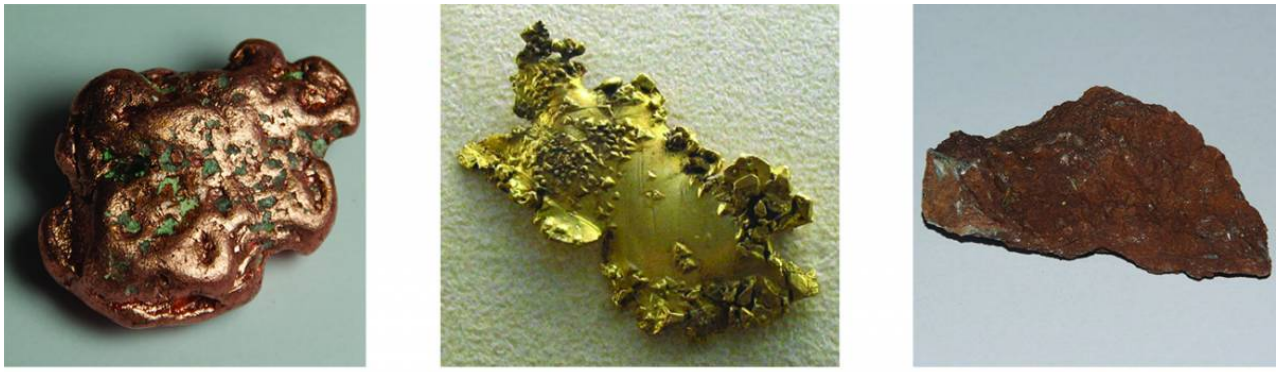
no reaction because Pt(*s*) will not be oxidized by H^+

40.2 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 40.5). 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 40.4
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.

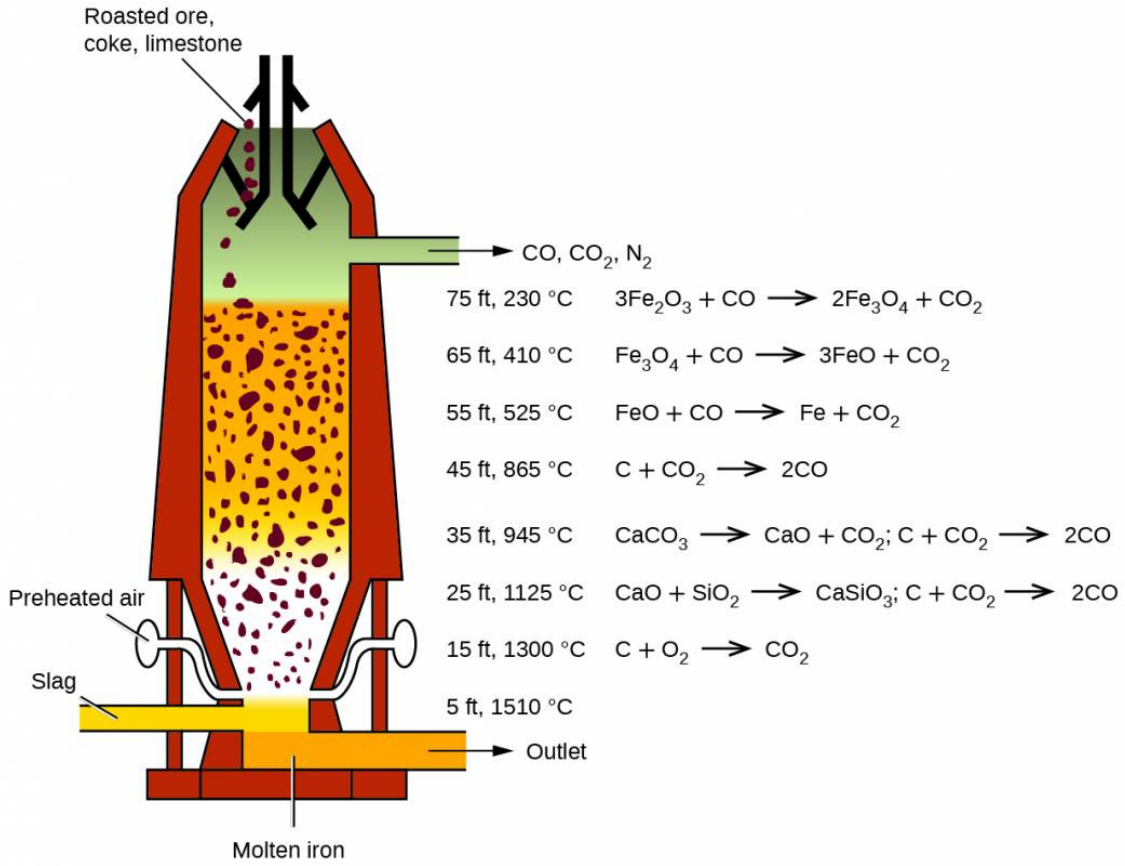
40.3 Isolation of Iron

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 19.6) 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 40.5

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:

$$2\mathrm{Ag_2\,S}(s) + 8\mathrm{CN}^-(aq) + \mathrm{O_2}(g) + 2\mathrm{H_2O}(l) \longrightarrow 4[\mathrm{Ag(CN)_2}]^-(aq) + 2\mathrm{S}(s) + 4\mathrm{OH}^-(aq)$$

The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 40.6.

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:

$$2[\mathrm{Ag(CN)_2}]^-(aq) + \mathrm{Zn}(s) \longrightarrow 2\mathrm{Ag}(s) + [\mathrm{Zn(CN)_4}]^{2-}(aq)$$

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 40.7).

Figure 40.6

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.

LINK TO LEARNING

You can watch an animation of steelmaking that walks you through the process.

40.4 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:

$$4\mathrm{Ag}(s) + 8\mathrm{CN}^{-}(aq) \longrightarrow 4[\mathrm{Ag(CN)}_2]^{-}(aq)?$$

$$\mathrm{Fe}(s) + 2\mathrm{FeCl}_3(s) \longrightarrow 3\mathrm{FeCl}_2(s)$$

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:

$$\mathrm{Co(OH)}_2(s) + 2\mathrm{HBr}(aq) \longrightarrow \mathrm{CoBr}_2(aq) + 2\mathrm{H}_2\mathrm{O}(l)$$

$$\mathrm{SiCl}_4(l) + 2\mathrm{H}_2\mathrm{O}(l) \longrightarrow \mathrm{SiO}_2(s) + 4\mathrm{HCl}(aq)$$

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 40.8). 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 40.7

Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: "Tortie tude"/Wikimedia Commons)

40.5 Isolation of Silver

Silver sometimes occurs in large nuggets (Figure 40.9) 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. 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,

$$\mathrm{FeC_2O_4}(s) \longrightarrow \mathrm{FeO}(s) + \mathrm{CO}(g) + \mathrm{CO_2}(g)$$

from silver metal or silver-containing compounds such as Ag_2S and AgCl. Representative equations are:

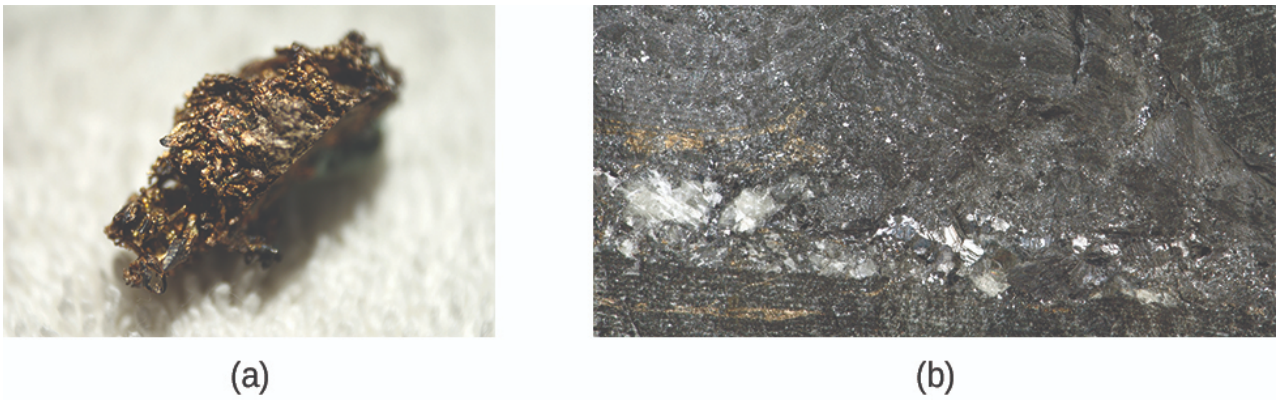
$$\mathrm{CoO}(s) + 2\mathrm{HNO_3}(aq) \longrightarrow \mathrm{Co(NO_3)_2}(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{VO_4}^{3-},$$

$$\mathrm{MnO_4}^{-}.$$

Figure 40.8

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)



(a) (b)

The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:

$$\mathrm{Co}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) \longrightarrow \mathrm{Co(OH)}_2(s)$$

EXAMPLE 40.5.1

Refining Redox

One of the steps for refining silver involves converting silver into dicyanoargenate(I) ions:

$$\mathrm{Ni}^{2+}(aq) + \mathrm{CO_3}^{2-} \longrightarrow \mathrm{NiCO_3}(s)$$

Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:

$$\mathrm{Ni(OH)_2}(s) + 2\mathrm{H_3O}^{+}(aq) + 2\mathrm{ClO_4}^{-}(aq) \longrightarrow \mathrm{Ni}^{2+}(aq) + 2\mathrm{ClO_4}^{-}(aq) + 4\mathrm{H_2O}(l)$$

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.

