CH105: ALLIED HEALTH CHEMISTRY II



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CH105: Allied Health Chemistry II

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Glossary

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Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

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1.1: Kinetic Molecular Theory - A Model for Gases

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. It is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic; that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure **1.1.1** shows a representation of how we mentally picture the gas phase.

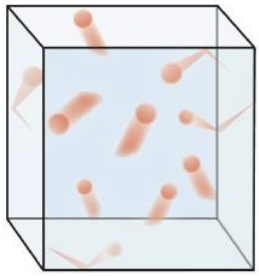


Figure **1.1.1**: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements so well that the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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1.2: Pressure

Learning Objectives

- Define *pressure*.
- Learn the units of pressure and how to convert between them.

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. The accumulation of all these forces distributed over the area of the walls of the container causes something we call pressure. **Pressure** (P) is defined as the force of all the gas particle/wall collisions divided by the area of the wall:

$$pressure = \frac{force}{area} \tag{1.2.1}$$

All gases exert pressure; it is one of the fundamental measurable quantities of this phase of matter. Even our atmosphere exerts pressure—in this case, the gas is being "held in" by the earth's gravity, rather than the gas being in a container. The pressure of the atmosphere is about 14.7 pounds of force for every square inch of surface area: 14.7 lb/in^2.

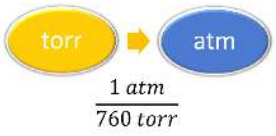
Pressure has a variety of units. The formal, SI-approved unit of pressure is the *pascal* (Pa), which is defined as 1 N/m^2 (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the **atmosphere** (atm), which was originally defined as the average atmospheric pressure at sea level.

However, "average atmospheric pressure at sea level" is difficult to pinpoint because of atmospheric pressure variations. A more reliable and common unit is **millimeters of mercury** (mmHg), which is the amount of pressure exerted by a column of mercury exactly 1 mm high. An equivalent unit is the **torr**, which equals 1 mmHg. (The torr is named after Evangelista Torricelli, a seventeenth-century Italian scientist who invented the mercury barometer.) With these definitions of pressure, the atmosphere unit is redefined: 1 atm is defined as exactly 760 mmHg, or 760 torr. We thus have the following equivalences:

$$1\ atm = 760\ mmHg = 760\ torr$$

We can use these equivalences as with any equivalences—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

Example 1.2.1: Pressure Conversion

	Example **1.2.1** How many atmospheres are there in 595 torr
Steps for Problem Solving	**Unit Conversion**
Identify the "given" information and what the problem is asking you to "find."	Given: 595 torr Find: ?atm
List other known quantities.	1 atm = 760 torr
Prepare a concept map.	
Cancel units and calculate.	$595\ \cancel{torr} \times \frac{1\ atm}{760\ \cancel{torr}} = 0.783\ atm$
Think about your result.	595 torr is less than 760 torr so the final answer should be less than 1 atm

Exercise 1.2.1

How many atmospheres are there in 1,022 torr?

Answer

1.345 atm

Example 1.2.2: Mars

	Example **1.2.2** The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atmospheres?
Steps for Problem Solving	**Unit Conversion**
Identify the "given" information and what the problem is asking you to "find."	Given: 6.01mmHg Find: ?atm
List other known quantities.	1 atm = 760 mmHg
Prepare a concept map.	mmHg → atm $\frac{1\ atm}{760\ mmHg}$
Cancel units and calculate.	$6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$
Think about your result.	6.01 is a very small number relative to 760 mmHg just like the value in atmospheres.

Exercise 1.2.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

Answer

652 torr

Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

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1.3: Gases - Pressure and Volume

Learning Objectives

- Learn what is meant by the term *gas laws*.
- Express the mathematical relationship between pressure and volume for a gas sample with fixed moles at a fixed temperature.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (P) and volume (V), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [n]), if the temperature (T) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. We say that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{ constant at constant n and T} \tag{1.3.1}$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled P_1 and V_1 and the new conditions are labeled P_2 and V_2, we have

$$P_1V_1 = \text{constant} = P_2V_2 \tag{1.3.2}$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant n and T} \tag{1.3.3}$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. Figure **1.3.1** shows two representations of how this gas law works.

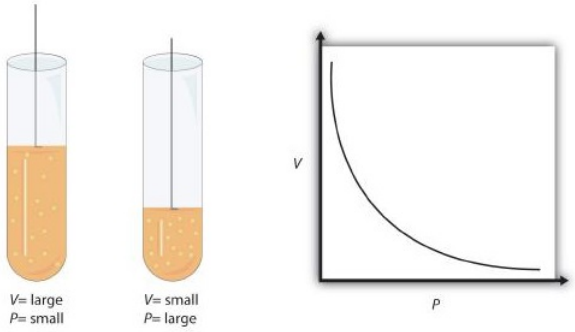


Figure **1.3.1**: The Relationship between Pressure and Volume for a Gas. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

This gas law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

Example 1.3.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: P_1 = 2.44 atm and V_1 = 4.01 L P_2 = 1.93 atm Find: V_2 = ? L
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{P_1 \times V_1}{P_2} \quad (1.3.4)$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.44 \cancel{\text{ atm}} \times 4.01 \text{ L}}{1.93 \cancel{\text{ atm}}} = 5.07 \text{ L} \quad (1.3.5)$$
Think about your result.	We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

Exercise 1.3.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer

124 mL

As mentioned, you can use any units for pressure or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

Example 1.3.2:

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: P_1 = 722 torr and V_1 = 88.8 mL V_2 = 0.633 L Find: P_2 = ? torr
List other known quantities.	1 L = 1000 mL to have the same units for volume.
Plan the problem.	1. Perform the conversion of the second volume unit from L to mL. 2. Rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times V_1}{V_2} \quad (1.3.6)$$
Cancel units and calculate.	1. $$0.663 \cancel{L} \times \frac{1000\,ml}{1\,\cancel{L}} = 663\,ml \quad (1.3.7)$$ 2. Substitute the known quantities into the equation and solve. $$P_2 = \frac{722\ \text{torr} \times 88.8\ \cancel{mL}}{663\ \cancel{mL}} = 96.7\ \text{torr} \quad (1.3.8)$$
Think about your result.	When the volume increased, the pressure decreased, which is as expected for Boyle's law.

Exercise 1.3.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

Summary

- The behavior of gases can be modeled with gas laws.
- A gas's pressure and volume are inversely related at constant temperature and amount.

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1.4: Gases - Volume and Temperature

Learning Objectives

- Express the mathematical relationship between temperature and volume for a gas sample with fixed moles at a fixed pressure.

The smell and taste of freshly-baked bread can be delightful for many. It is light and fluffy as a result of the action of yeast on sugar. The yeast converts the sugar to carbon dioxide, which at high temperatures causes the dough to expand.

The volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant. The absolute temperature is temperature measured with the Kelvin scale. The Kelvin scale must be used because zero on the Kelvin scale corresponds to a complete stoppage of molecular motion.

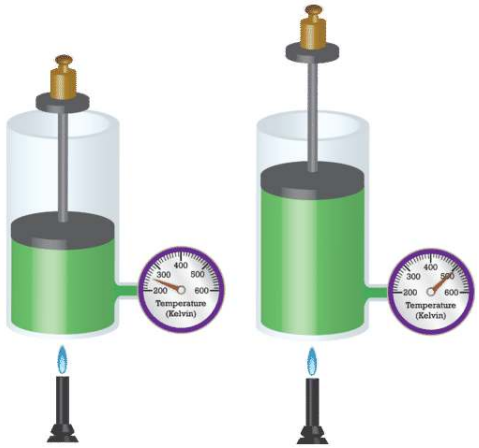


Figure **1.4.1**: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

Mathematically, the direct relationship can be represented by the following equation:

$$\frac{V}{T} = k \tag{1.4.1}$$

As with the previous gas law, k is constant only for a given gas sample. The table below shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

Table **1.4.1**: Temperature-Volume Data

Temperature (K)	**Volume (mL)**	$\frac{V}{T} = k \left(\frac{\text{mL}}{\text{K}}\right)$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in the figure below.

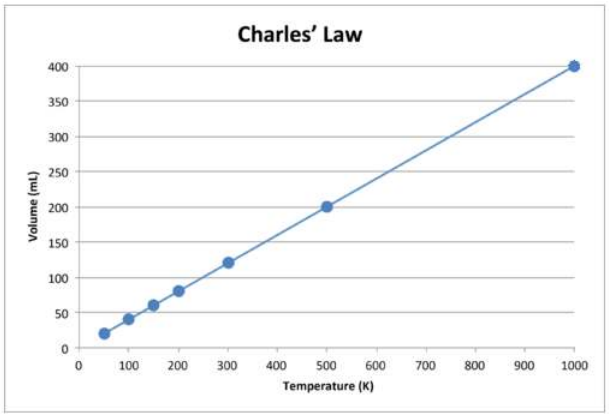


Figure 1.4.2:The volume of a gas increases as the Kelvin temperature increases.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero. The temperature at which this change into the liquid state occurs varies for different gases.

This law can also be used to compare changing conditions for a gas. Now we use V_1 and T_1 to stand for the initial volume and temperature of a gas, while V_2 and T_2 stand for the final volume and temperature. The mathematical relationship becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{1.4.2}$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that $\mathrm{K} = {}^\circ\mathrm{C} + 273$.

Example 1.4.1:

A balloon is filled to a volume of $2.20\ \mathrm{L}$ at a temperature of $22^\circ\mathrm{C}$. The balloon is then heated to a temperature of $71^\circ\mathrm{C}$. Find the new volume of the balloon.

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: $V_1 = 2.20\ \mathrm{L}$ and $T_1 = 22^\circ\mathrm{C} = 295\ \mathrm{K}$ $T_2 = 71^\circ\mathrm{C} = 344\ \mathrm{K}$ Find: V_2 = ? L
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{V_1 \times T_2}{T_1} \tag{1.4.3}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.20\ \mathrm{L} \times 344\ \cancel{\mathrm{K}}}{295\ \cancel{\mathrm{K}}} = 2.57\ \mathrm{L} \tag{1.4.4}$$
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

Exercise 1.4.1

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

Example 1.4.2:

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must be the temperature of the gas for its volume to be 25.0 L?

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: Given:T_1 = -27°C and V_1 = 34.8 L V_2 = 25.0 L Find: T_2 = ? K
List other known quantities.	K = -27°C + 273
Plan the problem.	1. Convert the initial temperature to Kelvin 2. Rearrange the equation algebraically to solve for T_2. $$T_2 = \frac{V_2 \times T_1}{V_1} \quad (1.4.5)$$
Cancel units and calculate.	1. −67°C + 273 = 206 K 2. Substitute the known quantities into the equation and solve. $$T_2 = \frac{25.0 \cancel{\text{L}} \times 206 \text{ K}}{34.8 \cancel{\text{L}}} = 148 \text{ K} \quad (1.4.6)$$
Think about your result.	This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

Exercise 1.4.2

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer

235 K, or −38°C

Summary

- A gas's volume is proportional to temperature at constant pressure and amount.

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1.5: The Combined Gas Law

Learning Objectives

- Learn and apply the combined gas law.

One thing we notice about all the gas laws is that, collectively, volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **combined gas law**, and its mathematical form is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \; at \; constant \; n \tag{1.5.1}$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in Kelvin.

Example 1.5.1:

A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: V_1 = 8.33 L, P_1 = 1.82 atm, and T_1 = 286 K V2 = 5.72 L and T_2 = 355 K Find: P_2 = ? atm
List other known quantities	none
Plan the problem	First, rearrange the equation algebraically to solve for V_2. $P_2 = \frac{P_1V_1T_2}{T_1V_2}$
Calculate	Now substitute the known quantities into the equation and solve. $P_2 = \frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})} = 3.22atm$ (1.5.2)
Think about your result.	Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

Exercise 1.5.1

If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?

Answer

105 mL

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

- The combined gas law relates pressure, volume, and temperature of a gas.

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1.6: The Ideal Gas Law and Gas Stoichiometry

Learning Objectives

- Learn the ideal gas law.
- Apply the ideal gas law to any set of conditions of a gas.
- Apply the ideal gas law to molar volumes, density, and stoichiometry problems.

So far, the gas laws we have considered have all required that the gas change its conditions; then we predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant *R* is called the ideal gas law constant. Its value depends on the units used to express pressure and volume.

Table **1.6.1** - Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	$\frac{L.atm}{mol.K}$
62.36	$\frac{L.torr}{mol.K} = \frac{L.mmHg}{mol.K}$
8.314	$\frac{J}{mol.K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvins. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 1.6.1:

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

The first step is to convert temperature to kelvins:

34 + 273 = 307 K

Now we can substitute the conditions into the ideal gas law:

$$(1.21 atm)(V) = (4.22\, mol)(0.08205 \frac{L.atm}{mol.K})(307\, K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L$$

Then solving for volume, we get V = 87.9 L

Exercise 1.6.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

Example 1.6.2:

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\,\cancel{g\,Hg} \times \frac{1\,mol\,Hg}{200.59\,\cancel{g\,Hg}} = 0.0000165\,mol = 1.66 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00120\,mm\,Hg)(435\,L) = (1.66 \times 10^{-5} mol)(62.36 \frac{L.mmHg}{mol.K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T = \frac{(0.00120)(435)}{(1.66 \times 10^{-5})(62.36)} K$$

Then solving for K, we get T = 504 K.

Note that the number of moles was rounded before inserting that number into the ideal gas law. If you waited to round until the end, you may have calculated 505K. This is more accurate but makes it harder to show the intermediate steps of the calculation.

Exercise 1.6.2

For a 0.00554 mol sample of H_2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

The ideal gas law can also be used in stoichiometry problems.

Example 1.6.3:

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is

calculated:

$$55.8\,\cancel{g\,Zn} \times \frac{1\,\cancel{mol\,Zn}}{65.41\,\cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1\,\cancel{mol\,Zn}} = 0.853\,H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07atm)V = (0.853\,mol)(0.08205\frac{L.atm}{mol.K})(299\,K)$$

All the units cancel except for L, for volume, which means V = 19.6 L

Exercise 1.6.3

What pressure of HCl is generated if 3.44 g of Cl_2 are reacted in 4.55 L at 455 K?

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Answer

0.796 atm

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V = (1\,mol)(0.08205\frac{L.atm}{mol.K})(273\,K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure **1.6.1** Molar Volume). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are not at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

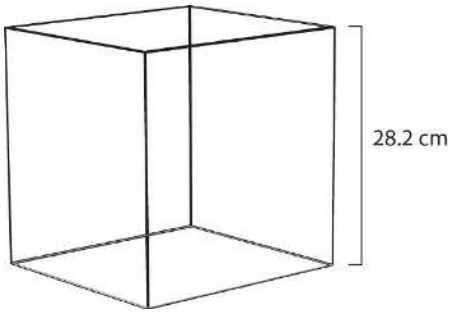


Figure **1.6.1**: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

Example 1.6.4:

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7 \cancel{L} \times \frac{1\,mol}{22.4\,\cancel{L}} = 1.73\,mol$$

Exercise 1.6.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

Example 1.6.5:

What volume of H_2 is produced at STP when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\,\cancel{g\,Zn} \times \frac{1\,\cancel{mol\,Zn}}{65.41\,\cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1\,\cancel{mol\,Zn}} = 0.853\,H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\,\cancel{mol\,H_2} \times \frac{22.4\,L}{1\,\cancel{mol\,H_2}} = 19.1\,L\,H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

Exercise 1.6.5

What volume of HCl is generated if 3.44 g of Cl_2 are reacted at STP?

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Answer

2.17 L

The ideal gas law can also be used to determine the density of gases. Density, recall, is defined as the mass of a substance divided by its volume:

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

Assume that you have exactly 1 mol of a gas. If you know the identity of the gas, you can determine the molar mass of the substance. Using the ideal gas law, you can also determine the volume of that mole of gas, using whatever the temperature and pressure conditions are. Then you can calculate the density of the gas by using

$$density = \frac{molar\ mass}{molar\ volume}$$

Example 1.6.6:

What is the density of N_2 at 25°C and 0.955 atm?

Solution

First, we must convert the temperature into kelvins:

$$25 + 273 = 298 \text{ K}$$

If we assume exactly 1 mol of N_2, then we know its mass: 28.0 g. Using the ideal gas law, we can calculate the volume:

$$(0.955\,atm)V = (1\,mol)(0.08205\frac{L.atm}{mol.K})(298\,K)$$

All the units cancel except for L, the unit of volume. So V = 25.6 L

Knowing the molar mass and the molar volume, we can determine the density of N_2 under these conditions:

$$d = \frac{28.0\,g}{25.6\,L} = 1.09\,g/L$$

Exercise 1.6.6

What is the density of CO_2 at a pressure of 0.0079 atm and 227 K? (These are the approximate atmospheric conditions on Mars.)

Answer

0.019 g/L

Chemistry Is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

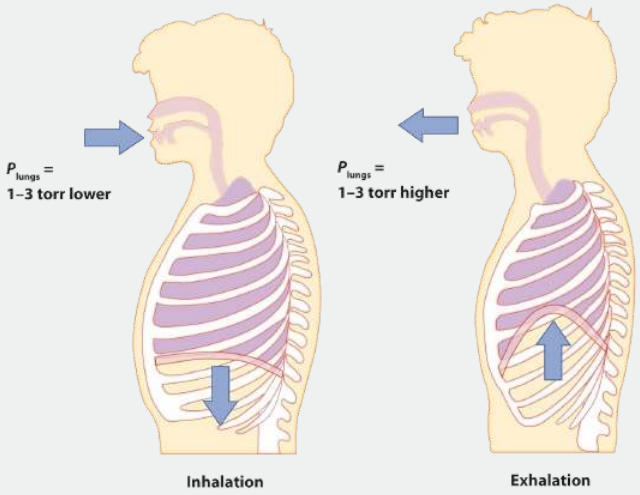


Figure **1.6.2** Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L) = n(0.08205\frac{L.atm}{mol.K})(295\,K)$$

Solving for the number of moles, we get

n = 0.021 mol air

This ends up being about 0.6 g of air per breath—not much, but enough to keep us alive.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems whose chemical reactions involve gases.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.
- The ideal gas law can be used to determine the density of gases.

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1.7: Partial Pressures

Learning Objectives

- To determine the contribution of each component gas to the total pressure of a mixture of gases

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{1.7.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressure, the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, ***the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases***. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as *Dalton's law of partial pressures*. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots \tag{1.7.2}$$

$$= \sum_{i=1}^{n} P_i \tag{1.7.3}$$

where P_{tot} is the total pressure and the other terms are the partial pressures of the individual gases (up to n component gases).

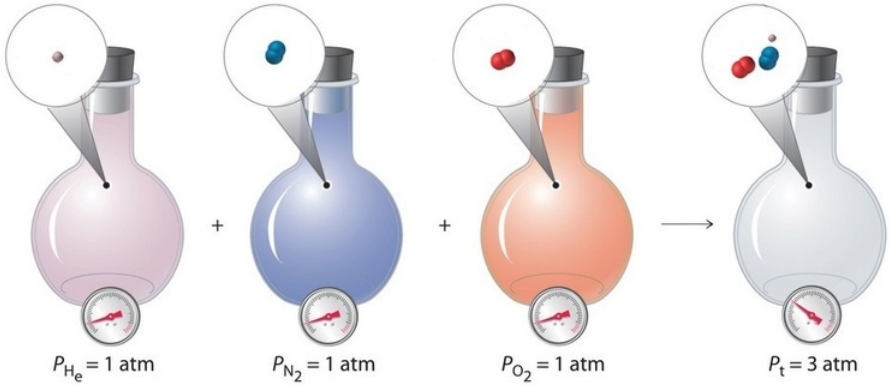


Figure 1.7.1: Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B \tag{1.7.4}$$

$$= n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) \tag{1.7.5}$$

$$= (n_A + n_B)\left(\frac{RT}{V}\right) \tag{1.7.6}$$

More generally, for a mixture of n component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{1.7.7}$$

$$= \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right) \tag{1.7.8}$$

Equation 1.7.8 restates Equation 1.7.6 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on only the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 1.7.8 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 1.7.1.

Example 1.7.1: The Bends

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called “the bends.” At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A. Calculate the number of moles of **He** and $\mathbf{O_2}$ present.
B. Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of **He** is

$$n_{\mathrm{He}} = \frac{326.4\ \mathrm{g}}{4.003\ \mathrm{g/mol}} = 81.54\ \mathrm{mol}$$

The number of moles of $\mathbf{O_2}$ is

$$n_{\mathrm{O_2}} = \frac{51.2\ \mathrm{g}}{32.00\ \mathrm{g/mol}} = 1.60\ \mathrm{mol}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\mathrm{He}} = \frac{n_{\mathrm{He}}RT}{V} = \frac{81.54\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 196.2\ \mathrm{atm}$$

$$P_{\mathrm{O_2}} = \frac{n_{\mathrm{O_2}}RT}{V} = \frac{1.60\ \mathrm{mol} \times 0.08206\ \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}} \times 293.15\ \mathrm{K}}{10.0\ \mathrm{L}} = 3.85\ \mathrm{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\mathrm{tot}} = P_{\mathrm{He}} + P_{\mathrm{O_2}} = (196.2 + 3.85)\ \mathrm{atm} = 200.1\ \mathrm{atm}$$

Exercise 1.7.1

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer

$P_{CH_4} = 137\ atm;\ P_{C_2H_6} = 13.4\ atm;\ P_{tot} = 151\ atm$

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (χ) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_{tot}):

$$\chi_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{1.7.9}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $\chi_A = 1.0$, then the sample is pure A, not a mixture. If $\chi_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_A RT/V$ and $P_{tot} = n_t RT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_A RT/V}{n_{tot} RT/V} = \frac{n_A}{n_{tot}} = \chi_A \tag{1.7.10}$$

Rearranging this equation gives

$$P_A = \chi_A P_{tot} \tag{1.7.11}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 1.7.11, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

Example 1.7.2: Exhaling Composition

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

	Inhaled Air / mmHg	Exhaled Air / mmHg
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_{tot}	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 1.7.11.

Solution:

The mole fraction of any gas A is given by

$$\chi_A = \frac{P_A}{P_{tot}}$$

where P_A is the partial pressure of A and P_{tot} is the total pressure. For example, the mole fraction of CO_2 is given as:

$$\chi_{CO_2} = \frac{48 \text{ mmHg}}{767 \text{ mmHg}} = 0.063$$

The following table gives the values of χ_A for the gases in the exhaled air.

Gas	Mole Fraction
N_2	0.741
O_2	0.151
H_2O	0.037
CO_2	0.063
Ar	0.010

Exercise 1.7.2

Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90. atm. The atmosphere consists of about 96% CO_2 and 3.0% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer

$$P_{CO_2} = 86 \text{ atm}$$

$$P_{N_2} = 2.7 \text{ atm}$$

Summary

The partial pressure of each gas in a mixture is proportional to its mole fraction. The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

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CHAPTER OVERVIEW

2: Phase Transitions and Liquids

2.1: Phase Transitions

2.2: Heating Curves

2.3: Intermolecular Forces

2.4: Properties of Liquids - Vapor Pressure and Surface Tension

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2.1: Phase Transitions

Learning Objective

- Describe what happens during a phase change.
- Calculate the energy change needed for a phase change.

Substances can change phase—often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous.

The process of a solid becoming a liquid is called **melting** (an older term that you may see sometimes is *fusion*). The opposite process, a liquid becoming a solid, is called **solidification**. For any pure substance, the temperature at which melting occurs—known as the **melting point**—is a characteristic of that substance. It requires energy for a solid to melt into a liquid. Every pure substance has a certain amount of energy it needs to change from a solid to a liquid. This amount is called the **enthalpy of fusion (or heat of fusion)** of the substance, represented as ΔH_{fus}. Some ΔH_{fus} values are listed in Table **2.1.1**; it is assumed that these values are for the melting point of the substance. Note that the unit of ΔH_{fus} is kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{fus} is always tabulated as a positive number. However, it can be used for both the melting and the solidification processes as long as you keep in mind that melting is always endothermic (so ΔH will be positive), while solidification is always exothermic (so ΔH will be negative).

Table **2.1.1**: Enthalpies of Fusion for Various Substances

Substance (Melting Point)	ΔH_{fus} (kJ/mol)
Water (0°C)	6.01
Aluminum (660°C)	10.7
Benzene (5.5°C)	9.95
Ethanol (−114.3°C)	5.02
Mercury (−38.8°C)	2.29

Example 2.1.1

What is the energy change when 45.7 g of $\mathbf{H_2O}$ melt at 0°C?

Solution

The ΔH_{fus} of $\mathbf{H_2O}$ is 6.01 kJ/mol. However, our quantity is given in units of grams, not moles, so the first step is to convert grams to moles using the molar mass of $\mathbf{H_2O}$, which is 18.0 g/mol. Then we can use ΔH_{fus} as a conversion factor. Because the substance is melting, the process is endothermic, so the energy change will have a positive sign.

$$45.7\ \cancel{g\ H_2O} \times \frac{1\ \cancel{mol\ H_2O}}{18.0\ \cancel{g}} \times \frac{6.01 kJ}{\cancel{mol}} = 15.3\ kJ$$

Without a sign, the number is assumed to be positive.

Exercise 2.1.1

What is the energy change when 108 g of $\mathbf{C_6H_6}$ freeze at 5.5°C?

Answer

−13.8 kJ

During melting, energy goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. Hence melting is an **isothermal** process because a substance stays at the same temperature. Only when all of a substance

is melted does any additional energy go to changing its temperature.

What happens when a solid becomes a liquid? In a solid, individual particles are stuck in place because the intermolecular forces cannot be overcome by the energy of the particles. When more energy is supplied (e.g., by raising the temperature), there comes a point at which the particles have enough energy to move around, but not enough energy to separate. This is the liquid phase: particles are still in contact, but are able to move around each other. This explains why liquids can assume the shape of their containers: the particles move around and, under the influence of gravity, fill the lowest volume possible (unless the liquid is in a zero-gravity environment—see Figure **2.1.1**.



Figure **2.1.1**: Liquids and Gravity. (a) A liquid fills the bottom of its container as it is drawn downward by gravity and the particles slide over each other. (b) A liquid floats in a zero-gravity environment. The particles still slide over each other because they are in the liquid phase, but now there is no gravity to pull them down. Source: Photo on the left © Thinkstock. Photo on the right courtesy of NASA, http://www.nasa.gov/mission_pages/st...image_009.html.

The phase change between a liquid and a gas has some similarities to the phase change between a solid and a liquid. At a certain temperature, the particles in a liquid have enough energy to become a gas. The process of a liquid becoming a gas is called **boiling (or vaporization)**, while the process of a gas becoming a liquid is called **condensation**. However, unlike the solid/liquid conversion process, the liquid/gas conversion process is noticeably affected by the surrounding pressure on the liquid because gases are strongly affected by pressure. This means that the temperature at which a liquid becomes a gas, the **boiling point**, can change with surrounding pressure. Therefore, we define the **normal boiling point** as the temperature at which a liquid changes to a gas when the surrounding pressure is exactly 1 atm, or 760 torr. Unless otherwise specified, it is assumed that a boiling point is for 1 atm of pressure.

Like the solid/liquid phase change, the liquid/gas phase change involves energy. The amount of energy required to convert a liquid to a gas is called the **enthalpy of vaporization** (or heat of vaporization), represented as ΔH_{vap}. Some ΔH_{vap} values are listed in Table **2.1.2**; it is assumed that these values are for the normal boiling point temperature of the substance, which is also given in the table. The unit for ΔH_{vap} is also kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{vap} is also always tabulated as a positive number. It can be used for both the boiling and the condensation processes as long as you keep in mind that boiling is always endothermic (so ΔH will be positive), while condensation is always exothermic (so ΔH will be negative).

Table **2.1.1**: Enthalpies of Vaporization for Various Substances

Substance (Normal Boiling Point)	ΔH_{vap} (kJ/mol)
Water (100°C)	40.68
Bromine (59.5°C)	15.4
Benzene (80.1°C)	30.8
Ethanol (78.3°C)	38.6
Mercury (357°C)	59.23

Example 2.1.2

What is the energy change when 66.7 g of $Br_2(g)$ condense to a liquid at 59.5°C?

Solution

The ΔH_{vap} of Br_2 is 15.4 kJ/mol. Even though this is a condensation process, we can still use the numerical value of ΔH_{vap} as long as we realize that we must take energy out, so the ΔH value will be negative. To determine the magnitude of the energy change, we must first convert the amount of Br_2 to moles. Then we can use ΔH_{vap} as a conversion factor.

$$66.7\ \cancel{g\ Br_2} \times \frac{1\ \cancel{mol\ Br_2}}{159.8\ \cancel{g}} \times \frac{15.4 kJ}{\cancel{mol}} = 6.43\ kJ$$

Because the process is exothermic, the actual value will be negative: $\Delta H = -6.43$ kJ.

Exercise 2.1.2

What is the energy change when 822 g of $C_2H_5OH(\ell)$ boil at its normal boiling point of 78.3°C?

Answer

689 kJ

As with melting, the energy in boiling goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. So boiling is also an isothermal process. Only when all of a substance has boiled does any additional energy go to changing its temperature.

What happens when a liquid becomes a gas? We have already established that a liquid is composed of particles in contact with each other. When a liquid becomes a gas, the particles separate from each other, with each particle going its own way in space. This is how gases tend to fill their containers. Indeed, in the gas phase most of the volume is empty space; only about 1/1,000th of the volume is actually taken up by matter (Figure 2.1.1). It is this property of gases that explains why they can be compressed, a fact that is considered in Chapter 6.

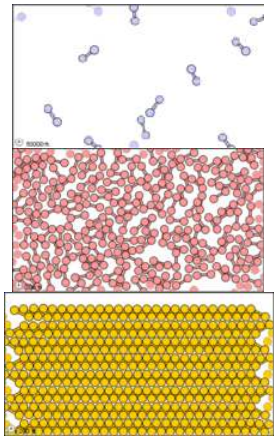


Figure 2.1.2: Sub-microscopic view of the diatomic molecules of the element bromine (a) in the gaseous state (above 58°C); (b) in liquid form (between -7.2 and 58.8°C); and (c) in solid form (below -7.2°C). As a solid, the molecules are fixed, but fluctuate. As a liquid, the molecules are in contact but are also able to move around each other. As a gas, most of the volume is actually empty space. The particles are not to scale; in reality, the dots representing the particles would be about 1/100th of the size depicted.