Check Your Learning

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).

40.6 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.

40.6.0.1 Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:

$$[\mathrm{Co(en)_3}]^{3+}$$

Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:

$$NO_3^-$$

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:

$$CO_3^{2-}$$

$$d_{z^2}$$

Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:

$$d_{z^2}$$

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:

$$I^- < Br^- < Cl^- < F^- < H_2O < C_2O_4^{2-} < NH_3 < en < NO_2^- < CN^-$$

a few ligands of the spectrochemical series, in order of increasing field strength of the ligand

$$\upsilon = \frac{c}{\lambda} \text{ so } \frac{3.00 \times 10^8 \text{ m/s}}{\frac{499 \text{ nm} \times 1 \text{ m}}{10^9 \text{ nm}}} = 6.01 \times 10^{14} \text{ Hz}$$

40.6.0.2 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:

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:

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

and

For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and $HMnO_4$, respectively.

40.6.0.3 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:

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:

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.

40.6.0.4 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:

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.

40.6.0.5 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:

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:

Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

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.

40.6.1 HOW SCIENCES INTERCONNECT

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.

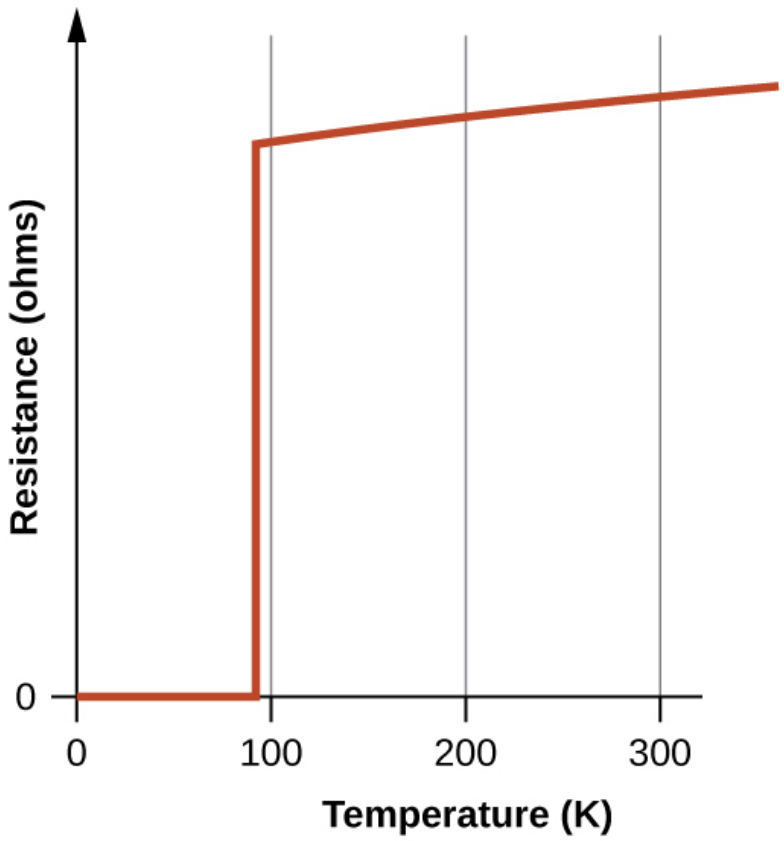
Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (−250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium 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 19.10), 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.

Further advances during the same period included materials that became superconducting at even higher temperatures and with a wider array of materials. The DuPont team led by Uma Chowdry and Arthur Sleight identified Bismouth-Strontium-Copper-Oxides that became superconducting at temperatures as high as 110 K and, importantly, did not contain rare earth elements. Advances continued through the subsequent decades until, in 2020, a team led by Ranga Dias at University of Rochester announced the development of a room-temperature superconductor, opening doors to widespread applications. More research and development is needed to realize the potential of these materials, but the possibilities are very promising.

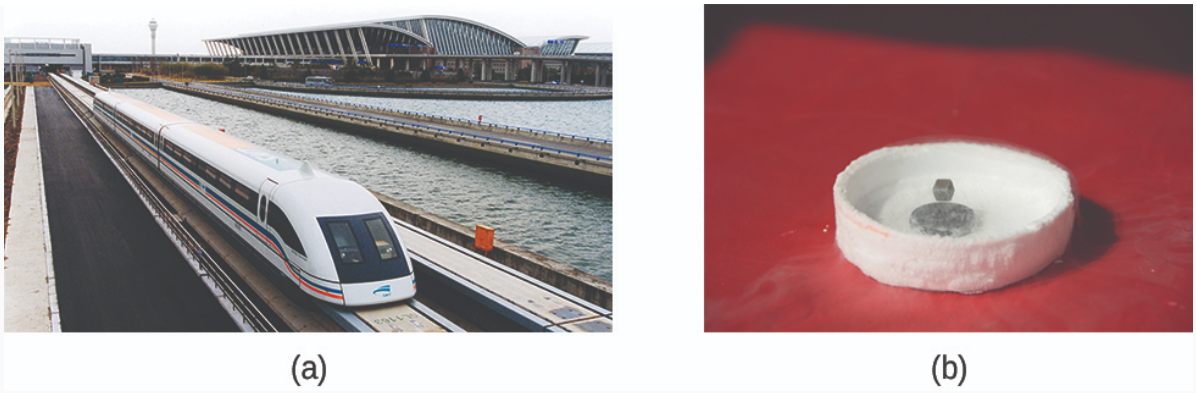
Figure 40.9
The resistance of the high-temperature superconductor $YBa_2Cu_3O_7$ varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.



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.

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 40.11).

Figure 40.10
(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)



(a) (b)

LINK TO LEARNING

Watch how a high-temperature superconductor levitates around a magnetic racetrack in the video.

Learning Objectives

By the end of this section, you will be able to:

- List the defining traits of coordination compounds
- Describe the structures of complexes containing monodentate and polydentate ligands
- Use standard nomenclature rules to name coordination compounds
- Explain and provide examples of geometric and optical isomerism
- Identify several natural and technological occurrences of coordination compounds

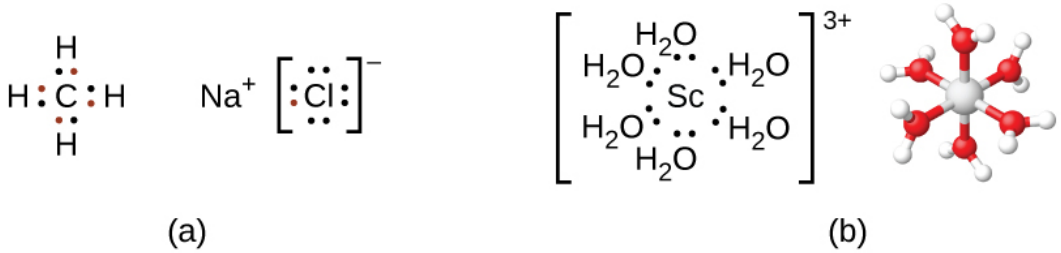
The hemoglobin in your blood, the chlorophyll in green plants, vitamin B-12, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure 19.12). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

Figure 40.11
Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with M = $Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure 40.13). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a central metal ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form coordination compounds. The Lewis base donors, called ligands, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a donor atom with a lone pair of electrons that can form a coordinate bond to the metal.

Figure 40.12

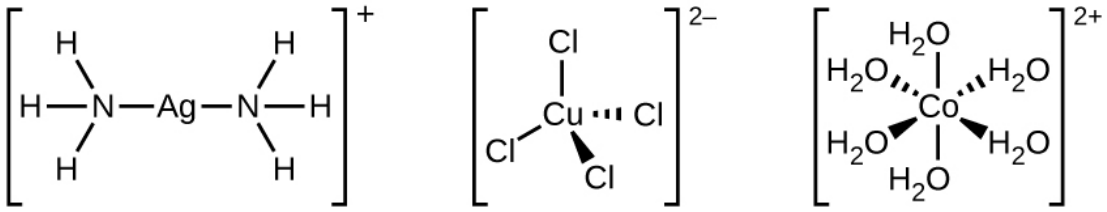
(a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)



The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure 40.14). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for "one toothed," meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.

Figure 40.13

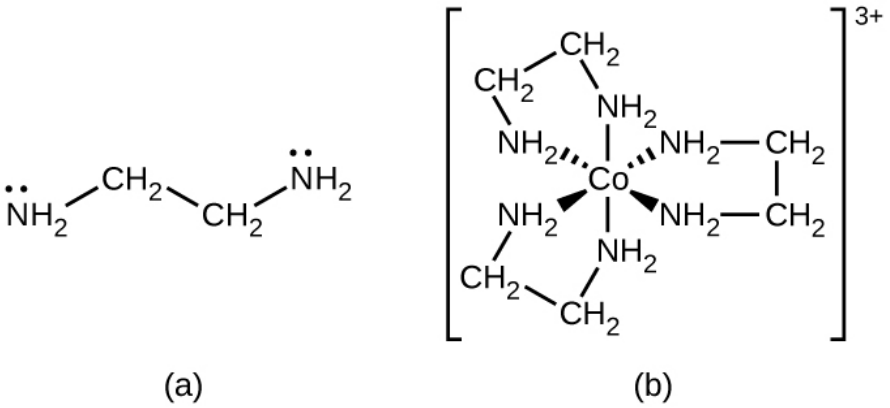
The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.