Under some circumstances, the solid phase can transition directly to the gas phase without going through a liquid phase, and a gas can directly become a solid. The solid-to-gas change is called **sublimation**, while the reverse process is called **deposition.** Sublimation is isothermal, like the other phase changes. There is a measurable energy change during sublimation; this energy change is called the **enthalpy of sublimation**, represented as ΔH_{sub}. The relationship between the ΔH_{sub} and the other enthalpy changes is as follows:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

As such, ΔH_{sub} is not always tabulated because it can be simply calculated from ΔH_{fus} and ΔH_{vap}.

There are several common examples of sublimation. A well-known product, dry ice, is actually solid CO_2. Dry ice is dry because it sublimes, with the solid bypassing the liquid phase and going straight to the gas phase. The sublimation occurs at temperature of −77°C, so it must be handled with caution. If you have ever noticed that ice cubes in a freezer tend to get smaller over time, it is because the solid water is very slowly subliming. "Freezer burn" isn't actually a burn; it occurs when certain foods, such as meats, slowly lose solid water content because of sublimation. The food is still good, but looks unappetizing. Reducing the temperature of a freezer will slow the sublimation of solid water.



Figure **2.1.3**: Freezer burn on a piece of beef. (Public Domain; RolloM).

Chemical equations can be used to represent a phase change. In such cases, it is crucial to use phase labels on the substances. For example, the chemical equation for the melting of ice to make liquid water is as follows:

$$H_2O(s) \rightarrow H_2O(\ell)$$

No chemical change is taking place; however, a physical change is taking place.

Summary

- Phase changes can occur between any two phases of matter.
- All phase changes occur with a simultaneous change in energy.
- All phase changes are isothermal.

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2.2: Heating Curves

Freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure **2.2.3** shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

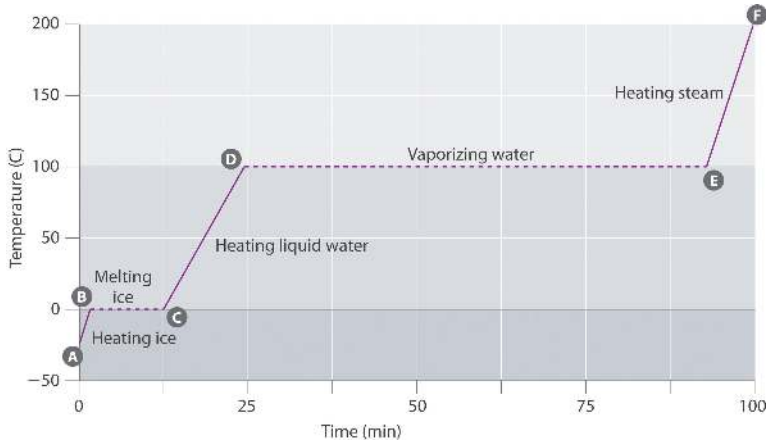


Figure **2.2.1**: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure **2.2.3**, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure **2.2.3**, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is

heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or "bump" the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a "boiling chip") in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure **2.2.4** plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure **2.2.3**, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

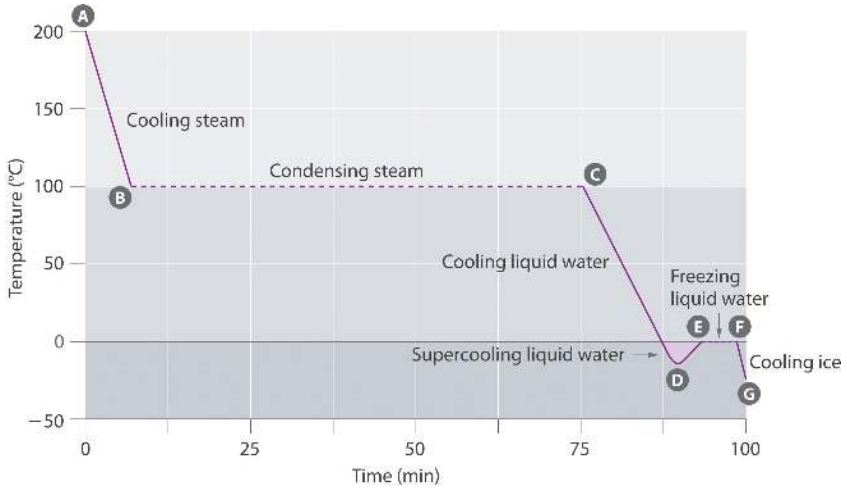


Figure **2.2.2**: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

Example 2.2.1: Cooling Hot Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost (Equation 5.39) to obtain the final temperature of the mixture.

Solution:

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T \tag{2.2.1}$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

Exercise 2.2.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 2.2.1

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

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2.3: Intermolecular Forces

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids but are more similar to solids.*

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law,.)

In this section, we explicitly consider three kinds of intermolecular interactions: There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure **2.3.1***a*.

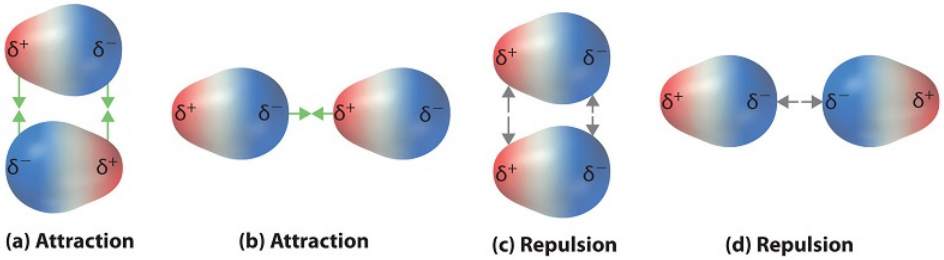


Figure **2.3.1**: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure **2.3.1***c*). Hence dipole–dipole interactions, such as those in Figure **2.3.1***b*, are *attractive intermolecular interactions*, whereas those in Figure **2.3.1***d* are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure **2.3.2**. On average, however, the attractive interactions dominate.

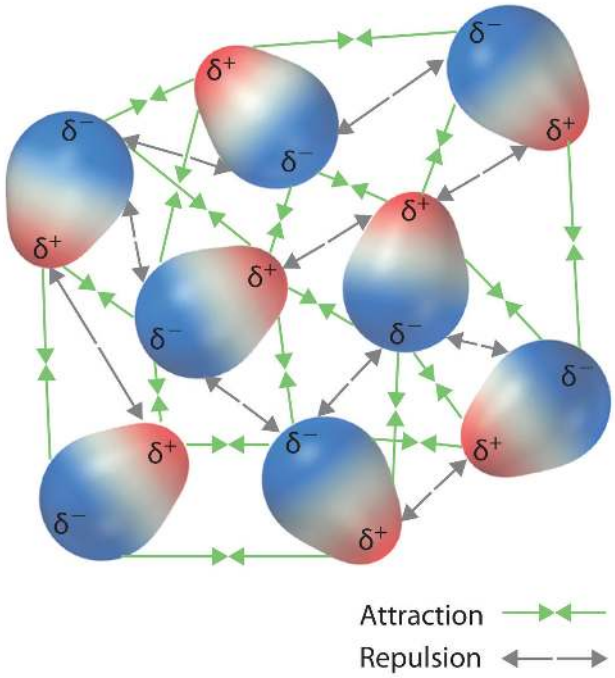


Figure **2.3.2**: Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as **HCl**, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas **NaCl**, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table **2.3.1**.

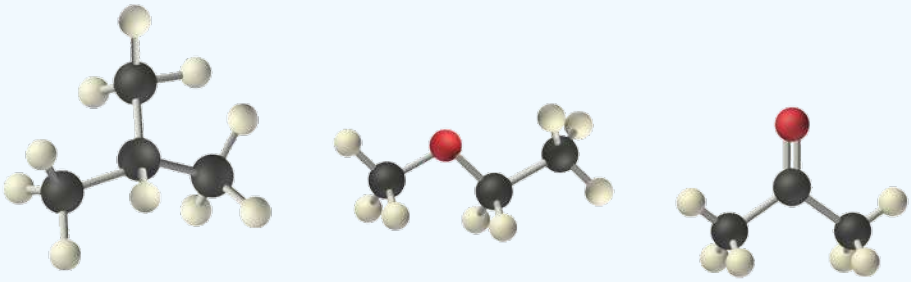
Table **2.3.1**: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*

Example 2.3.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane Ethyl methyl ether Acetone

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone.

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 2.3.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table **2.3.2**).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table **2.3.2**: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure **2.3.3**, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

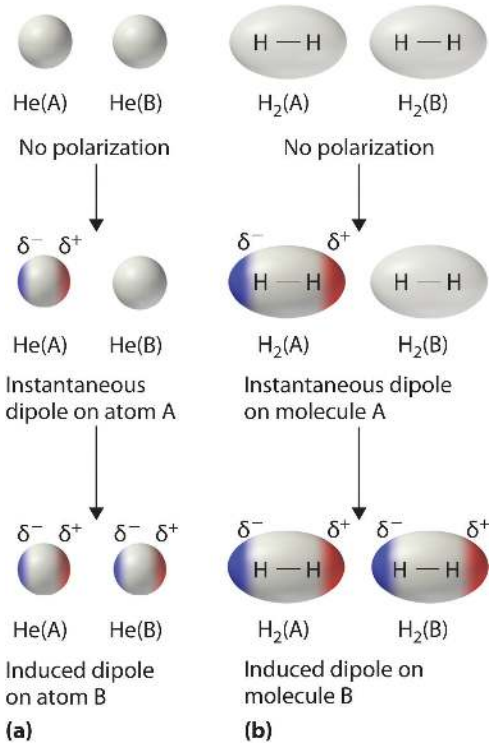


Figure **2.3.3**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure **2.3.3**, tends to become more pronounced as atomic and molecular masses increase (Table **2.3.2**). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure **2.3.4**). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure **2.3.4** shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

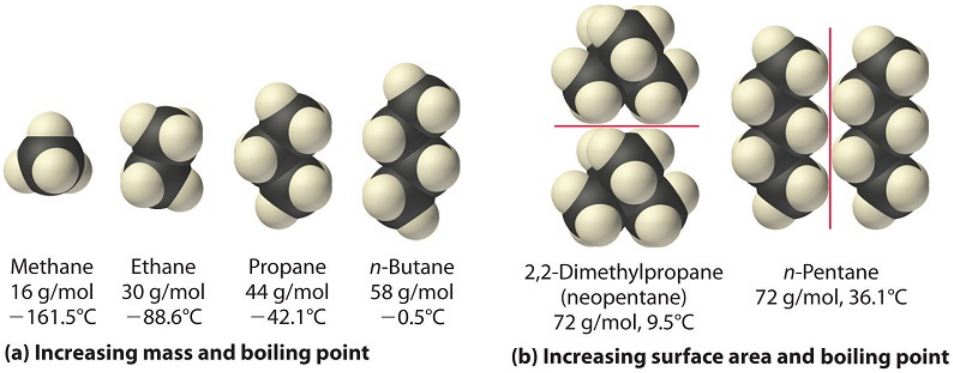


Figure **2.3.4**: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 2.3.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise 2.3.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure **2.3.5**. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted

on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

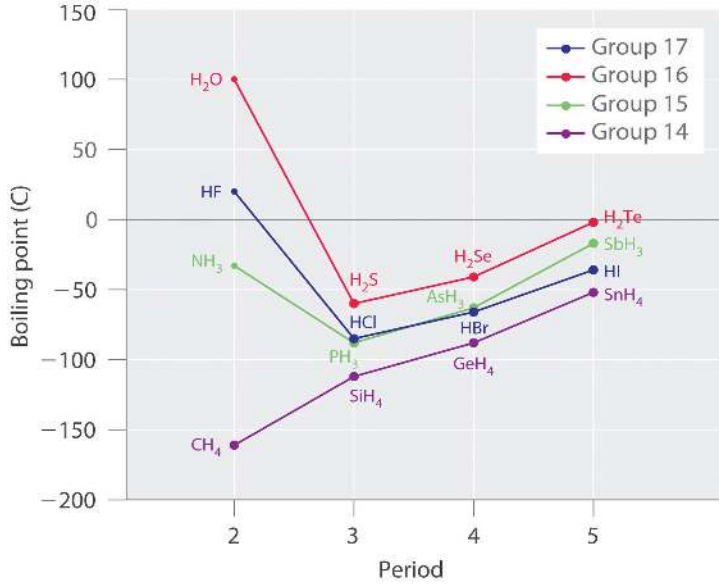


Figure **2.3.5**: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure **2.3.6**. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

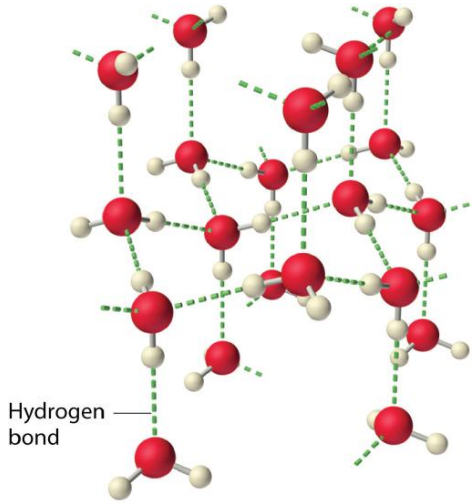


Figure **2.3.6**: The Hydrogen-Bonded Structure of Ice.

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Example 2.3.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

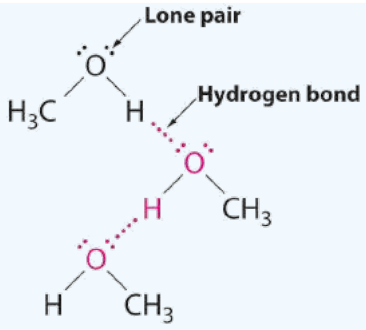
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



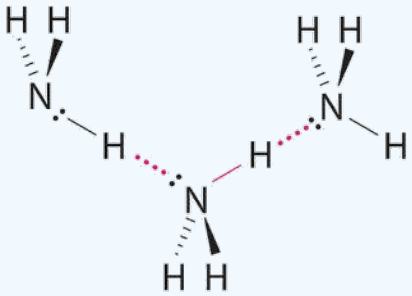
Hydrogen bonding in methanol

Exercise 2.3.3

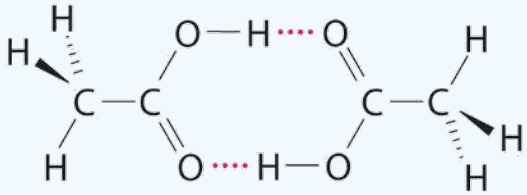
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 2.3.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass

is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269°C) < \text{Ar } (-185.7°C) < N_2O\ (-88.5°C) < C_{60}\ (>280°C) < \text{NaCl } (1465°C).$$

Exercise 2.3.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Example 2.3.5:

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.

b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 2.3.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than

smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

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2.4: Properties of Liquids - Vapor Pressure and Surface Tension

Learning Objective

- Define the vapor pressure of liquids.
- Explain the origin of both surface tension and capillary action.

There are some properties that all liquids have. A liquid that most are familiar with is water, and it has these properties. Other liquids have them as well, which is something to keep in mind.

All liquids have a certain portion of particles with enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (Figure **2.4.1** - Evaporation). The formation of a gas from a liquid at temperatures below the boiling point is called **evaporation**. At these temperatures, the material in the gas phase is called **vapor**, rather than gas; the term *gas* is reserved for when the gas phase is the stable phase.

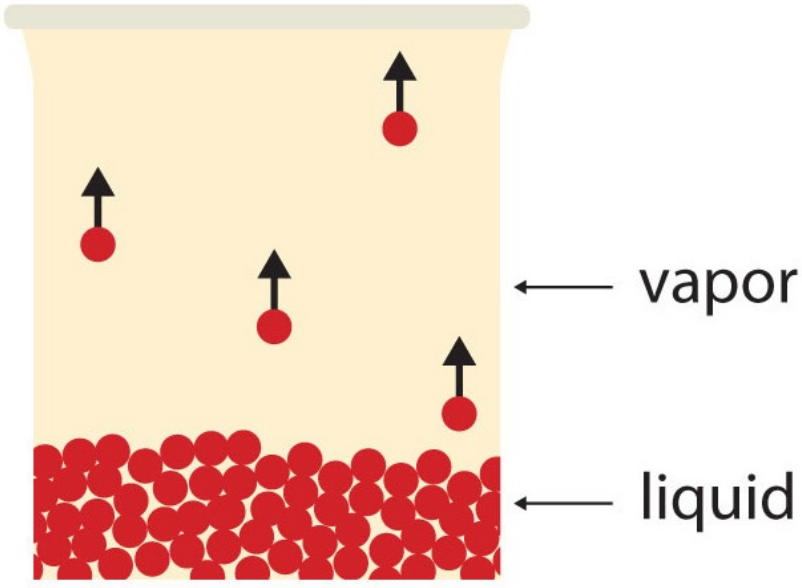


Figure **2.4.1** Evaporation. Some particles of a liquid have enough energy to escape the liquid phase to become a vapor.

If the available volume is large enough, eventually all the liquid will become vapor. But if the available volume is not enough, eventually some of the vapor particles will reenter the liquid phase (Figure **2.4.2** Equilibrium). At some point, the number of particles entering the vapor phase will equal the number of particles leaving the vapor phase, so there is no net change in the amount of vapor in the system. We say that the system is *at equilibrium*. The partial pressure of the vapor at equilibrium is called the *vapor pressure of the liquid*.

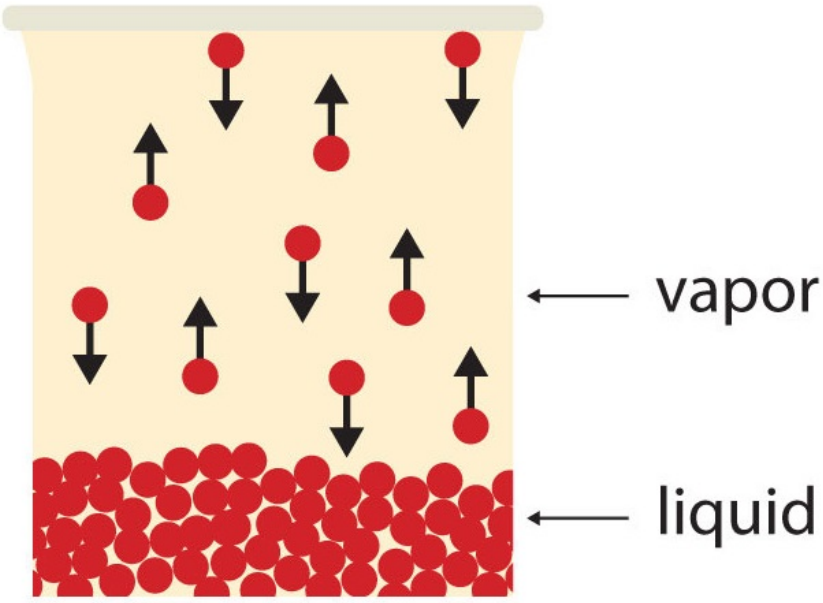


Figure10.4.2 Equilibrium. At some point, the number of particles entering the vapor phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.

Understand that the liquid has not stopped evaporating. The reverse process—condensation—is occurring as fast as evaporation, so there is no net change in the amount of vapor in the system. The term **dynamic equilibrium** represents a situation in which a process still occurs, but the opposite process also occurs at the same rate, so that there is no net change in the system.

The vapor pressure for a substance is dependent on the temperature of the substance; as the temperature increases, so does the vapor pressure. Figure **2.4.3** - Plots of Vapor Pressure versus Temperature for Several Liquids, is a plot of vapor pressure versus temperature for several liquids. Having defined vapor pressure, we can also redefine the *boiling point* of a liquid: the temperature at which the vapor pressure of a liquid equals the surrounding environmental pressure. The normal vapor pressure, then, is the temperature at which the vapor pressure is 760 torr, or exactly 1 atm. Thus boiling points vary with surrounding pressure, a fact that can have large implications on cooking foods at lower- or higher-than-normal elevations. Atmospheric pressure varies significantly with altitude.

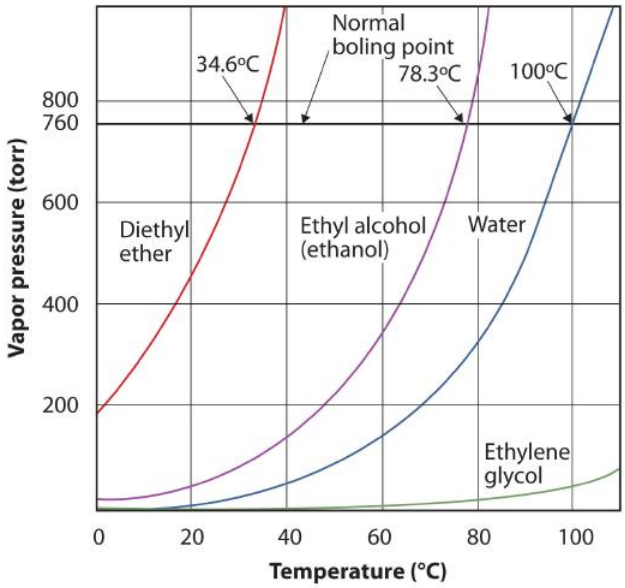


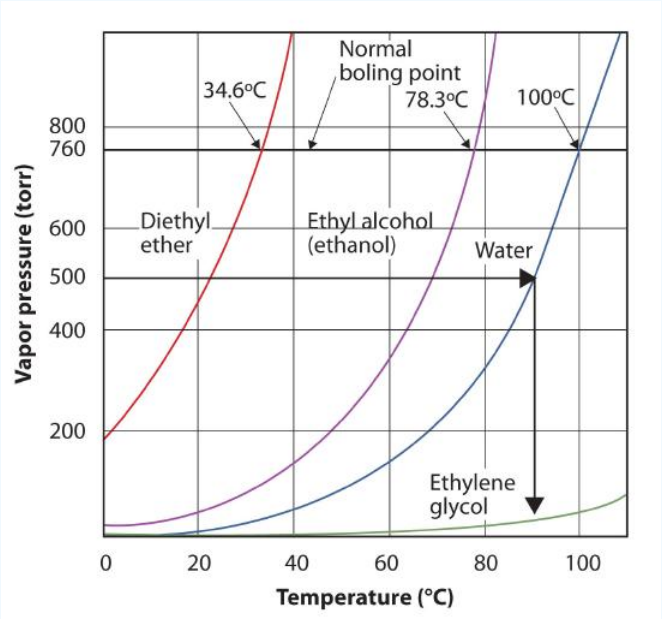
Figure **2.4.3** Plots of Vapor Pressure versus Temperature for Several Liquids. The vapor pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.

Example 2.4.1:

Use Figure **2.4.3** - Plots of Vapor Pressure versus Temperature for Several Liquids, to estimate the boiling point of water at 500 torr, which is the approximate atmospheric pressure at the top of Mount Everest.

Solution

See the accompanying figure. Five hundred torr is between 400 and 600, so we extend a line from that point on the *y*-axis across to the curve for water and then drop it down to the *x*-axis to read the associated temperature. It looks like the point on the water vapor pressure curve corresponds to a temperature of about 90°C, so we conclude that the boiling point of water at 500 torr is 90°C.



By reading the graph properly, you can estimate the boiling point of a liquid at different temperatures.

Exercise 2.4.1

Use Figure **2.4.3** - Plots of Vapor Pressure versus Temperature for Several Liquids, to estimate the boiling point of ethanol at 400 torr.

Answer

about 65°C

The vapor pressure curve for water is not exactly zero at the melting point 0°C. Even ice has a vapor pressure; that is why it sublimes over time. However, the vapor pressures of solids are typically much lower than that of liquids. At −1°C, the vapor pressure of ice is 4.2 torr. At a freezer temperature of 0°F (−17°C), the vapor pressure of ice is only 1.0 torr; so-called deep freezers can get down to −23°C, where the vapor pressure of ice is only 0.6 torr.

All liquids share some other properties as well. **Surface tension** is an effect caused by an imbalance of forces on the atoms at the surface of a liquid, as shown in Figure **2.4.4** - Surface Tension. The blue particle in the bulk of the liquid experiences intermolecular forces from all around, as illustrated by the arrows. However, the yellow particle on the surface does not experience any forces above it because there are no particles above it. This leads to an imbalance of forces, called surface tension.

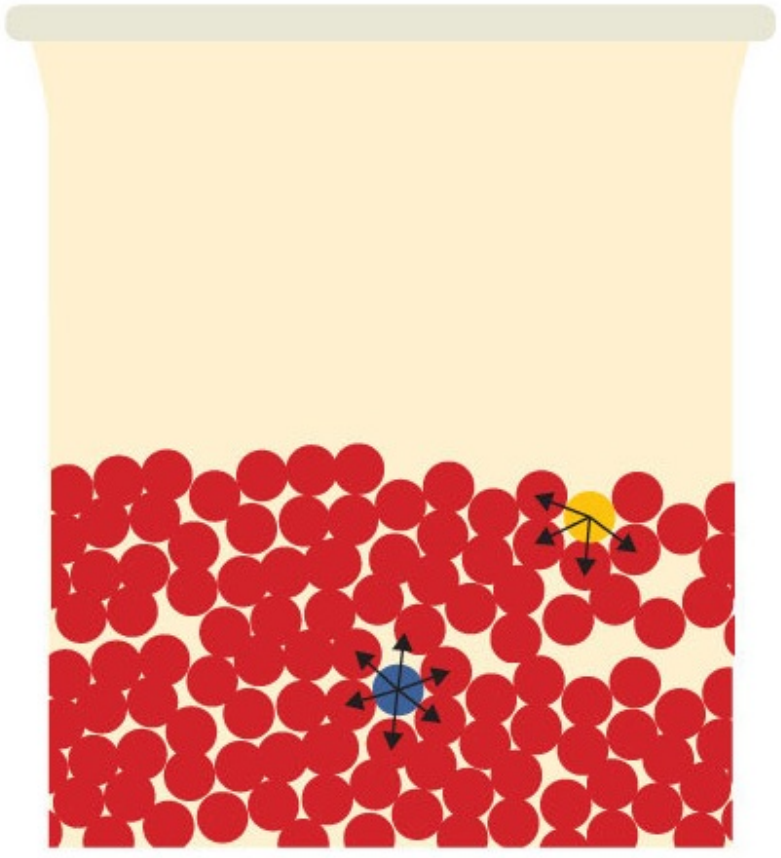


Figure 2.4.4 Surface Tension. Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.

Surface tension is responsible for several well-known behaviors of liquids, including water. Liquids with high surface tension tend to bead up when present in small amounts (Figure 2.4.5 - Effects of Surface Tension).



Figure 2.4.5 Effects of Surface Tension © Thinkstock. Water on the surface of this apple beads up due to the effect of surface tension.

Surface tension causes liquids to form spheres in free fall or zero gravity (See Figure 2.4.1 - Liquids and Gravity: the "floating" water isn't in the shape of a sphere by accident; it is the result of surface tension). Surface tension is also responsible for the fact that small insects can "walk" on water. Because of surface tension, it takes energy to break the surface of a liquid, and if an object (such as an insect) is light enough, there is not enough force due to gravity for the object to break through the surface, so the object stays on top of the water (Figure 2.4.6 - Walking on Water). Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.



Figure **2.4.6** Walking on Water © Thinkstock. Small insects can actually walk on top of water because of surface tension effects.

The fact that small droplets of water bead up on surfaces does not mean that water—or any other liquid—does not interact with other substances. Sometimes the attraction can be very strong. **Adhesion** is the tendency of a substance to interact with other substances because of intermolecular forces, while **cohesion** is the tendency of a substance to interact with itself. If cohesive forces within a liquid are stronger than adhesive forces between a liquid and another substance, then the liquid tends to keep to itself; it will bead up. However, if adhesive forces between a liquid and another substance are stronger than cohesive forces, then the liquid will spread out over the other substance, trying to maximize the interface between the other substance and the liquid. We say that the liquid *wets* the other substance.

Adhesion and cohesion are important for other phenomena as well. In particular, if adhesive forces are strong, then when a liquid is introduced to a small-diameter tube of another substance, the liquid will move up or down in the tube, as if ignoring gravity. Because tiny tubes are called capillaries, this phenomenon is called **capillary action.** For example, one type of capillary action, *capillary rise*, is seen when water or water-based liquids rise up in thin glass tubes (like the capillaries sometimes used in blood tests), forming an upwardly curved surface called a **meniscus**. Capillary action is also responsible for the "wicking" effect that towels and sponges use to dry wet objects; the matting of fibers forms tiny capillaries that have good adhesion with water. Cotton is a good material for this; polyester and other synthetic fabrics do not display similar capillary action, which is why you seldom find rayon bath towels. A similar effect is observed with liquid fuels or melted wax and their wicks. Capillary action is thought to be at least partially responsible for transporting water from the roots to the tops of trees, even tall ones.

On the other hand, some liquids have stronger cohesive forces than adhesive forces. In this case, in the presence of a capillary, the liquid is forced down from its surface; this is an example of a type of capillary action called *capillary depression*. In this case, the meniscus curves downward. Mercury has very strong cohesive forces; when a capillary is placed in a pool of mercury, the surface of the mercury liquid is depressed (Figure **2.4.7** - Capillary Action).



Figure **2.4.7** Capillary Action. (a) Capillary rise is seen when adhesion is strong, such as with water in a thin glass tube. (b) Capillary depression is seen when cohesive forces are stronger than adhesive forces, such as with mercury and thin glass tubes.

Chemistry Is Everywhere: Waxing a Car

Responsible car owners are encouraged to wax their cars regularly. In addition to making the car look nicer, it also helps protect the surface, especially if the surface is metal. Why?

The answer has to do with cohesion and adhesion (and, to a lesser extent, rust). Water is an important factor in the rusting of iron, sometimes used extensively in outer car bodies. Keeping water away from the metal is one way to minimize rusting. A coat of paint helps with this. However, dirty or scratched paint can attract water, and adhesive forces will allow the water to wet the surface, maximizing its contact with the metal and promoting rust.

Wax is composed of long hydrocarbon molecules that do not interact well with water. (Hydrocarbons are compounds with C and H atoms; for more information on hydrocarbons, see Chapter 16). That is, a thin layer of wax will not be wetted by water. A freshly waxed car has low adhesive forces with water, so water beads up on the surface, as a consequence of its cohesion and surface tension. This minimizes the contact between water and metal, thus minimizing rust.



Figure **2.4.8** Waxing a car © Thinkstock. Droplets of water on a freshly waxed car do not wet the car well because of low adhesion between water and the waxed surface. This helps protect the car from rust.

Summary:

- All liquids evaporate.
- If volume is limited, evaporation eventually reaches a dynamic equilibrium, and a constant vapor pressure is maintained.
- All liquids experience surface tension, an imbalance of forces at the surface of the liquid.
- All liquids experience capillary action, demonstrating either capillary rise or capillary depression in the presence of other substances.