Many other ligands coordinate to the metal in more complex fashions. Bidentate ligands are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 40.15). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

Figure 40.14

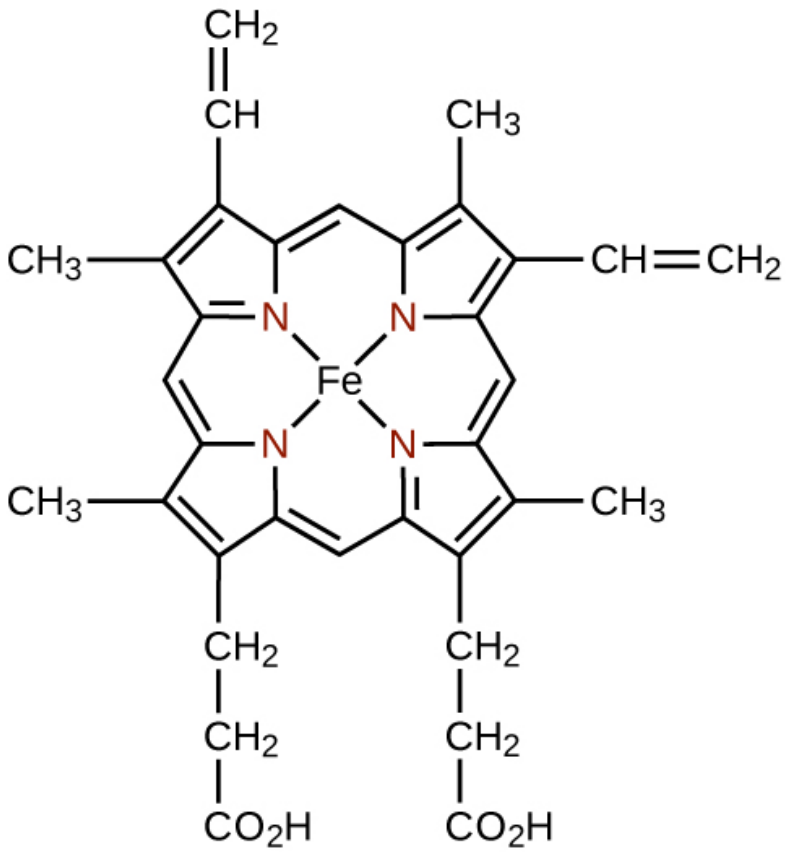
(a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex contains three of these ligands, each forming two bonds to the cobalt ion.



Any ligand that bonds to a central metal ion by more than one donor atom is a polydentate ligand (or "many teeth") because it can bite into the metal center with more than one bond. The term chelate (pronounced "KEY-late") from the Greek for "claw" is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A chelating ligand is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab's claw would hold a marble. Figure 40.15 showed one example of a chelate. The heme complex in hemoglobin is another important example (Figure 40.16). It contains a polydentate ligand with four donor atoms that coordinate to iron.

Figure 40.15

The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

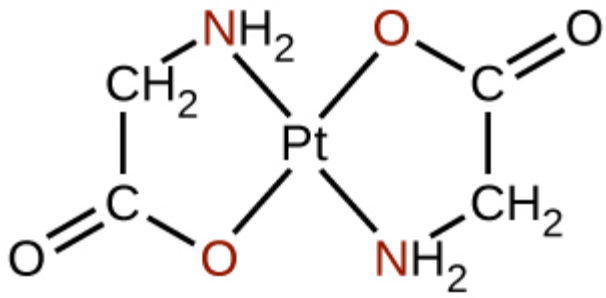


Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $H_2NCH_2CH_2NH_2$, and the anion of the acid glycine,

(Figure 40.17) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The ligand in heme (Figure 40.16) is a tetradentate ligand.

Figure 40.16

Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.



40.7 The Naming of Complexes

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds. The following five rules are used for naming complexes:

1. If a coordination compound is ionic, name the cation first and the anion second, in accordance with the usual nomenclature.
2. Name the ligands first, followed by the central metal. Name the ligands alphabetically. Negative ligands (anions) have names formed by adding *-o* to the stem name of the group. For examples, see Table 19.1. For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *ammine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO). For example, name $[Pt(NH_3)_2Cl_4]$ as diamminetetrachloroplatinum(IV).
   Table 40.17

   Examples of Anionic Ligands

Anionic Ligand	Name
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
	nitrato
OH^-	hydroxo
O^{2-}	oxo
	oxalato
	carbonato

3. If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes, the prefixes *bis-* (for two), *tris-* (for three), and *tetrakis-* (for four) are used when the name of the ligand already includes *di-*, *tri-*, or *tetra-*, or when the ligand name begins with a vowel. For example, the ion bis(bipyridyl)osmium(II) uses bis- to signify that there are two ligands attached to Os, and each bipyridyl ligand contains two pyridine groups (C_5H_4N).

When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly like the name of the element and is followed by a Roman numeral in parentheses to indicate its oxidation state (Table 41.2 and Table 41.3). When the complex is an anion, the suffix -ate is added to the stem of the name of the metal, followed by the Roman numeral designation of its oxidation state (Table 41.4). Sometimes, the Latin name of the metal is used when the English name is clumsy. For example, *ferrate* is used instead of *ironate*, *plumbate* instead *leadate*, and *stannate* instead of *tinate*. The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[Cr(H_2O)_4Cl_2]Br$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: +1 = −2 + *x*, so the oxidation state (*x*) is equal to 3+.

Table 40.18

Examples in Which the Complex Is a Cation

$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) chloride
$[Pt(NH_3)_4Cl_2]^{2+}$	tetraamminedichloroplatinum(IV) ion
$[Ag(NH_3)_2]^+$	diamminesilver(I) ion
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichlorochromium(III) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate

Table 40.19

Examples in Which the Complex Is Neutral

$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
$[Ni(H_2NCH_2CH_2NH_2)_2Cl_2]$	dichlorobis(ethylenediamine)nickel(II)

Table 40.20

Examples in Which the Complex Is an Anion

$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion
$Na_2[SnCl_6]$	sodium hexachlorostannate(IV)

LINK TO LEARNING

Do you think you understand naming coordination complexes? You can look over more examples and test yourself with online quizzes at the University of Sydney's site.

EXAMPLE 40.7.1

Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.
(a) $Na_2[PtCl_6]$

(b) $K_3[Fe(C_2O_4)_3]$

(c) $[Co(NH_3)_5Cl]Cl_2$

Solution

(a) There are two Na^+ ions, so the coordination sphere has a negative two charge: $[PtCl_6]^{2-}$. There are six anionic chloride ligands, so $-2 = -6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six. (b) The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $-3 = -6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six. (c) In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = -1 + x$ and is 3+, so the complex is pentaamminechlorocobalt(III) chloride and the coordination number is six.

Check Your Learning

The complex potassium dicyanoargenate(I) is used to make antiseptic compounds. Give the formula and coordination number.

Answer

$K[Ag(CN)_2]$; coordination number two

The Structures of Complexes

For transition metal complexes, the coordination number determines the geometry around the central metal ion. The most common structures of the complexes in coordination compounds are square planar, tetrahedral, and octahedral, corresponding to coordination numbers of four, four, and six, respectively. Coordination numbers greater than six are less common and yield a variety of structures (see Figure 40.18 and Table 40.5):

Figure 40.21

These are geometries of some complexes with coordination numbers of seven and eight.

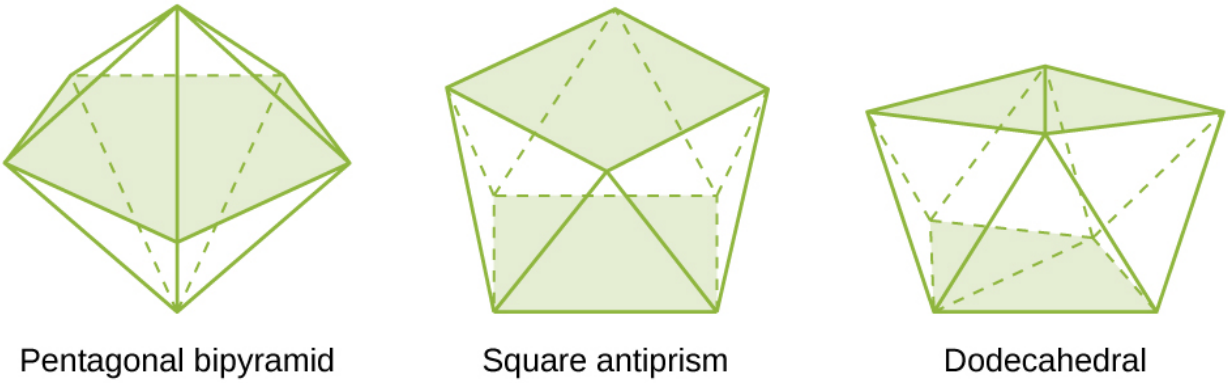


Table 40.22

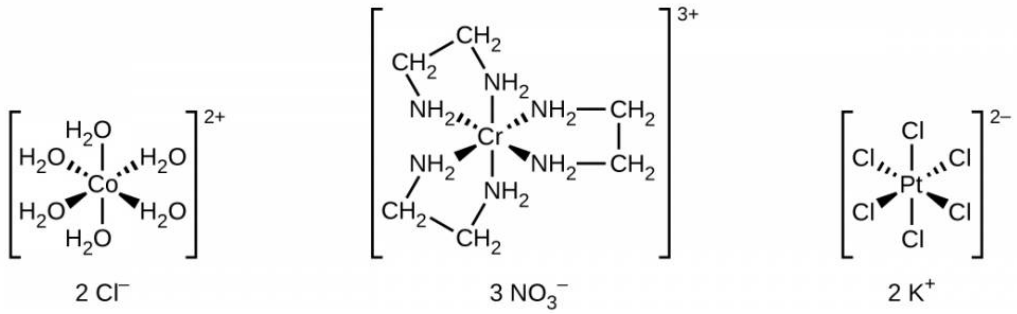
Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Ni(CO)_4]$
4	square planar (d^8)	$[Ni(CN)_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding *d*-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in Figure 40.19. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.

Figure 40.23

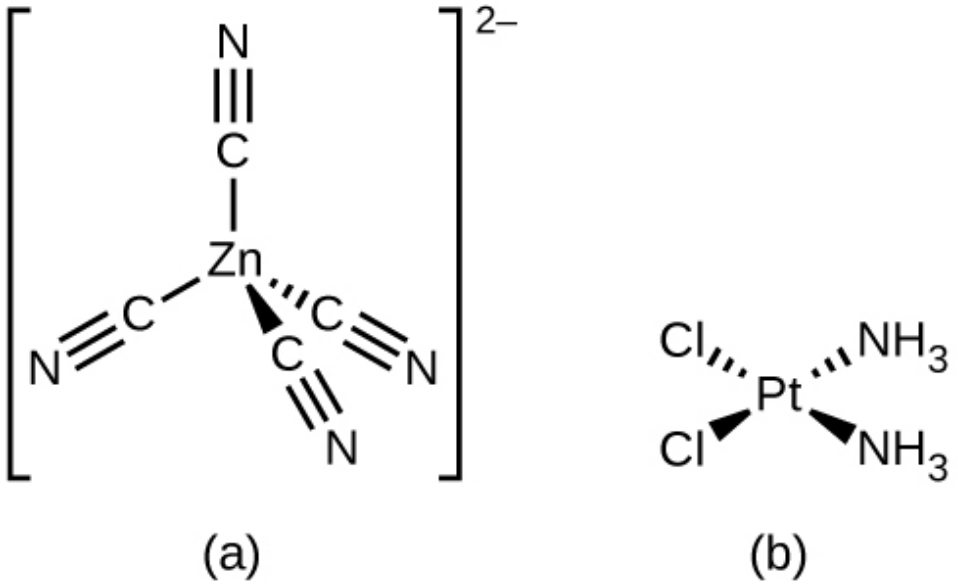
Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.



For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (Figure 40.20), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.

Figure 40.24

Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$.



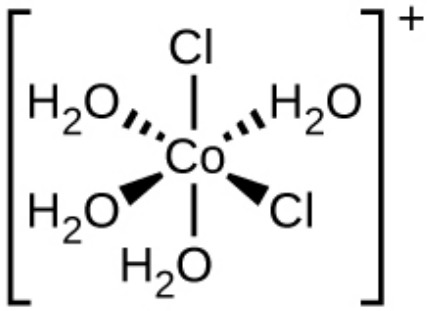
40.8 Isomerism in Complexes

Isomers are different chemical species that have the same chemical formula. Transition metal complexes often exist as **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral $[Co(NH_3)_4Cl_2]^+$ ion has two isomers. In the *cis* configuration, the two chloride ligands are adjacent to each other (Figure 40.21). The other isomer, the *trans* configuration, has the two chloride ligands directly across from one another.

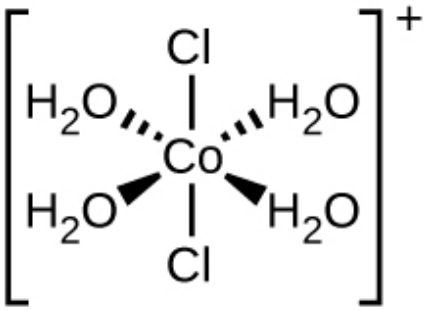
Figure 40.25

The cis and trans isomers of $[Co(H_2O)_4Cl_2]^+$ contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.

Violet, *cis* form



Green, *trans* form



Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[Co(NH_3)_4Cl_2]NO_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two $[Co(NH_3)_4Cl_2]NO_3$ isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

EXAMPLE 40.8.1

Geometric Isomers

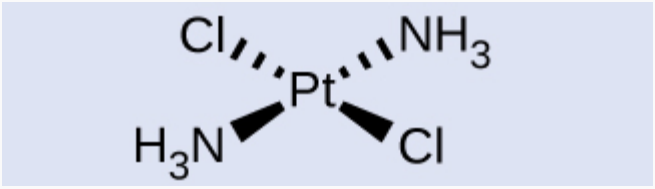
Identify which geometric isomer of $[Pt(NH_3)_2Cl_2]$ is shown in Figure 40.20. Draw the other geometric isomer and give its full name.

Solution

In the Figure 40.20, the two chlorine ligands occupy *cis* positions. The other form is shown in Figure 40.22. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diamminedichloroplatinum(II).

Figure 40.26

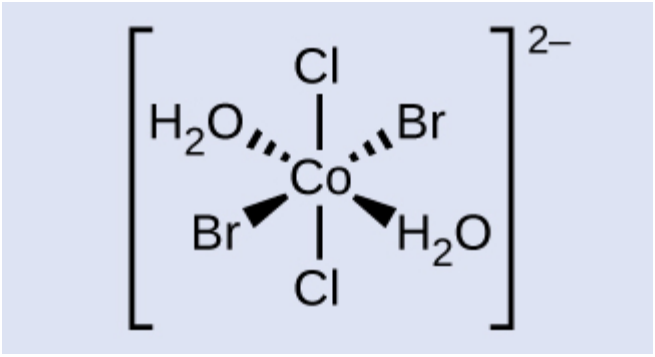
The trans isomer of $[Pt(NH_3)_2Cl_2]$ has each ligand directly across from an adjacent ligand.



Check Your Learning

Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).

Answer

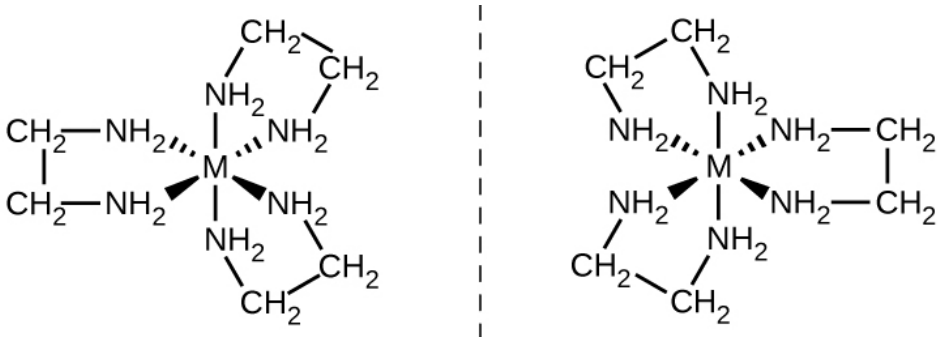


Another important type of isomers are optical isomers, or enantiomers, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in Figure 40.23. These two isomers will react differently with other optical isomers. For example, DNA helices are

optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.

Figure 40.27

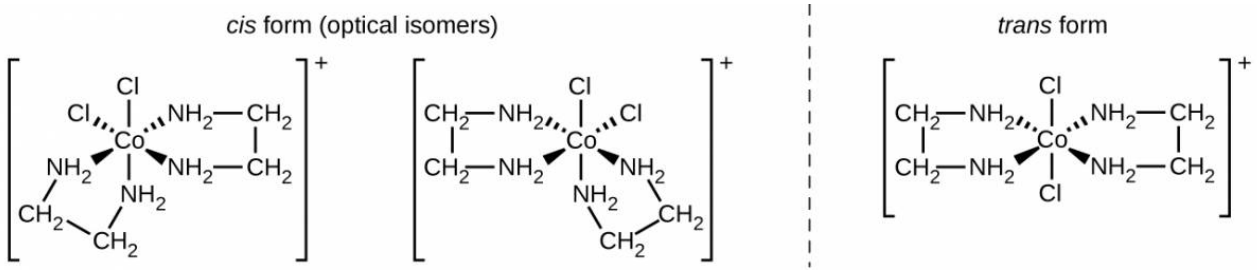
The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.



The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis*/*trans*), and its *cis* isomer exists as a pair of optical isomers (Figure 40.24).

Figure 40.28

Three isomeric forms of $[Co(en)_2Cl_2]^+$ exist. The trans isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the cis isomers. The mirror images of the cis isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.



Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly, SCN− can be bound through the sulfur or nitrogen atom, affording two distinct compounds ($[Co(NH_3)_5SCN]^{2+}$ or $[Co(NH_3)_5NCS]^{2+}$).