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CHAPTER OVERVIEW

3: Solutions

3.1: Introduction to Solutions
3.2: Units of Concentration
3.3: Dilutions
3.4: Concentrations as Conversion Factors and Solution Stoichiometry
3.5: Colligative Properties
3.6: Osmosis

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3.1: Introduction to Solutions

Learning Objective

- Learn some terminology involving solutions.
- Recognize which terminology is qualitative and which terminology is quantitative.
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. "Major" and "minor" indicate whichever component has the greater or lesser presence by mass or moles, respectively. Sometimes this becomes confusing, especially when considering substances with very different molar masses. We will confine the discussion here to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water; soda water is a solution of gaseous CO_2 in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent.

Example 3.1.1: Sugar Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is sucrose, so it is the solute. Water—the majority component—is the solvent. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 3.1.1

A solution is made by dissolving 3.33 g of HCl(g) in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: HCl(g); solvent: CH_3OH

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called **concentration**. Various words are used to describe the relative amounts of solute. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table **3.1.1** lists the solubilities of some simple ionic compounds. These solubilities vary widely: NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table **3.1.1**: Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated but rather concentrated. Ideally, we need more precise ways of specifying the amount of solute in a solution. We will introduce such ways in Section 11.3.

In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.

It should be obvious that some solutes dissolve in certain solvents but not others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not water. What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in Chapter 10). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane but not in polar water. This concept leads to the general rule that "like dissolves like" for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

Example 3.1.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Exercise 3.1.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O because both experience hydrogen bonding

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration is the expression of the amount of solute in a given amount of solvent and can be described by several qualitative terms.
- Solubility is a specific amount of solute that can dissolve in a given amount of solvent.
- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

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3.2: Units of Concentration

Learning Objective

- Learn to determine specific concentrations with several common units.

Rather than qualitative terms (Section 11.2 - Definitions), we need quantitative ways to express the amount of solute in a solution; that is, we need specific units of concentration. In this section, we will introduce several common and useful units of concentration.

Molarity (M) is defined as the number of moles of solute divided by the number of liters of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution}$$

which can be simplified as

$$M = \frac{mol}{L},\ or\ mol/L$$

As with any mathematical equation, if you know any two quantities, you can calculate the third, unknown, quantity.

For example, suppose you have 0.500 L of solution that has 0.24 mol of NaOH dissolved in it. The concentration of the solution can be calculated as follows:

$$molarity = \frac{0.24\ mol\ NaOH}{0.500 L} = 0.48\ M\ NaOH$$

The concentration of the solution is 0.48 M, which is spoken as "zero point forty-eight molarity" or "zero point forty-eight molar." If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L? First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\ \cancel{g HCl} \times \frac{1\ mol\ Hcl}{36.5\ \cancel{g HCl}} = 0.614\ M\ HCl$$

Now we can use the definition of molarity to determine a concentration:

$$M = \frac{0.614\ mol\ HCl}{1.56 L} = 0.394\ M$$

Example 3.2.1:

What is the molarity of a solution made when 32.7 g of NaOH are dissolved to make 445 mL of solution?

Solution

To use the definition of molarity, both quantities must be converted to the proper units. First, convert the volume units from milliliters to liters:

$$445\ \cancel{mL} \times \frac{1\ L}{1000\ \cancel{mL}} = 0.445\ L$$

Now we convert the amount of solute to moles, using the molar mass of NaOH, which is 40.0 g/mol:

$$32.7\ \cancel{g NaOH} \times \frac{1\ mol\ NaOH}{40.0\ \cancel{g NaOH}} = 0.818\ mol\ NaOH$$

Now we can use the definition of molarity to determine the molar concentration:

$$M = \frac{0.818\ mol\ NaOH}{0.445 L} = 1.84\ M\ NaOH$$

Exercise 3.2.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M

Another way to specify an amount is **percentage composition by mass** (or *mass percentage*, % m/m). It is defined as follows:

$$\%m/m = \frac{mass\ of\ solute}{mass\ of\ entire\ sample} \times 100\%$$

It is not uncommon to see this unit used on commercial products (Figure **3.2.1** - Concentration in Commercial Applications)



Figure **3.2.1** Concentration in Commercial Applications © Thinkstock.

The percentage of urea in this package is 5% m/m, meaning that there are 5 g of urea per 100 g of product.

Example 3.2.1:

What is the mass percentage of Fe in a piece of metal with 87.9 g of Fe in a 113 g sample?

Solution

Using the definition of mass percentage, we have

$$\%m/m = \frac{87.9\,g\,Fe}{113\,g\,sample} \times 100\% = 77.8\%\,Fe$$

Exercise 3.2.1

What is the mass percentage of H_2O_2 in a solution with 1.67 g of H_2O_2 in a 55.5 g sample?

Answer

3.01%

Related concentration units are **parts per thousand (ppth), parts per million (ppm)** and **parts per billion (ppb).** Parts per thousand is defined as follows:

$$ppth = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1000$$

There are similar definitions for parts per million and parts per billion:

$$ppm = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000$$

and

$$ppb = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000,000$$

Each unit is used for progressively lower and lower concentrations. The two masses must be expressed in the same unit of mass, so conversions may be necessary.

Example 3.2.1:

If there is 0.6 g of Pb present in 277 g of solution, what is the Pb concentration in parts per thousand?

Solution

Use the definition of parts per thousand to determine the concentration. Substituting

$$\frac{0.6g\ Pb}{277g\ solution} \times 1000 = 2.17\ ppth$$

Exercise 3.2.1

If there is 0.551 mg of As in 348 g of solution, what is the As concentration in ppm?

Answer

1.58 ppm

For ionic solutions, we need to differentiate between the concentration of the salt versus the concentration of each individual ion. Because the ions in ionic compounds go their own way when a compound is dissolved in a solution, the resulting concentration of the ion may be different from the concentration of the complete salt. For example, if 1 M NaCl were prepared, the solution could also be described as a solution of 1 M $Na^+(aq)$ and 1 M $Cl^-(aq)$ because there is one Na^+ ion and one Cl^- ion per formula unit of the salt. However, if the solution were 1 M $CaCl_2$, there are two $Cl^-(aq)$ ions for every formula unit dissolved, so the concentration of $Cl^-(aq)$ would be 2 M, not 1 M.

In addition, the total ion concentration is the sum of the individual ion concentrations. Thus for the 1 M NaCl, the total ion concentration is 2 M; for the 1 M $CaCl_2$, the total ion concentration is 3 M.

Key Takeaway

- Quantitative units of concentration include molarity, mass percentage, parts per thousand (ppth), parts per million (ppm), and parts per billion (ppb).

Exercise 3.2.1

1. What is the molarity of a solution made by dissolving 13.4 g of $NaNO_3$ in 345 mL of solution?
2. What is the molarity of a solution made by dissolving 332 g of $C_6H_{12}O_6$ in 4.66 L of solution?
3. What are the individual ion concentrations and the total ion concentration in 0.66 M $Mg(NO_3)_2$?
4. What are the individual ion concentrations and the total ion concentration in 1.04 M $Al_2(SO_4)_3$?

5. If the $C_2H_3O_2^-$ ion concentration in a solution is 0.554 M, what is the concentration of $Ca(C_2H_3O_2)_2$?

6. If the Cl^- ion concentration in a solution is 2.61 M, what is the concentration of $FeCl_3$?

Answers

1. 0.457 M
2.
3. Mg^{2+} = 0.66 M; NO_3^- = 1.32 M; total: 1.98 M
4.
5. 0.277 M

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3.3: Dilutions

Learning Objective

- Learn how to dilute and concentrate solutions.

Often, a worker will need to change the concentration of a solution by changing the amount of solvent. **Dilution** is the addition of solvent, which decreases the concentration of the solute in the solution. **Concentration** is the removal of solvent, which increases the concentration of the solute in the solution. (Do not confuse the two uses of the word *concentration* here!)

In both dilution and concentration, the amount of solute stays the same. This gives us a way to calculate what the new solution volume must be for the desired concentration of solute. From the definition of molarity,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

we can solve for the number of moles of solute:

$$\textbf{moles of solute} = \textbf{(molarity)(liters of solution)}$$

A simpler way of writing this is to use M to represent molarity and V to represent volume. So the equation becomes

$$\textbf{moles of solute} = MV$$

Because this quantity does not change before and after the change in concentration, the product MV must be the same before and after the concentration change. Using numbers to represent the initial and final conditions, we have

$$M_1V_1 = M_2V_2$$

as the **dilution equation**. The volumes must be expressed in the same units. Note that this equation gives only the initial and final conditions, not the amount of the change. The amount of change is determined by subtraction.

Example 3.3.1

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

Solution

It does not matter which set of conditions is labeled 1 or 2, as long as the conditions are paired together properly. Using the dilution equation, we have

$$(2.19\text{ M})(25.0\text{ mL}) = M_2(72.8\text{ mL})$$

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

$$M_2 = 0.752\text{ M}$$

The concentration of the solution has decreased. In going from 25.0 mL to 72.8 mL, 72.8 − 25.0 = 47.8 mL of solvent must be added.

Exercise 3.3.1

A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

135.4 mL

Concentrating solutions involves removing solvent. Usually this is done by evaporating or boiling, assuming that the heat of boiling does not affect the solute. The dilution equation is used in these circumstances as well.

Chemistry Is Everywhere: Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure **3.3.1** Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.

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

$$(10\%)V_1 = (0.50\%)(100\text{ mL})V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Summary

- Calculate the new concentration or volume for a dilution or concentration of a solution.

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3.4: Concentrations as Conversion Factors and Solution Stoichiometry

Learning Objective

- Apply concentration units as conversion factors.

Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition. For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

$$0.108\ \cancel{L\ NaCl} \times \frac{0.887\ mol\ NaCl}{\cancel{L\ NaCl}} = 0.0958\ mol\ NaCl$$

(There is an understood 1 in the denominator of the conversion factor.) If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 3.4.1

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:

$$4.88\ \cancel{mol\ CuSO_4} \times \frac{1\ L}{2.35\ \cancel{mol}} = 2.08\ L\ of\ solution$$

Exercise 3.4.1

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer:

1.74 L

Of course, once quantities in moles are available, another conversion can give the mass of the substance, using molar mass as a conversion factor.

Example 3.4.2

What mass of solute is present in 0.765 L of 1.93 M NaOH?

Solution

This is a two-step conversion, first using concentration as a conversion factor to determine the number of moles and then the molar mass of NaOH (40.0 g/mol) to convert to mass:

$$0.765\ \cancel{L} \times \frac{1.93\ \cancel{mol\ NaOH}}{\cancel{L\ solution}} \times \frac{40.0 g\ NaOH}{1\ \cancel{mol\ NaOH}} = 59.1\ g\ NaOH$$

Exercise 3.4.2

What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?

Answer

6.12 g

More complex stoichiometry problems using balanced chemical reactions can also use concentrations as conversion factors. For example, suppose the following equation represents a chemical reaction:

$$2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)$$

If we wanted to know what volume of 0.555 M $CaCl_2$ would react with 1.25 mol of $AgNO_3$, we first use the balanced chemical equation to determine the number of moles of $CaCl_2$ that would react and then use concentration to convert to liters of solution:

$$1.25\ \cancel{mol\ AgNO_3} \times \frac{1\ \cancel{mol\ CaCl_2}}{2\ \cancel{mol\ AgNO_3}} \times \frac{1 L\ solution}{0.555\ \cancel{mol\ CaCl_2}} = 1.13\,L\,CaCl_2$$

This can be extended by starting with the mass of one reactant, instead of moles of a reactant.

Example 3.4.3

What volume of 0.0995 M $Al(NO_3)_3$ will react with 3.66 g of Ag according to the following chemical equation?

$$3\,Ag\,(s) + Al(NO_3)_3\,(aq) \longrightarrow 3\,AgNO_3 + Al\,(s)$$

Solution

Here, we first must convert the mass of Ag to moles before using the balanced chemical equation and then the definition of molarity as a conversion factor:

$$3.66\ \cancel{g\ Ag} \times \frac{1\ \cancel{mol\ Ag}}{107.97\ \cancel{g\ Ag}} \times \frac{1\ \cancel{mol\ Al(NO_3)_3}}{3\ \cancel{mol\ Ag}} \times \frac{1 L\ solution}{0.0995\ \cancel{mol\ Al(NO_3)_3}} = 0.114\,L$$

The strikeouts show how the units cancel.

Exercise 3.4.3

What volume of 0.512 M NaOH will react with 17.9 g of $H_2C_2O_4(s)$ according to the following chemical equation?

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

Answer:

0.777 L

We can extend our skills even further by recognizing that we can relate quantities of one solution to quantities of another solution. Knowing the volume and concentration of a solution containing one reactant, we can determine how much of another solution of another reactant will be needed using the balanced chemical equation.

Example 3.4.4

A student takes a precisely measured sample, called an *aliquot*, of 10.00 mL of a solution of $FeCl_3$. The student carefully adds 0.1074 M $Na_2C_2O_4$ until all the $Fe^{3+}(aq)$ has precipitated as $Fe_2(C_2O_4)_3(s)$. Using a precisely measured tube called a burette, the student finds that 9.04 mL of the $Na_2C_2O_4$ solution was added to completely precipitate the $Fe^{3+}(aq)$. What was the concentration of the $FeCl_3$ in the original solution? (A precisely measured experiment like this, which is meant to determine the amount of a substance in a sample, is called a *titration*.) The balanced chemical equation is as follows:

$$2\,FeCl_3\,(aq) + 3\,Na_2C_2O_4\,(aq) \longrightarrow Fe_2(C_2O_4)_3\,(s) + 6\,NaCl\,(aq)$$

Solution

First we need to determine the number of moles of $Na_2C_2O_4$ that reacted. We will convert the volume to liters and then use the concentration of the solution as a conversion factor:

$$9.04\,\cancel{mL} \times \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \times \frac{0.1074 mol\,Na_2C_2O_4}{\cancel{L}} = 0.000971\,mol\,Na_2C_2O_4$$

Now we will use the balanced chemical equation to determine the number of moles of Fe^{3+}(aq) that were present in the initial aliquot:

$$0.000971\,\cancel{mol\,Na_2C_2O_4} \times \frac{2 mol\,FeCl_3}{3\,\cancel{mol Na_2C_2O_4}} = 0.000647 mol\,FeCl_3$$

Then we determine the concentration of $FeCl_3$ in the original solution. Converting 10.00 mL into liters (0.01000 L), we use the definition of molarity directly:

$$M = \frac{mol}{L} = \frac{0.000647 mol\,FeCl_3}{0.01000 L} = 0.0647 M\,FeCl_3$$

Exercise 3.4.4

A student titrates 25.00 mL of H_3PO_4 with 0.0987 M KOH. She uses 54.06 mL to complete the chemical reaction. What is the concentration of H_3PO_4?

$$H_3PO_4\,(aq) + 3\,KOH\,(aq) \longrightarrow K_3PO_4\,(aq) + 3\,H_2O$$

Answer:

0.0711 M



Figure **3.4.1** Titration © Thinkstock. When a student performs a titration, a measured amount of one solution is added to another reactant.

We have used molarity exclusively as the concentration of interest, but that will not always be the case. The next example shows a different concentration unit being used.