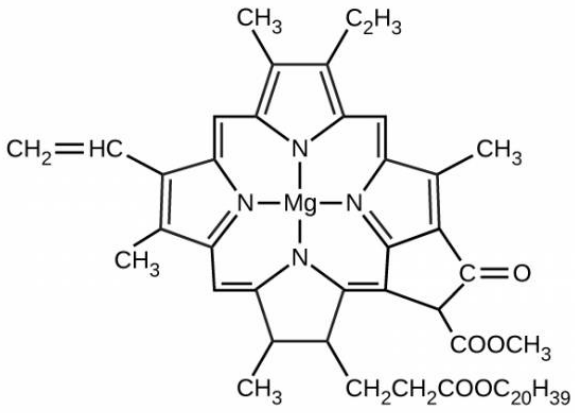
Ionization isomers (or coordination isomers) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are $[CoCl_6][Br]$ and $[CoCl_5Br][Cl]$.

40.9 Coordination Complexes in Nature and Technology

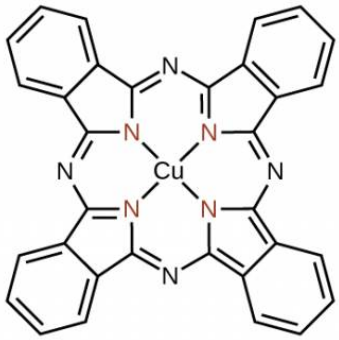
Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 40.25). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

Figure 40.29

(a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.



(a)



(b)

40.9.1 CHEMISTRY IN EVERYDAY LIFE

Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see Figure 40.26). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

Figure 40.30

(a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)

(a)

(b)

(c)

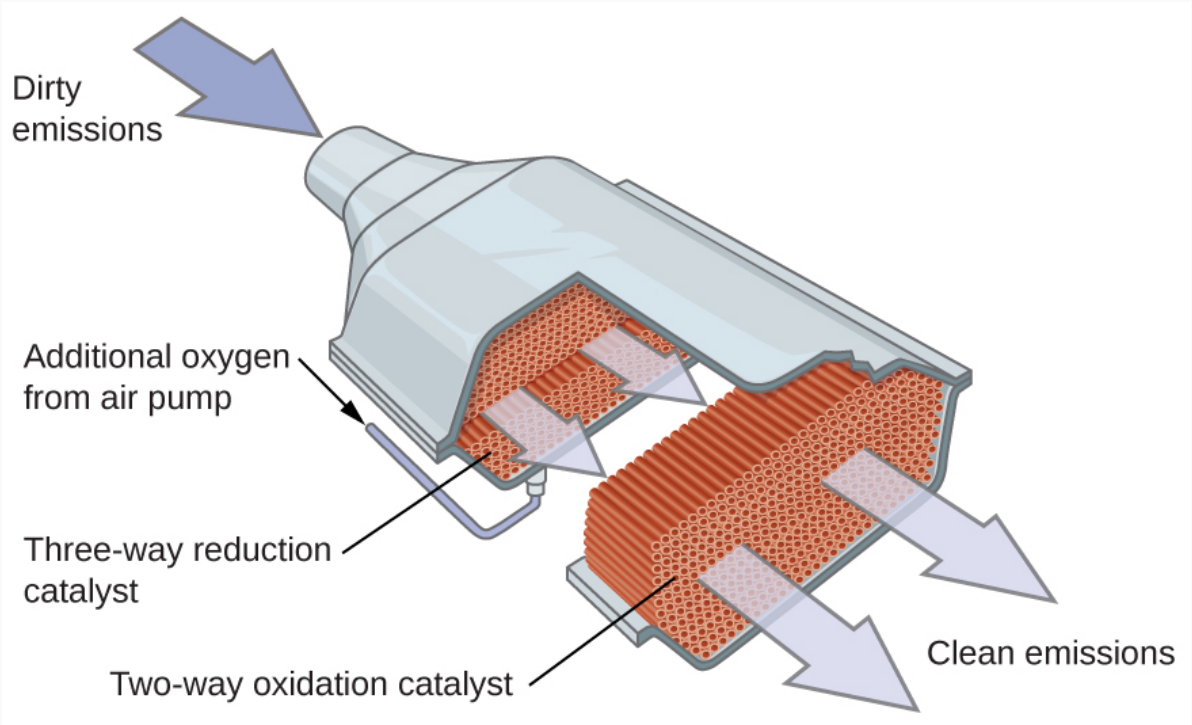
40.9.2 PORTRAIT OF A CHEMIST

Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see Figure 19.27).

Figure 40.31

Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.



Another project involves the development of porous, sponge-like materials that are "photoactive." The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this video to learn more about this research and listen to Dr. D'Alessandro (shown in Figure 40.28) describe what it is like being a research chemist.

Figure 40.32

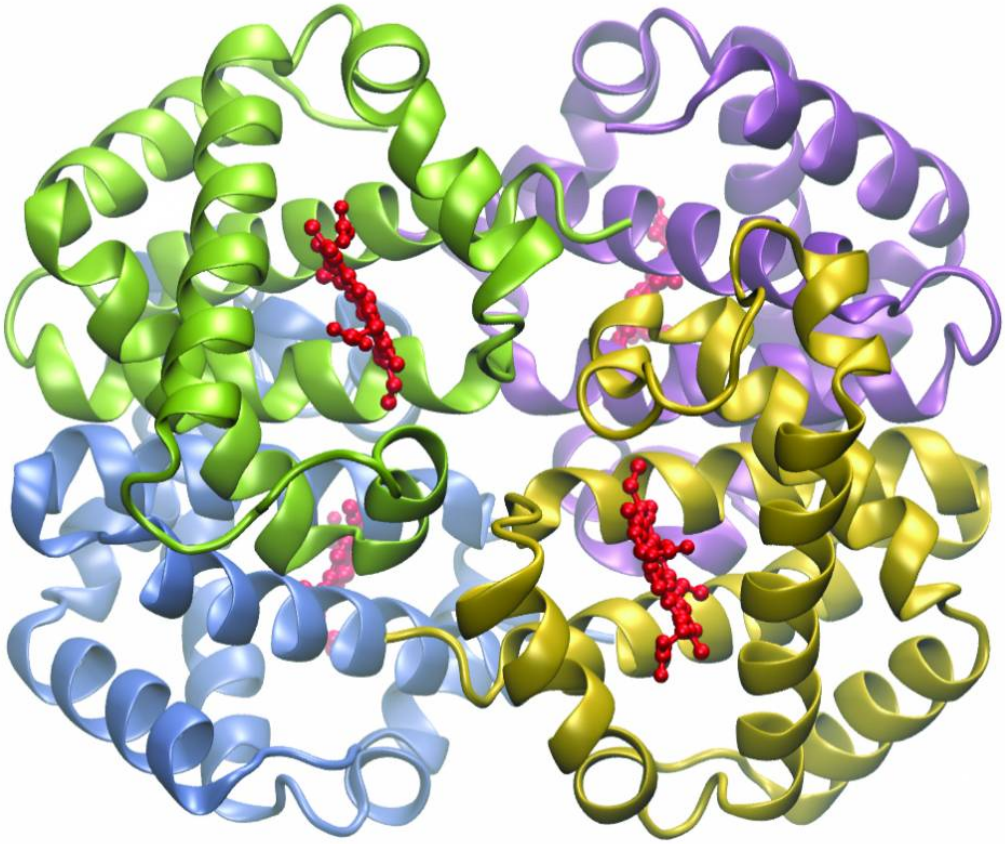
Dr. Deanna D'Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 40.25) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (Figure 40.29), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.

Figure 40.33

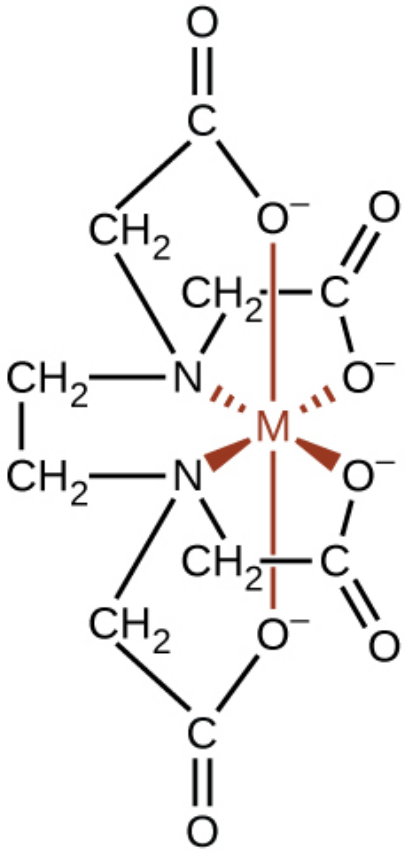
Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.



Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (Figure 40.30). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.

Figure 40.34

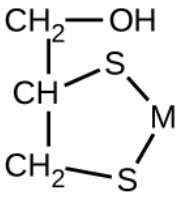
The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.



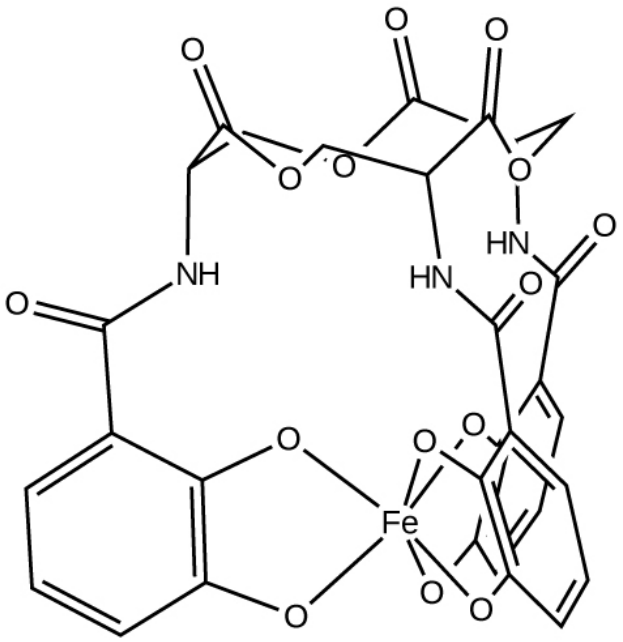
Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (Figure 40.31). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.