Example 3.4.5:

H_2O_2 is used to determine the amount of Mn according to this balanced chemical equation:

$$2\,MnO_4^-(aq) + 5\,H_2O_2(aq) + 6\,H_3O^+(aq) \longrightarrow 2\,Mn_2^+(aq) + 5\,O_2(g) + 14\,H_2O(\ell)$$

What mass of 3.00% m/m H_2O_2 solution is needed to react with 0.355 mol of MnO_4^-(aq)?

Solution

Because we are given an initial amount in moles, all we need to do is use the balanced chemical equation to determine the number of moles of H_2O_2 and then convert to find the mass of H_2O_2. Knowing that the H_2O_2 solution is 3.00% by mass, we can determine the mass of solution needed:

$$3.55\ \cancel{mol\ MnO_4^-} \times \frac{5\ \cancel{mol\ H_2O_2}}{2\ \cancel{mol MnO_4^-}} \times \frac{34.02\ g\ \cancel{H_2O_2}}{\cancel{mol\ H_2O_2}} \times \frac{100 g\ solution}{3\ g\ \cancel{H_2O_2}} = 1006 g\ sol$$

The first conversion factor comes from the balanced chemical equation, the second conversion factor is the molar mass of H_2O_2, and the third conversion factor comes from the definition of percentage concentration by mass.

Exercise 3.4.5

Use the balanced chemical reaction for MnO_4^- and H_2O_2 to determine what mass of O_2 is produced if 258 g of 3.00% m/m H_2O_2 is reacted with MnO_4^-.

Answer

7.28 g

Summary

Know how to apply concentration units as conversion factors.

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3.5: Colligative Properties

Learning Objectives

- To describe how the properties of solutions differ from those of pure solvents.

Solutions are likely to have properties similar to those of their major component—usually the solvent. However, some solution properties differ significantly from those of the solvent. Here, we will focus on liquid solutions that have a solid solute, but many of the effects we will discuss in this section are applicable to all solutions.

Colligative Properties

Solutes affect some properties of solutions that depend only on the concentration of the dissolved particles. These properties are called **colligative properties**. Four important colligative properties that we will examine here are vapor pressure depression, boiling point elevation, freezing point depression, and osmotic pressure.

Molecular compounds separate into individual molecules when they are dissolved, so for every 1 mol of molecules dissolved, we get 1 mol of particles. In contrast, **ionic** compounds separate into their constituent ions when they dissolve, so 1 mol of an ionic compound will produce more than 1 mol of dissolved particles. For example, **every mole of NaCl** that dissolves yields **1 mol of Na^+ ions** and **1 mol of Cl^- ions**, for a **total of 2 mol** of particles in solution. Thus, the effect on a solution's properties by dissolving NaCl may be twice as large as the effect of dissolving the same amount of moles of glucose ($C_6H_{12}O_6$).

Vapor Pressure Depression

All liquids evaporate. In fact, given enough volume, a liquid will turn completely into a vapor. If enough volume is not present, a liquid will evaporate only to the point where the rate of evaporation equals the rate of vapor condensing back into a liquid. The pressure of the vapor at this point is called the **vapor pressure** of the liquid.

The presence of a dissolved solid lowers the characteristic vapor pressure of a liquid so that it evaporates more slowly. (The exceptions to this statement are if the solute itself is a liquid or a gas, in which case the solute will also contribute something to the evaporation process. We will not discuss such solutions here.) This property is called vapor pressure depression and is depicted in Figure **3.5.1**.

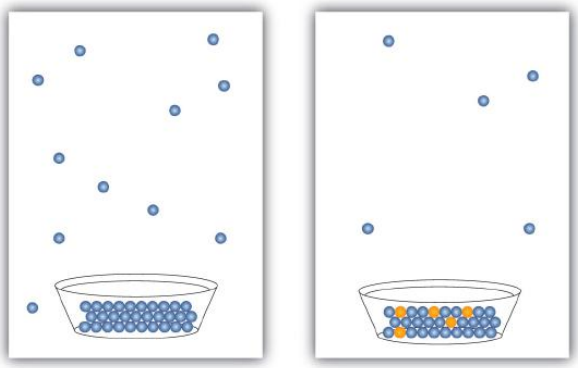


Figure **3.5.1**: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

Boiling Point and Freezing Point Effects

A related property of solutions is that their boiling points are higher than the boiling point of the pure solvent. Because the presence of solute particles decreases the vapor pressure of the liquid solvent, a higher temperature is needed to reach the boiling point. This phenomenon is called boiling point elevation. **For every mole of particles dissolved in a liter of water, the boiling point of water increases by about 0.5°C.** The addition of one mole of sucrose (molecular compound) in one liter of water will raise the boiling point from 100^0C to 100.5^0C but the addition of one mole of NaCl in one liter of water will raise the boiling point by 2 x 0.5^0C = 1^0C. Furthermore, the addition of one mole of $CaCl_2$ in one liter of water will raise the boiling point by 3 x 0.5^0C = 1.5^0C.

Some people argue that putting a pinch or two of salt in water used to cook spaghetti or other pasta makes a solution that has a higher boiling point, so the pasta cooks faster. In actuality, the amount of solute is so small that the boiling point of the water is practically unchanged.

The presence of solute particles has the opposite effect on the freezing point of a solution. When a solution freezes, only the solvent particles come together to form a solid phase, and the presence of solute particles interferes with that process. Therefore, for the liquid solvent to freeze, more energy must be removed from the solution, which lowers the temperature. Thus, solutions have lower freezing points than pure solvents do. This phenomenon is called freezing point depression. **For every mole of particles in a liter of water, the freezing point decreases by about 1.9°C.**

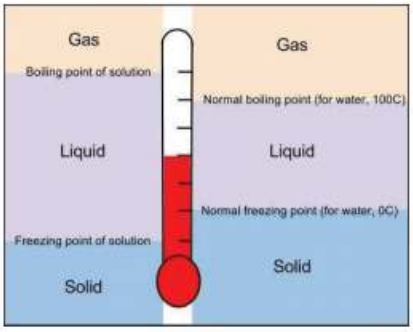


Figure **3.5.2**: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Both boiling point elevation and freezing point depression have practical uses. For example, solutions of water and ethylene glycol ($C_2H_6O_2$) are used as coolants in automobile engines because the boiling point of such a solution is greater than 100°C, the normal boiling point of water. In winter, salts like NaCl and $CaCl_2$ are sprinkled on the ground to melt ice or keep ice from forming on roads and sidewalks (Figure **3.5.2**). This is because the solution made by dissolving sodium chloride or calcium chloride in water has a lower freezing point than pure water, so the formation of ice is inhibited.



Figure **3.5.2**: Effect of Freezing Point Depression. The salt sprinkled on this sidewalk makes the water on the sidewalk have a lower freezing point than pure water, so it does not freeze as easily. This makes walking on the sidewalk less hazardous in winter. © Thinkstock

Example 3.5.1

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $CaCl_2$?

Solution

Colligative properties depend on the number of dissolved particles, so the solution with the greater number of particles in solution will show the greatest deviation. When NaCl dissolves, it separates into two ions, Na^+ and Cl^-. But when $CaCl_2$ dissolves, it separates into three ions—one Ca^{2+} ion and two Cl^- ions. Thus, mole for mole, $CaCl_2$ will have 50% more impact on freezing point depression than NaCl.

Exercise 3.5.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $CaCl_2$ or a 1 M solution of $MgSO_4$?

Answer

$CaCl_2$

Example 3.5.2

Estimate the boiling point of 0.2 M $CaCl_2$ solution.

Solution

The boiling point increases 0.5^0C for every mole of solute per liter of water. For this estimation, let's assume that 1 liter of solution is roughly the same volume as 1 liter of water. A 0.2 M $CaCl_2$ solution contains 0.2 moles of $CaCl_2$ solution formula units per liter of solution. Each $CaCl_2$ unit separates into three ions.

$$0.2 \text{ mol } CaCl_2 \times \frac{3 \text{ mol ions}}{1 \text{ mol } CaCl_2} \times \frac{0.5 \text{ deg C}}{1 \text{ mol ion}} = 0.3 \text{ deg C}$$

The normal boiling point of water is 100^0C, so the boiling point of the solution is raised to 100.3^0C.

Exercise 3.5.2

Estimate the freezing point of 0.3 M $CaCl_2$ solution.

Answer

minus 1.7^0C

Osmotic Pressure

The last colligative property of solutions we will consider is a very important one for biological systems. It involves **osmosis**, the process by which solvent molecules can pass through certain membranes but solute particles cannot. When two solutions of different concentration are present on either side of these membranes (called *semipermeable membranes*), there is a tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal. This tendency is called **osmotic pressure**. External pressure can be exerted on a solution to counter the flow of solvent; the pressure required to halt the osmosis of a solvent is equal to the osmotic pressure of the solution.

Osmolarity (osmol) is a way of reporting the total number of particles in a solution to determine osmotic pressure. It is defined as the molarity of a solute times the number of particles a formula unit of the solute makes when it dissolves (represented by *i*):

$$osmol = M \times i \tag{3.5.1}$$

If more than one solute is present in a solution, the individual osmolarities are additive to get the total osmolarity of the solution. Solutions that have the same osmolarity have the same osmotic pressure. If solutions of differing osmolarities are present on opposite sides of a semipermeable membrane, solvent will transfer from the lower-osmolarity solution to the higher-osmolarity solution. Counterpressure exerted on the high-osmolarity solution will reduce or halt the solvent transfer. An even higher pressure can be exerted to force solvent from the high-osmolarity solution to the low-osmolarity solution, a process called *reverse osmosis*. Reverse osmosis is used to make potable water from saltwater where sources of fresh water are scarce.

Example 3.5.3

A 0.50 M NaCl aqueous solution and a 0.30 M $Ca(NO_3)_2$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Solution

The solvent will flow into the solution of higher osmolarity. The NaCl solute separates into two ions—Na^+ and Cl^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol (NaCl)} = 0.50\ \text{M} \times 2 = 1.0\ \text{osmol}$$

The $Ca(NO_3)_2$ solute separates into three ions—one Ca^{2+} and two NO_3^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol } [Ca(NO_3)_2] = 0.30\ \text{M} \times 3 = 0.90\ \text{osmol}$$

The osmolarity of the $Ca(NO_3)_2$ solution is lower than that of the NaCl solution, so water will transfer through the membrane from the $Ca(NO_3)_2$ solution to the NaCl solution.

Exercise 3.5.3

A 1.5 M $C_6H_{12}O_6$ aqueous solution and a 0.40 M $Al(NO_3)_3$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Answer

osmol $C_6H_{12}O_6$ = 1.5; osmol $Al(NO_3)_3$ = 1.6

The solvent flows from $C_6H_{12}O_6$ solution (lower osmolarity) to $Al(NO_3)_3$ solution (higher osmolarity).

To Your Health: Dialysis

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called *hemodialysis*, a patient's blood is passed though a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). A section of tubing composed of a semipermeable membrane is immersed in a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules and excess water through the membrane into the sterile solution. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.



Figure **3.5.3**: A patient undergoing hemodialysis depends on osmosis to cleanse the blood of waste products that the kidneys are incapable of removing due to disease. from Wikipedia.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.

Cell walls are semipermeable membranes, so the osmotic pressures of the body's fluids have important biological consequences. If solutions of different osmolarity exist on either side of the cells, solvent (water) may pass into or out of the cells, sometimes with disastrous results. Consider what happens if red blood cells are placed in a *hypotonic* solution, meaning a solution of lower osmolarity than the liquid inside the cells. The cells swell up as water enters them, disrupting cellular activity and eventually causing the cells to burst. This process is called *hemolysis*. If red blood cells are placed in a *hypertonic* solution, meaning one having a higher osmolarity than exists inside the cells, water leaves the cells to dilute the external solution, and the red blood cells shrivel and die. This process is called *crenation*. Only if red blood cells are placed in *isotonic* solutions that have the same

osmolarity as exists inside the cells are they unaffected by negative effects of osmotic pressure. **Glucose solutions of about 0.31 M, or sodium chloride solutions of about 0.16 M, are isotonic with blood plasma.**

The concentration of an isotonic sodium chloride (NaCl) solution is only half that of an isotonic glucose ($C_6H_{12}O_6$) solution because NaCl produces two ions when a formula unit dissolves, while molecular $C_6H_{12}O_6$ produces only one particle when a formula unit dissolves. The osmolarities are therefore the same even though the concentrations of the two solutions are different.

Osmotic pressure explains why you should not drink seawater if you are abandoned in a life raft in the middle of the ocean. Its osmolarity is about three times higher than most bodily fluids. You would actually become thirstier as water from your cells was drawn out to dilute the salty ocean water you ingested. Our bodies do a better job coping with hypotonic solutions than with hypertonic ones. The excess water is collected by our kidneys and excreted.

Osmotic pressure effects are used in the food industry to make pickles from cucumbers and other vegetables and in brining meat to make corned beef. It is also a factor in the mechanism of getting water from the roots to the tops of trees!

Career Focus: Perfusionist

A perfusionist is a medical technician trained to assist during any medical procedure in which a patient's circulatory or breathing functions require support. The use of perfusionists has grown rapidly since the advent of open-heart surgery in 1953.

Most perfusionists work in operating rooms, where their main responsibility is to operate heart-lung machines. During many heart surgeries, the heart itself must be stopped. In these situations, a heart-lung machine keeps the patient alive by aerating the blood with oxygen and removing carbon dioxide. The perfusionist monitors both the machine and the status of the blood, notifying the surgeon and the anesthetist of any concerns and taking corrective action if the status of the blood becomes abnormal.

Despite the narrow parameters of their specialty, perfusionists must be highly trained. Certified perfusion education programs require a student to learn anatomy, physiology, pathology, chemistry, pharmacology, math, and physics. A college degree is usually required. Some perfusionists work with other external artificial organs, such as hemodialysis machines and artificial livers.

Concept Review Exercises

1. What are the colligative properties of solutions?
2. Explain how the following properties of solutions differ from those of the pure solvent: vapor pressure, boiling point, freezing point, and osmotic pressure.

Answers

1. Colligative properties are characteristics that a solution has that depend on the number, not the identity, of solute particles.
2. In solutions, the vapor pressure is lower, the boiling point is higher, the freezing point is lower, and the osmotic pressure is higher.

Exercises

1. In each pair of aqueous systems, which will have the lower vapor pressure?
   a. pure water or 1.0 M NaCl
   b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
   c. 1.0 M $CaCl_2$ or 1.0 M $(NH_4)_3PO_4$
2. In each pair of aqueous systems, which will have the lower vapor pressure?
   a. 0.50 M $Ca(NO_3)_2$ or 1.0 M KBr
   b. 1.5 M $C_{12}H_{22}O_{11}$ or 0.75 M $Ca(OH)_2$
   c. 0.10 M $Cu(NO_3)_2$ or pure water

3. In each pair of aqueous systems, which will have the higher boiling point?

   a. pure water or a 1.0 M NaCl
   b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
   c. 1.0 M $CaCl_2$ or 1.0 M $(NH_4)_3PO_4$

4. In each pair of aqueous systems, which will have the higher boiling point?

   a. 0.50 M $Ca(NO_3)_2$ or 1.0 M KBr
   b. 1.5 M $C_{12}H_{22}O_{11}$ or 0.75 M $Ca(OH)_2$
   c. 0.10 M $Cu(NO_3)_2$ or pure water

5. Estimate the boiling point of each aqueous solution. The boiling point of pure water is 100.0°C.

   a. 0.50 M NaCl
   b. 1.5 M Na_2SO_4
   c. 2.0 M $C_6H_{12}O_6$

6. Estimate the freezing point of each aqueous solution. The freezing point of pure water is 0.0°C.

   a. 0.50 M NaCl
   b. 1.5 M Na_2SO_4
   c. 2.0 M $C_6H_{12}O_6$

7. Explain why salt (NaCl) is spread on roads and sidewalks to inhibit ice formation in cold weather.

8. Salt (NaCl) and calcium chloride ($CaCl_2$) are used widely in some areas to minimize the formation of ice on sidewalks and roads. One of these ionic compounds is better, mole for mole, at inhibiting ice formation. Which is that likely to be? Why?