Figure 40.35

Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.



(a)



(b)

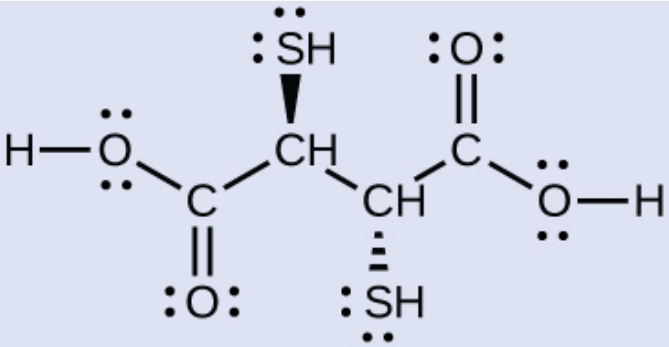
EXAMPLE 40.9.3

Chelation Therapy

Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in Figure 40.32. Identify which atoms in this molecule could act as donor atoms.

Figure 40.36

Dimercaptosuccinic acid is used to treat heavy metal poisoning.



Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

Check Your Learning

Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.[1] Identify at least two biologically important metals that could be disrupted by chelation therapy.

Answer

Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$,

and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Learning Objectives

By the end of this section, you will be able to:

- Outline the basic premise of crystal field theory (CFT)
- Identify molecular geometries associated with various d-orbital splitting patterns
- Predict electron configurations of split d orbitals for selected transition metal atoms or ions
- Explain spectral and magnetic properties in terms of CFT concepts

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the *d* orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three *p* orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

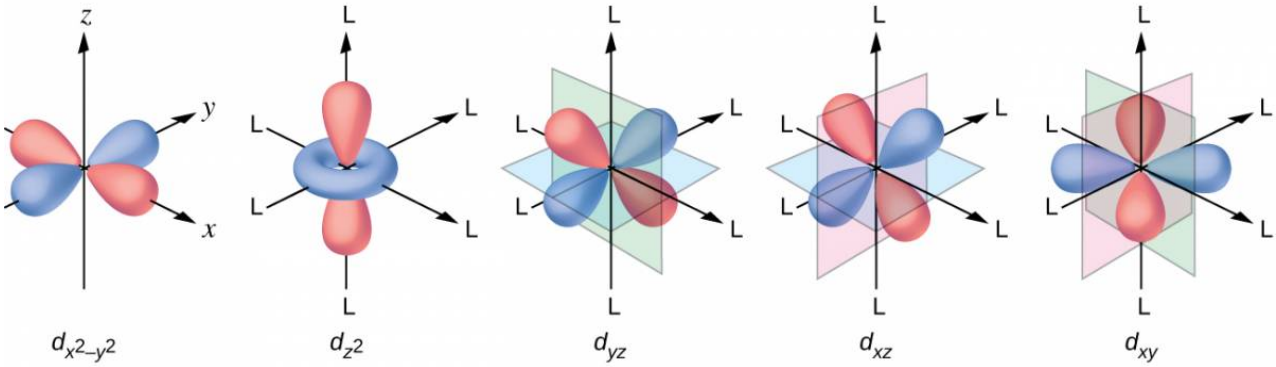
40.10 Crystal Field Theory

To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized *d* orbitals of the central metal atom has been developed. This electrostatic model is crystal field theory (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized *d* orbitals in an octahedral complex. The five *d* orbitals consist of lobe-shaped regions and are arranged in space, as shown in Figure 19.33. In an octahedral complex, the six ligands coordinate along the axes.

Figure 40.37
The directional characteristics of the five d orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the orbital so that the axis labels could be shown.



In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five *d* orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the *d* orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five *d* orbitals, the

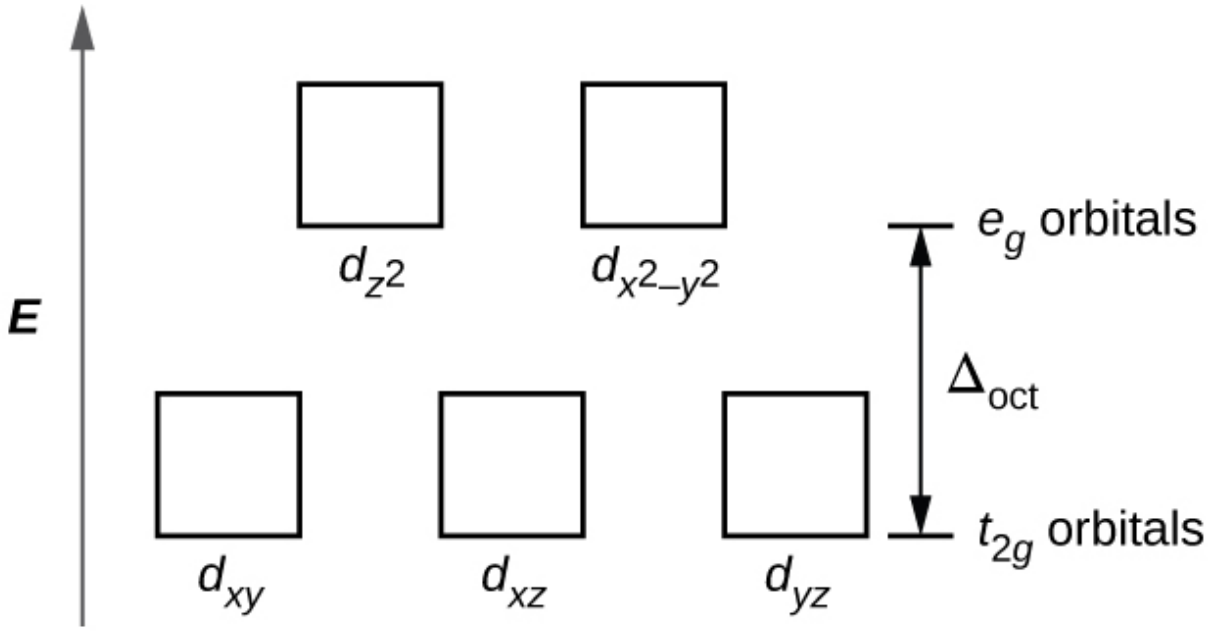
and

orbitals, point toward the ligands (Figure 40.33). These two orbitals are called the e_g orbitals (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the d_{xy}, d_{xz}, and d_{yz} orbitals, have lobes that point between the ligands and are called the t_{2g} orbitals (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the *d* orbitals of the metal ion. However, the repulsions between the electrons in the e_g orbitals (the

and

orbitals) and the ligands are greater than the repulsions between the electrons in the t_{2g} orbitals (the d_{zy}, d_{xz}, and d_{yz} orbitals) and the ligands. This is because the lobes of the e_g orbitals point directly at the ligands, whereas the lobes of the t_{2g} orbitals point between them. Thus, electrons in the e_g orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the t_{2g} orbitals. The difference in energy may be represented as shown in Figure 40.34.

Figure 40.38
In octahedral complexes, the e_g orbitals are destabilized (higher in energy) compared to the t_{2g} orbitals because the ligands interact more strongly with the d orbitals at which they are pointed directly.



The difference in energy between the e_g and the t_{2g} orbitals is called the crystal field splitting and is symbolized by Δ_{oct}, where oct stands for octahedral.

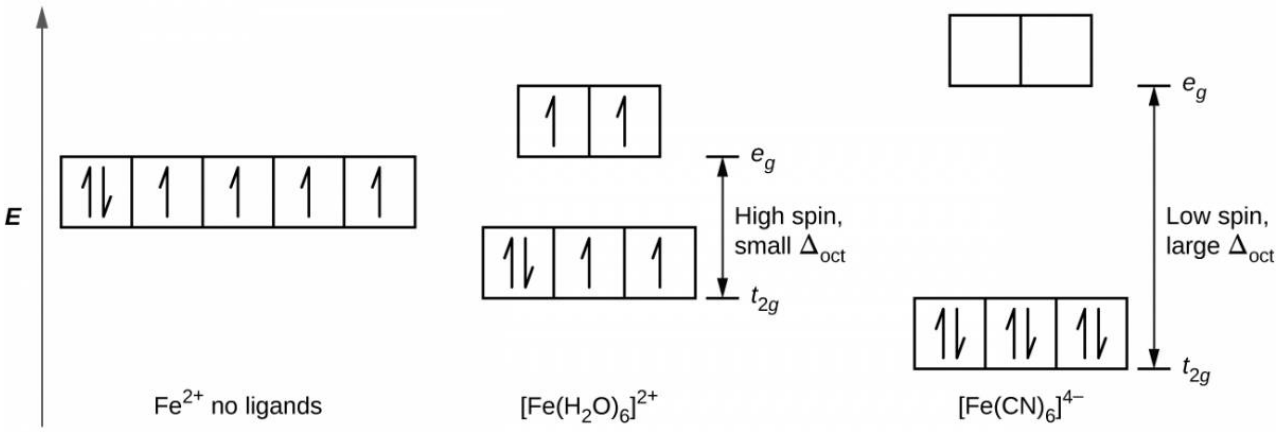
The magnitude of Δ_{oct} depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using 3*d*, 4*d*, or 5*d* orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the spectrochemical series, a short version of which is given here:

In this series, ligands on the left cause small crystal field splittings and are weak-field ligands, whereas those on the right cause larger splittings and are strong-field ligands. Thus, the Δ_{oct} value for an octahedral complex with iodide ligands (I^-) is much smaller than the Δ_{oct} value for the same metal with cyanide ligands (CN^-).