9. What is the osmolarity of each aqueous solution?

   a. 0.500 M NH_2CONH_2
   b. 0.500 M NaBr
   c. 0.500 M $Ca(NO_3)_2$

10. What is the osmolarity of each aqueous solution?

    a. 0.150 M KCl
    b. 0.450 M $(CH_3)_2CHOH$
    c. 0.500 M $Ca_3(PO_4)_2$

11. A 1.0 M solution of an unknown soluble salt has an osmolarity of 3.0 osmol. What can you conclude about the salt?

12. A 1.5 M NaCl solution and a 0.75 M $Al(NO_3)_3$ solution exist on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and the direction of solvent flow, if any, across the membrane.

Answers

1. a. 1.0 M NaCl
   b. 1.0 M NaCl
   c. 1.0 M $(NH_4)_3PO_4$

2.
   a. 1.0 M KBr
   b. 0.75 M $Ca(OH)_2$
   c. 0.10 M $Cu(NO_3)_2$

3.

a. 1.0 M NaCl
b. 1.0 M NaCl
c. 1.0 M $(NH_4)_3PO_4$

4.

a. 1.0 M KBr
b. 0.75 M $Ca(OH)_2$
c. 0.10 M $Cu(NO_3)_2$

5.

a. 100.5°C
b. 102.3°C
c. 101°C

6.

a. -1.9°C
b. -8.6°C
c. -3.8°C

7. NaCl lowers the freezing point of water, so it needs to be colder for the water to freeze.

8. $CaCl_2$ splits up into 3 ions while NaCl splits up into 2 ions only. $CaCl_2$ will be more effective.

9.

a. 0.500 osmol
b. 1.000 osmol
c. 1.500 osmol

10.

a. 0.300 osmol
b. 0.450 osmol
c. 2.50 osmol

11. It must separate into three ions when it dissolves.

12. Both NaCl and $Al(NO_3)_3$ have 3.0 osmol. There will be no net difference in the solvent flow.

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3.6: Osmosis

Learning Outcomes

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions.
- Describe a semipermeable membrane.
- Predict behavior of blood cells in different solution types.
- Describe flow of solvent molecules across a membrane.
- Identify the polar and nonpolar regions of a cell membrane.
- Explain the components present in a phospholipid.

Fish cells, like all cells, have semipermeable membranes. Eventually, the concentration of "stuff" on either side of them will even out. A fish that lives in salt water will have somewhat salty water inside itself. Put it in freshwater, and the freshwater will, through osmosis, enter the fish, causing its cells to swell, and the fish will die. What will happen to a freshwater fish in the ocean?

Osmosis

Imagine you have a cup that has $100\ \text{mL}$ water, and you add $15\ \text{g}$ of table sugar to the water. The sugar dissolves and the mixture that is now in the cup is made up of a **solute** (the sugar) that is dissolved in the **solvent** (the water). The mixture of a solute in a solvent is called a **solution**.

Imagine now that you have a second cup with $100\ \text{mL}$ of water, and you add $45\ \text{g}$ of table sugar to the water. Just like the first cup, the sugar is the solute, and the water is the solvent. But now you have two mixtures of different solute concentrations. In comparing two solutions of unequal solute concentration, the solution with the higher solute concentration is **hypertonic**, and the solution with the lower solute concentration is **hypotonic**. Solutions of equal solute concentration are **isotonic**. The first sugar solution is hypotonic to the second solution. The second sugar solution is hypertonic to the first.

You now add the two solutions to a beaker that has been divided by a semipermeable membrane, with pores that are too small for the sugar molecules to pass through, but are big enough for the water molecules to pass through. The hypertonic solution is one side of the membrane and the hypotonic solution on the other. The hypertonic solution has a lower water concentration than the hypotonic solution, so a concentration gradient of water now exists across the membrane. Water molecules will move from the side of higher water concentration to the side of lower concentration until both solutions are isotonic. At this point, **equilibrium** is reached.

Red blood cells behave the same way (see figure below). When red blood cells are in a hypertonic (higher concentration) solution, water flows out of the cell faster than it comes in. This results in *crenation* (shriveling) of the blood cell. On the other extreme, a red blood cell that is hypotonic (lower concentration outside the cell) will result in more water flowing into the cell than out. This results in swelling of the cell and potential *hemolysis* (bursting) of the cell. In an isotonic solution, the flow of water in and out of the cell is happening at the same rate.

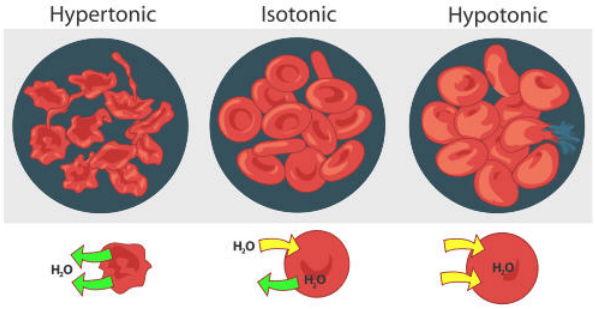


Figure 9.7.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

Osmosis is the diffusion of water molecules across a semipermeable membrane from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water). Water moves into and

out of cells by osmosis.

- If a cell is in a hypertonic solution, the solution has a lower water concentration than the cell cytosol, and water moves out of the cell until both solutions are isotonic.
- Cells placed in a hypotonic solution will take in water across their membranes until both the external solution and the cytosol are isotonic.

A red blood cell will swell and undergo hemolysis (burst) when placed in a hypotonic solution. When placed in a hypertonic solution, a red blood cell will lose water and undergo *crenation* (shrivel). Animal cells tend to do best in an isotonic environment, where the flow of water in and out of the cell is occurring at equal rates.

Diffusion

Passive transport is a way that small molecules or ions move across the cell membrane without input of energy by the cell. The three main kinds of passive transport are diffusion (or simple diffusion), osmosis, and facilitated diffusion. Simple diffusion and osmosis do not involve transport proteins. Facilitated diffusion requires the assistance of proteins.

Diffusion is the movement of molecules from an area of high concentration of the molecules to an area with a lower concentration. For cell transport, diffusion is the movement of small molecules across the cell membrane. The difference in the concentrations of the molecules in the two areas is called the **concentration gradient**. The kinetic energy of the molecules results in random motion, causing diffusion. In simple diffusion, this process proceeds without the aid of a transport protein. It is the random motion of the molecules that causes them to move from an area of high concentration to an area with a lower concentration.

Diffusion will continue until the concentration gradient has been eliminated. Since diffusion moves materials from an area of higher concentration to the lower, it is described as moving solutes "down the concentration gradient". The end result is an equal concentration, or **equilibrium**, of molecules on both sides of the membrane. At equilibrium, movement of molecules does not stop. At equilibrium, there is equal movement of materials in both directions.

Not everything can make it into your cells. Your cells have a plasma membrane that helps to guard your cells from unwanted intruders.

The Plasma Membrane and Cytosol

If the outside environment of a cell is water-based, and the inside of the cell is also mostly water, something has to make sure the cell stays intact in this environment. What would happen if a cell dissolved in water, like sugar does? Obviously, the cell could not survive in such an environment. So something must protect the cell and allow it to survive in its water-based environment. All cells have a barrier around them that separates them from the environment and from other cells. This barrier is called the **plasma membrane**, or cell membrane.

The Plasma Membrane

The plasma membrane (see figure below) is made of a double layer of special lipids, known as **phospholipids**. The phospholipid is a lipid molecule with a hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails. Because of the hydrophilic and hydrophobic nature of the phospholipid, the molecule must be arranged in a specific pattern as only certain parts of the molecule can physically be in contact with water. Remember that there is water outside the cell, and the **cytoplasm** inside the cell is mostly water as well. So the phospholipids are arranged in a double layer (a bilayer) to keep the cell separate from its environment. Lipids do not mix with water (recall that oil is a lipid), so the phospholipid bilayer of the cell membrane acts as a barrier, keeping water out of the cell, and keeping the cytoplasm inside the cell. The cell membrane allows the cell to stay structurally intact in its water-based environment.

The function of the plasma membrane is to control what goes in and out of the cell. Some molecules can go through the cell membrane to enter and leave the cell, but some cannot. The cell is therefore not completely permeable. "Permeable" means that anything can cross a barrier. An open door is completely permeable to anything that wants to enter or exit through the door. The plasma membrane is **semipermeable**, meaning that some things can enter the cell, and some things cannot.

Molecules that cannot easily pass through the bilayer include ions and small hydrophilic molecules, such as glucose, and macromolecules, including proteins and RNA. Examples of molecules that can easily diffuse across the plasma membrane include

carbon dioxide and oxygen gas. These molecules diffuse freely in and out of the cell, along their concentration gradient. Though water is a polar molecule, it can also diffuse through the plasma membrane.

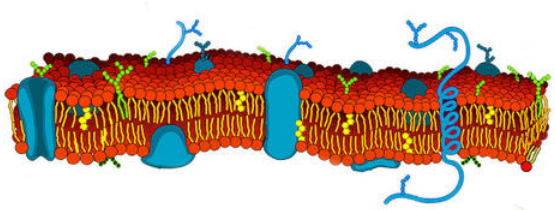


Figure 9.7.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side of the bilayer. There are many proteins throughout the membrane.

Cytosol

The inside of all cells also contain a jelly-like substance called **cytosol**. Cytosol is composed of water and other molecules, including **enzymes**, which are proteins that speed up the cell's chemical reactions. Everything in the cell sits in the cytosol, like fruit in a Jell-o mold. The term cytoplasm refers to the cytosol and all of the organelles, the specialized compartments of the cell. The cytoplasm does not include the nucleus. As a prokaryotic cell does not have a nucleus, the DNA is in the cytoplasm.

Supplemental Resources

- The Plasma Membrane: www.youtube.com/watch?v=moPJkCbKjBs

Concept Review Exercises

1. What are some of the features of a semipermeable membrane?

2. What do the prefixes hyper, hypo, and iso mean?

Answers

1. A semipermeable membrane allows some substances to pass through but not others.

2. hyper – higher; hypo – lower; iso - same

Key Takeaways

- Water moves into and out of cells by osmosis.
- Water (solvent) moves from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water).

EXERCISES

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

a. Which one has a higher concentration?
b. Which way will water molecules flow?
c. Which volume will increase?
d. Which volume will decrease?
e. What will happen to the concentration of solution A?
f. What will happen to the concentration of solution B?

2. Two solutions with different concentrations and compositions are separated by a semipermeable membrane. The left-hand solution is a .50 M solution of $MgSO_4$, while the right-hand solution contains $CaCl_2$ at a concentration of .40 M. Determine the direction of the flow of solvent, left or right.

3. Given the following situations, wherein two tanks of different solutions are separated by a semipermeable membrane, determine the direction of the flow of solvent (water).

a. Solution A contains a 0.40 M concentration of $CaCl_2$, while Solution B contains a 0.45 M concentration of KI

b. Solution A contains a 1.00 M concentration of NH_4Cl, while Solution B contains a 1.00 M concentration of CH_2O

4. Cells are placed in a solution and the cells then undergo hemolysis. What can be said about the relative concentrations of solute in the cell and the solution?

5. Describe the relative concentrations inside and outside a red blood cell when crenation occurs.

6. A saltwater fish is placed in a freshwater tank. What will happen to the fish? Describe the flow of water molecules to explain the outcome.

7. What makes up the "head" region of a phospholipid? Is it hydrophobic or hydrophilic?

8. What makes up the "tail" region of a phospholipid? Is it hydrophobic or hydrophilic?

Answers

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

a. Solution B
b. A → → B
c. B
d. A
e. increase
f. decrease

2. Water (solvent) flows from left to right.

3.

a. Water flows from Solution B to Solution A.

b. Water flows from Solution B to Solution A.

4. Cells contain fluid with higher concentration than solution outside the cell.

5. Cells contain fluid with a lower concentration than the solution outside the cell.

6. Water molecules will flow from the tank water into the fish because the fish has a higher concentration of salt. If the fish absorbs too much water, it will die.

7. The "head" region is a phosphate group and it is hydrophilic.

8. The "tail" is a hydrocarbon tail and it is hydrophobic.

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CHAPTER OVERVIEW

4: Reactions- Equilibrium and Net Ionic Equations

4.1: The Equilibrium Constant

4.2: Le Chatelier's Principle

4.3: Ionic Equations - A Review

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4.1: The Equilibrium Constant

Learning Outcomes

- Explain chemical equilibrium.
- Write expression for calculating K.
- Calculate K values.
- Predict relative amounts of reactants and products based on equilibrium constant K.

Hydrogen and iodine gases react to form hydrogen iodide according to the following reaction:

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)} \tag{4.1.1}$$

$$\text{Forward reaction: } \mathrm{H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)} \tag{4.1.2}$$
$$\text{Reverse reaction: } \mathrm{2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)} \tag{4.1.3}$$

Initially, only the forward reaction occurs because no HI is present. As soon as some HI has formed, it begins to decompose back into $\mathrm{H_2}$ and $\mathrm{I_2}$. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of $\mathrm{H_2}$ and $\mathrm{I_2}$ to produce HI becomes equal to the rate of decomposition of HI into $\mathrm{H_2}$ and $\mathrm{I_2}$. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

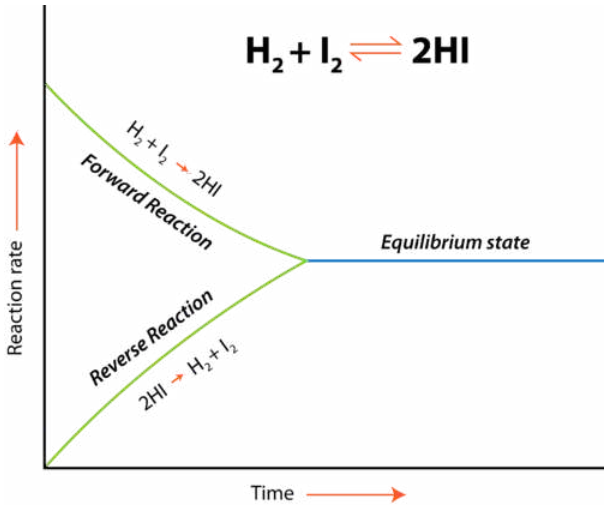


Figure 9.5.1: Equilibrium in reaction: $\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)}$.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. The figure below shows changes in concentration of $\mathrm{H_2}$, $\mathrm{I_2}$, and HI for two different reactions. In the reaction depicted by the graph on the left (A), the reaction begins with only $\mathrm{H_2}$ and $\mathrm{I_2}$ present. There is no HI initially. As the reaction proceeds towards equilibrium, the concentrations of the $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually decrease, while the concentration of the HI gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. At equilibrium, concentrations of all substances are constant.