Electrons in the *d* orbitals follow the aufbau ("filling up") principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the pairing energy (P). Electrons will always singly occupy each orbital in a degenerate set before pairing. P is similar in magnitude to Δ_{oct}. When electrons fill the *d* orbitals, the relative magnitudes of Δ_{oct} and P determine which orbitals will be occupied.

In $[Fe(CN)_6]^{4-}$, the strong field of six cyanide ligands produces a large Δ_{oct}. Under these conditions, the electrons require less energy to pair than they require to be excited to the e_g orbitals (Δ_{oct} > P). The six 3*d* electrons of the Fe^{2+} ion pair in the three t_{2g} orbitals (Figure 40.35). Complexes in which the electrons are paired because of the large crystal field splitting are called low-spin complexes because the number of unpaired electrons (spins) is minimized.

Figure 40.39
Iron(II) complexes have six electrons in the 5d orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as $[Fe(CN)_6]^{4-}$, Δ_{oct} is greater than P, and the electrons pair in the lower energy t_{2g} orbitals before occupying the eg orbitals. With weak-field ligands such as H_2O, the ligand field splitting is less than the pairing energy, Δ_{oct} less than P, so the electrons occupy all d orbitals singly before any pairing occurs.



In $[Fe(H_2O)_6]^{2+}$, on the other hand, the weak field of the water molecules produces only a small crystal field splitting (Δ_{oct} < P). Because it requires less energy for the electrons to occupy the e_g orbitals than to pair together, there will be an electron in each of the five 3*d* orbitals before pairing occurs. For the six *d* electrons on the iron(II) center in $[Fe(H_2O)_6]^{2+}$, there will be one pair of electrons and four unpaired electrons (Figure 40.35). Complexes such as the $[Fe(H_2O)_6]^{2+}$ ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called high-spin complexes because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the $[Fe(CN)_6]^{3-}$ ion is a low-spin complex with only one unpaired electron, whereas both the $[Fe(H_2O)_6]^{3+}$ and $[FeF_6]^{3-}$ ions are high-spin complexes with five unpaired electrons.

EXAMPLE 40.10.1

High- and Low-Spin Complexes

Predict the number of unpaired electrons.
(a) $K_3[CrI_6]$

(b) $[Cu(en)_2(H_2O)_2]Cl_2$

(c) $Na_3[Co(NO_2)_6]$

Solution

The complexes are octahedral.
(a) Cr^{3+} has a d^3 configuration. These electrons will all be unpaired.

(b) Cu^{2+} is d^9, so there will be one unpaired electron.

(c) Co^{3+} has d^6 valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the t_{2g} orbitals, leaving 0 unpaired.

Check Your Learning

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which *d*-electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

Answer

d^4, d^5, d^6, and d^7

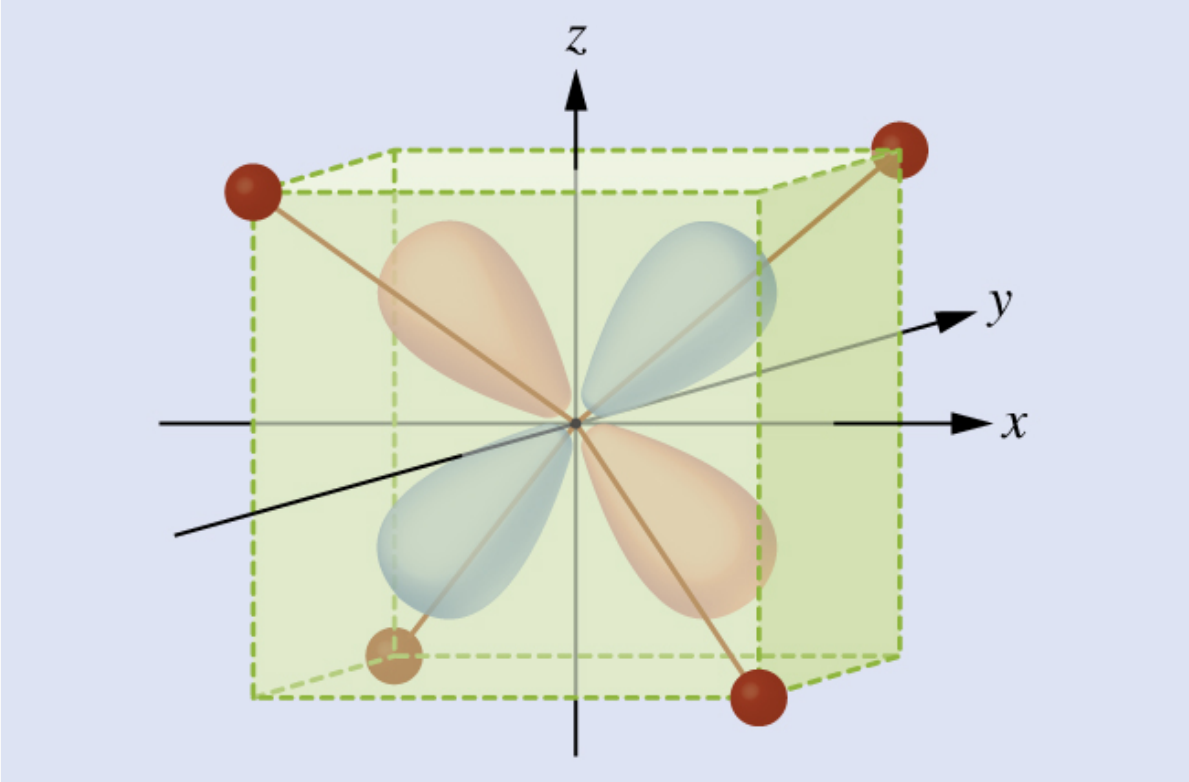
EXAMPLE 40.10.2

CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the e_g set point directly at the ligands. For tetrahedral complexes, the *d* orbitals remain in place, but now we have only four ligands located between the axes (Figure 40.36). None of the orbitals points directly at the tetrahedral ligands. However, the e_g set (along the Cartesian axes) overlaps with the ligands less than does the t_{2g} set. By analogy with the octahedral case, predict the energy diagram for the *d* orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral e_g set becomes a tetrahedral *e* set, and the octahedral t_{2g} set becomes a t_2 set.

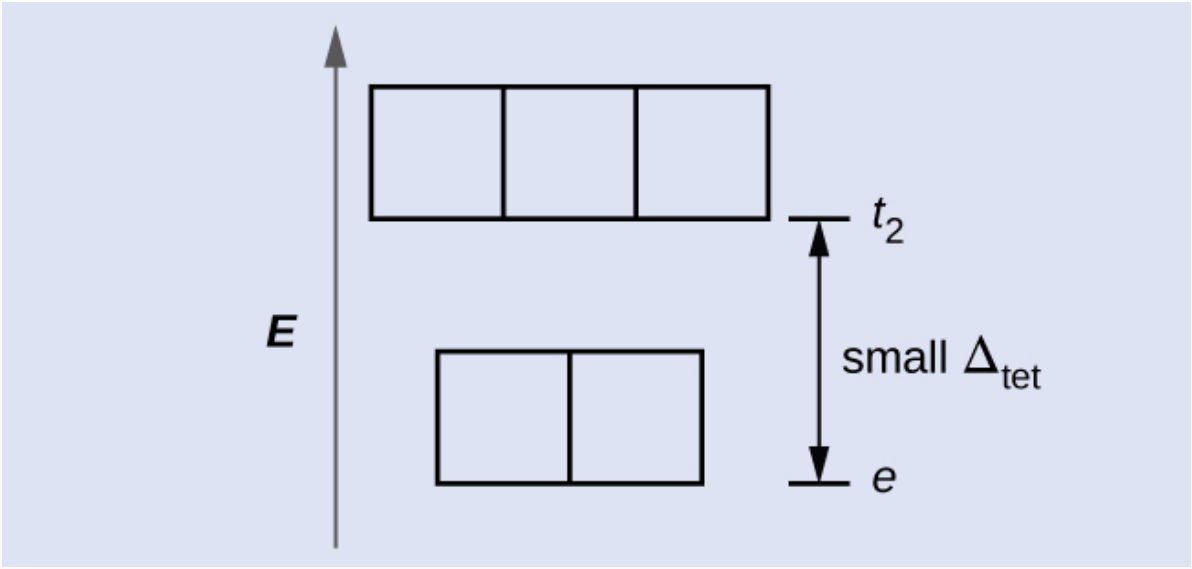
Figure 40.40

This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.



Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so Δ_{tet} is usually small



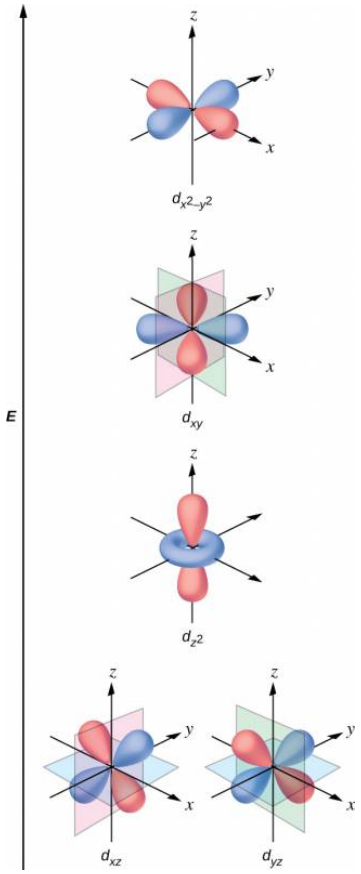
Check Your Learning

Explain how many unpaired electrons a tetrahedral d^4 ion will have.

Answer

4; because Δ_{tet} is small, all tetrahedral complexes are high spin and the electrons go into the t_2 orbitals before pairing

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the *z*-axis. This changes the distribution of the *d* orbitals, as orbitals on or near the *z*-axis become more stable, and those on or near the *x*- or *y*-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated pattern, as depicted below:



40.11 Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

40.12 Colors of Transition Metal Complexes

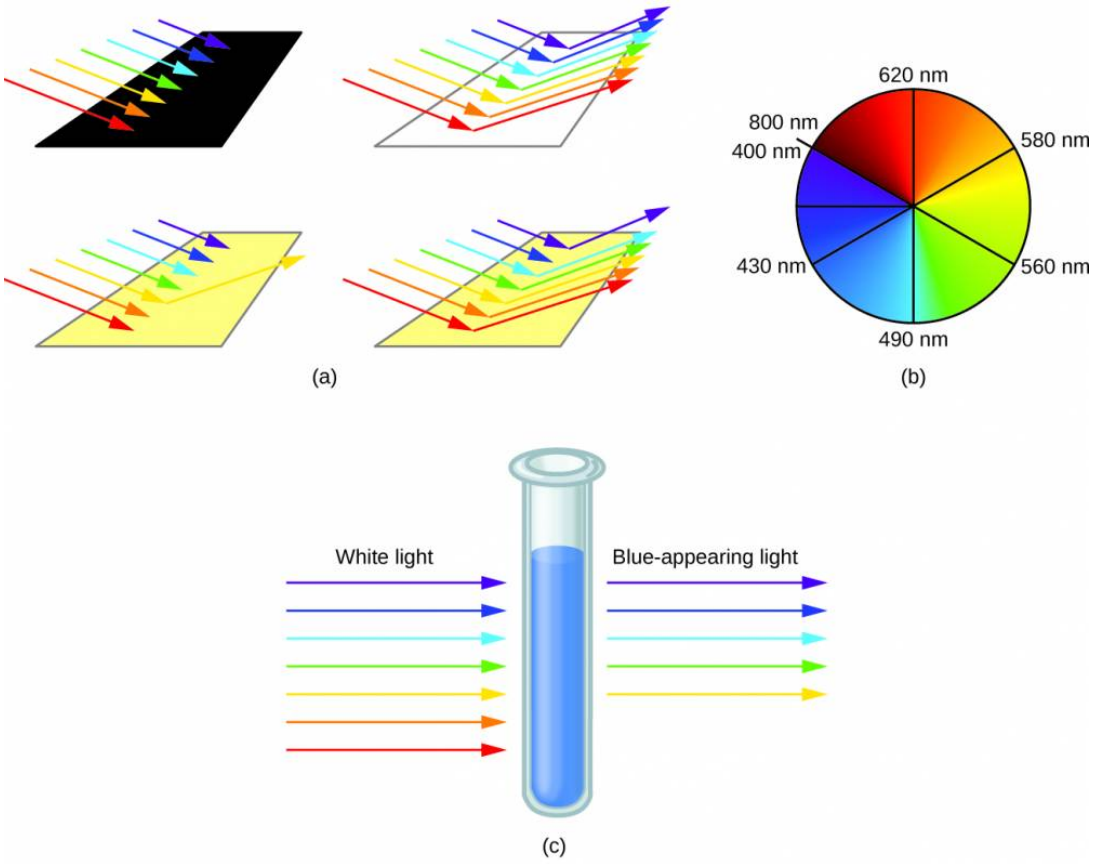
When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the *d* orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is

missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure 40.37).

Figure 40.41

(a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.



EXAMPLE 40.12.1

Colors of Complexes

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single *d* electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{oct} and occurs at 499 nm. Calculate the value of Δ_{oct} in Joules and predict what color the solution will appear.

Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Check Your Learning

A complex that appears green, absorbs photons of what wavelengths?

Answer

red, 620–800 nm

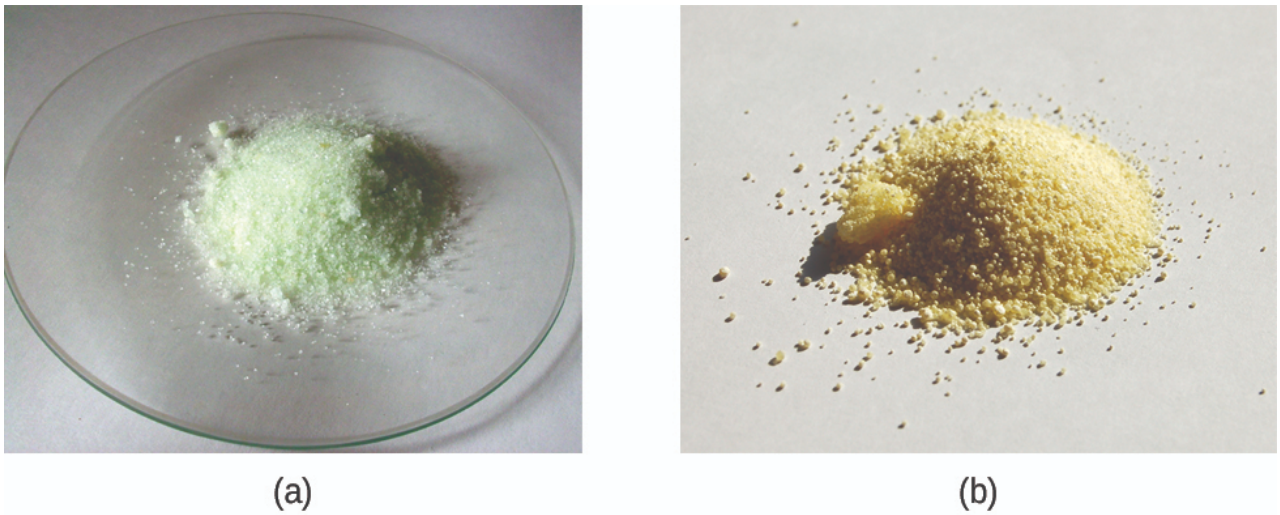
Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 40.38, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.

Figure 40.42
The partially filled d orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 40.39). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.

Figure 40.43

Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.



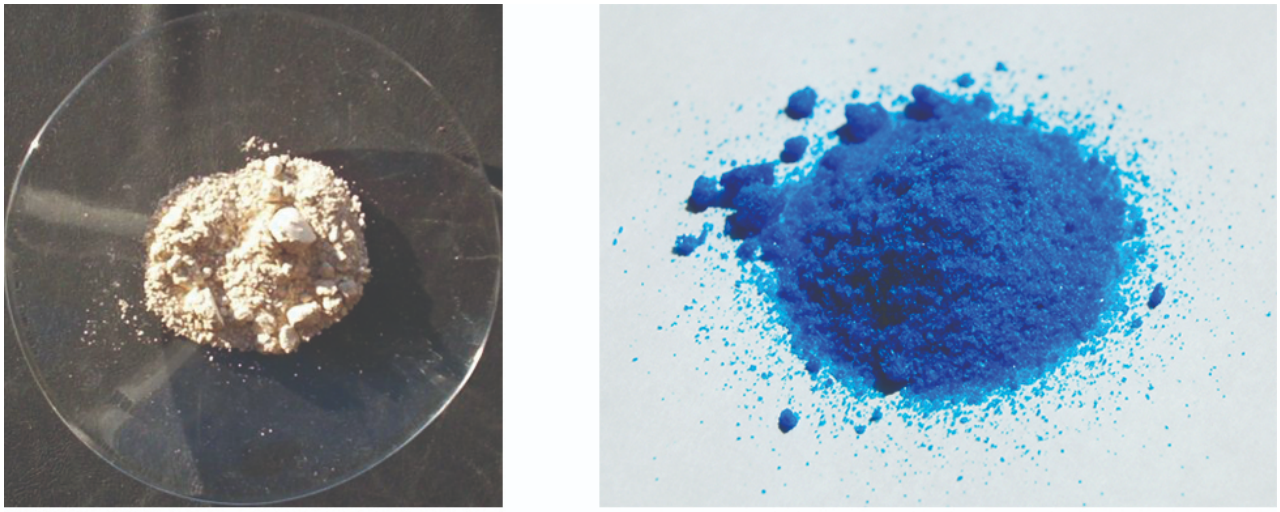
LINK TO LEARNING

Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light. On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the 4*p* orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 40.40). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.

Figure 40.44
(a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2{\cdot}5H_2O$ are brightly colored.



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