In reaction B, the process begins with only HI and no $\mathrm{H_2}$ or $\mathrm{I_2}$. In this case, the concentration of HI gradually decreases while the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of HI at equilibrium is significantly higher than the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$. This is true whether the reaction began with all reactants or all products. The position of equilibrium is a property of the particular reversible reaction and does not depend upon how equilibrium was achieved.

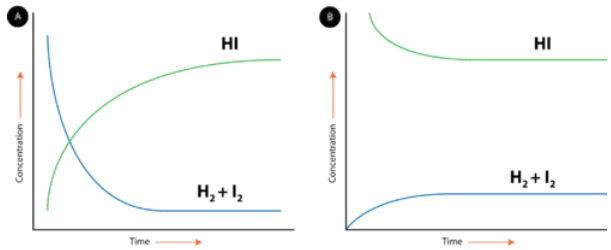


Figure 9.5.2: Equilibrium between reactants and products is achieved regardless of whether the reaction starts with the reactants or products.

Conditions for Equilibrium and Types of Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both forward and reverse are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

The description of equilibrium in this concept refers primarily to equilibrium between reactants and products in a chemical reaction. Other types of equilibrium include phase equilibrium and solution equilibrium. A phase equilibrium occurs when a substance is in equilibrium between two states. For example, a stoppered flask of water attains equilibrium when the rate of evaporation is equal to the rate of condensation. A solution equilibrium occurs when a solid substance is in a saturated solution. At this point, the rate of dissolution is equal to the rate of recrystallization. Although these are all different types of transformations, most of the rules regarding equilibrium apply to any situation in which a process occurs reversibly.



Figure **4.1.3**: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

Red blood cells transport oxygen to the tissues so they can function. In the absence of oxygen, cells cannot carry out their biochemical responsibilities. Oxygen moves to the cells attached to hemoglobin, a protein found in the red cells. In cases of carbon monoxide poisoning, CO binds much more strongly to the hemoglobin, blocking oxygen attachment and lowering the amount of oxygen reaching the cells. Treatment involves the patient breathing pure oxygen to displace the carbon monoxide. The equilibrium reaction shown below illustrates the shift toward the right when excess oxygen is added to the system:

$$\mathrm{Hb(CO)_4}\,(aq) + 4\mathrm{O_2}\,(g) \rightleftharpoons \mathrm{Hb(O_2)_4}\,(aq) + 4\mathrm{CO}\,(g) \tag{4.1.4}$$

Equilibrium Constant

Consider the hypothetical reversible reaction in which reactants **A** and **B** react to form products **C** and **D**. This equilibrium can be shown below, where the lowercase letters represent the coefficients of each substance.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \tag{4.1.5}$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentration for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** (K_{eq}) is the ratio of the mathematical product of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{eq} = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \tag{4.1.6}$$

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units ($\mathrm{mol/L}$).

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the above section, the position of equilibrium for a given reaction does not depend on the starting concentrations and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

The equilibrium constant can vary over a wide range of values. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reducing agent and Cl_2 is a good oxidizing agent, the reaction proceeds essentially to completion.

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad K = 1.6 \times 10^{33} \text{ at } 300\mathrm{K}$$

In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants. An example is the decomposition of water. No wonder you won't find water a very good source of oxygen gas and hydrogen gas at ordinary temperatures!

$$H_2O_{(g)} \rightleftharpoons H_{2(g)} + \tfrac{1}{2}O_{2(g)} \quad K = 8 \times 10^{-41} \text{ at } 25^\circ\mathrm{C}$$

Figure 4.1.4 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products.

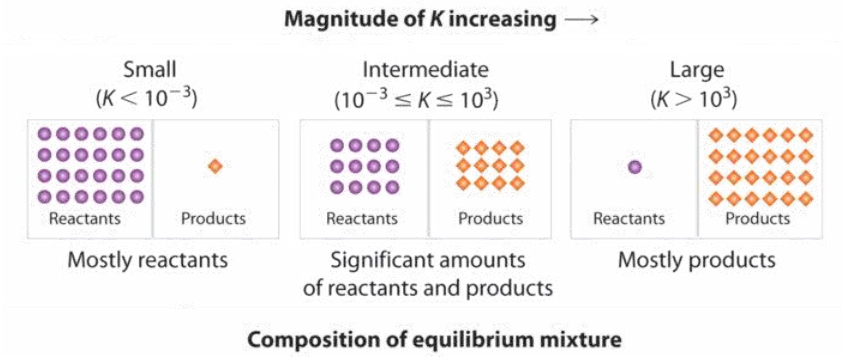


Figure 4.1.4: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

- When K is a very **large** number, the reaction is essentially irreversible, products predominate at equilibrium.
- When K is between 1 and 1000, more products than reactants are present at equilibrium
- When K is between 1 and 0.001, more reactants than products are present at equilibrium.
- When K is a very **small** number, the reaction produces almost no products; only reactants are present at equilibrium.

Example 4.1.1

Write the expression for the equilibrium constant K for the following reaction:

$N_2\ (g) + 3\ H_2\ (g) \rightleftarrows 2\ NH_3\ (g)$

Solution

The equilibrium constant equation is the ratio of the concentration of the products (NH_3) to the concentration of the reactants (N_2 and H_2), each raised to the power of its coefficient in the balanced chemical equation.

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Exercise 4.1.1

Write the expression of the equilibrium constant K for the following reaction:.

$2\ NOCl\ (g) \rightleftarrows 2\ NO\ (g) + Cl_2\ (g)$

Answer

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

Example 4.1.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Solution

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 4.1.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{4.1.7}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. At which temperature would you expect to find the highest proportion of ammonia in the equilibrium mixture?

Answer

a. 327°C, where K is smallest

b. 25°C

Concept Review Exercises

1. What is chemical equilibrium?

2. What does the equilibrium constant tell us?

Answers

1. The rate of the forward reaction equals the rate of the reverse reaction.

2. The ratio of products and reactants when the system is at equilibrium.

Key Takeaway

- As a chemical change proceeds, the quantities of the reactants/products will decrease, and those of the products/reactants will increase. Eventually the reaction slows down and the composition of the system stops changing. At this point the reaction is in its *equilibrium state*, and no further change in composition will occur as long as the system is left undisturbed.

EXERCISES

1. If the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is at equilibrium, do the concentrations of HI, H_2, and I_2 have to be equal?

2. Do the concentrations at equilibrium depend upon how the equilibrium was reached?

3. What does it mean if the K_{eq} is > 1?

4. What does it mean if the K_{eq} is < 1?

5. Does the equilibrium state depend on the starting concentrations?

6. Write an expression for the equilibrium constant K equation.

a. $PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g)$

b. $2O_3\ (g) \rightleftharpoons 3O_2\ (g)$

7. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K would make this reaction most useful commercially? Explain your answer.

a. $K \approx 0.01$

b. $K \approx 1$

c. $K \approx 10$.

8. Tell whether the reactants or the products are favored at equilibrium:

a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K = 172$

b. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K = 0.230$

c. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K = 4.6\times10^4$

d. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K = 0.050$

AnswerS

1. No, the concentrations are constant but the concentrations do not have to be equal.

2. No.

3. More products than reactants are present at equilibrium.

4. More reactants than products present at equilibrium.

5. No. The equilibrium ratio does not depend on the initial concentrations.

6.

a. $K = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b. $K = \frac{[O_2]^3}{[O_3]^2}$

7. The answer is c. $K \approx 10$.

Since $K = \frac{[C_6H_6]^2}{[C_2H_2]^3}$ (K≈10), this means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

8.

a. products

b. reactants

c. products

d. reactants

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4.2: Le Chatelier's Principle

Learning Outcomes

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

Original Equilibrium	**Favored Reaction**	**Result**	
$\mathrm{A} \rightleftharpoons \mathrm{B}$	Forward: $\mathrm{A} \rightarrow \mathrm{B}$	[A] decreases; [B] increases	(4.2.1)
$\mathrm{A} \rightleftharpoons \mathrm{B}$	Reverse: $\mathrm{A} \leftarrow \mathrm{B}$	[A] increases; [B] decreases	

Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightleftharpoons 2\mathrm{NH_3}\,(g) \tag{4.2.2}$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more $\mathbf{N_2}$ is added, the forward reaction will be favored because the forward reaction uses up $\mathbf{N_2}$ and converts it to $\mathbf{NH_3}$. The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more $\mathbf{NH_3}$ is produced. The concentration of $\mathbf{NH_3}$ increases, while the concentrations of $\mathbf{N_2}$ and $\mathbf{H_2}$ decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more $\mathbf{N_2}$ is added, a new equilibrium is achieved by the system. The new concentration of $\mathbf{NH_3}$ is higher because of the favoring of the forward reaction. The new concentration of the $\mathbf{H_2}$ is lower .The concentration of $\mathbf{N_2}$ is higher than in the original equilibrium, but went down slightly following the addition of the $\mathbf{N_2}$ that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_{eq}, does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more $\mathbf{NH_3}$ were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of $\mathbf{NH_3}$ would result in increased formation of the reactants, $\mathbf{N_2}$ and $\mathbf{H_2}$.

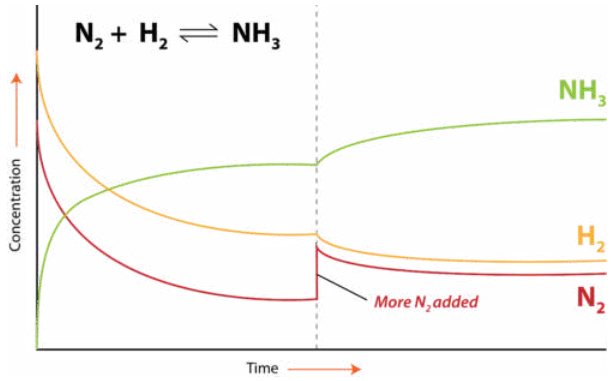


Figure 9.6.2: *The Haber-Bosch process is an equilibrium between reactants* $\mathbf{N_2}$ *and* $\mathbf{H_2}$ *and product* $\mathbf{NH_3}$.

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, $\mathbf{NH_3}$ is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more $\mathbf{NH_3}$ is produced. The concentrations of $\mathbf{N_2}$ and $\mathbf{H_2}$ decrease. Continued removal of $\mathbf{NH_3}$ will eventually force the reaction to go to completion until all of the reactants are used up. If either $\mathbf{N_2}$ or $\mathbf{H_2}$ were removed from the equilibrium system, the reverse reaction would be favored and the concentration of $\mathbf{NH_3}$ would decrease.

The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 9.6.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

Example 4.2.1

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{4.2.3}$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift to the right (toward products) to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift to the left (toward reactants) to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift to the right (toward products) to replace the product removed.

Exercise 4.2.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g) \tag{4.2.4}$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answer

1. shift to the left (toward reactants)
2. shift to the left (toward reactants)

Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).

$$\mathrm{N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 91\ kJ} \tag{4.2.5}$$

The forward reaction is the exothermic direction: the formation of $\mathrm{NH_3}$ releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as $\mathrm{NH_3}$ decomposes to $\mathrm{N_2}$ and $\mathrm{H_2}$, heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of $\mathrm{NH_3}$ will increase and the amount of $\mathrm{N_2}$ and $\mathrm{H_2}$ will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq} is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

Le Chatelier's principle as related to temperature changes can be illustrated easily be the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.

$$\mathrm{N_2O_4\,(g) + heat \rightleftharpoons 2NO_2\,(g)} \tag{4.2.6}$$

Dinitrogen tetroxide ($\mathrm{N_2O_4}$) is colorless, while nitrogen dioxide ($\mathrm{NO_2}$) is dark brown in color. When $\mathrm{N_2O_4}$ breaks down into $\mathrm{NO_2}$, heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

Example 4.2.2

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ \tag{4.2.7}$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts to the left (back toward reactants).

Exercise 4.2.2

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2 \tag{4.2.8}$$

Answer

Equilibrium shifts to the left (toward reactants).

Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

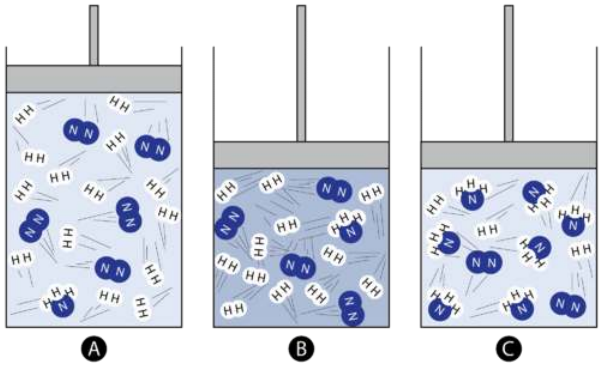


Figure 9.6.3: *Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.*

On the far left, the reaction system contains primarily $\mathbf{N_2}$ and $\mathbf{H_2}$, with only one molecule of $\mathbf{NH_3}$ present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more $\mathbf{NH_3}$ is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which $\mathbf{NH_3}$ decomposes to $\mathbf{N_2}$ and $\mathbf{H_2}$. This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

Table 9.6.2

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:

$$\mathbf{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + O_2\,(g)} \tag{4.2.9}$$

Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of $\mathbf{CaCO_3}$ because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of $\mathbf{HCl}$ from $\mathbf{H_2}$ and $\mathbf{Cl_2}$.

$$\mathbf{H_2}\,(g) + \mathbf{Cl_2}\,(g) \rightleftharpoons \mathbf{2HCl}\,(g) \tag{4.2.10}$$

Example 4.2.3

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{4.2.11}$$

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts to the right (toward the products side).

Exercise 4.2.3

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g) \tag{4.2.12}$$

Answer

Reaction shifts to the left (toward reactants).

Application of Le Chatelier's Principle

Oxygen transport by the blood

In aerobic respiration, oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

hemoglobin + O_2 $\rightleftharpoons$ oxyhemoglobin

The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Concept Review Exercises

1. Define Le Chatelier’s principle.

2. List the three factors types of changes that can disturb the equilibrium of a system.

Answers

1. Le Chatelier’s principle states that a system at equilibrium is disturbed, it will respond in a way to minimize the disturbance.

2. temperature, change in amount of substance, change in pressure through change in volume

Key Takeaways

- In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio* of *Products/Reactants* (*equilibrium constant*), *K* is unchanged.
- If temperature is changed, the numeric value *K* will change. If a reaction is *exothermic* (releases heat), an increase in the **temperature** will force the equilibrium to the left, causing the system to absorb heat and thus partially offsetting the rise in temperature. The opposite effect occurs for *endothermic* reactions, which are shifted to the right by rising temperature.

- The effect of **pressure** on an equilibrium is significant only for reactions which involve different numbers of moles of gases on the two sides of the equation. An increase in the total pressure will shift to the side with fewer moles of gas. A decrease in pressure will shift to the side with more moles of gas.

EXERCISES

1. How will each change affect the reaction?

$PCl_5(g)$ + heat $\rightleftharpoons PCl_3(g) + Cl_2(g)$

a. Addition of PCl_5
b. Addition of Cl_2
c. Removal of PCl_3
d. Increasing temperature
e. Decreasing temperature
f. Decreasing volume

2. How will each change affect the reaction?

$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

a. Removal of HNO_2
b. Addition of HCl (i.e. adding more H^+)
c. Increasing volume
d. Decreasing volume
e. Removal of NO_2^-
f. Addition of OH^- (which will react with and remove H^+)

3. How will each change affect the reaction?

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ $\Delta H = 172.5 kJ$

a. Addition of CO_2
b. Removal of CO_2
c. Increasing temperature
d. Decreasing temperature
e. Increasing volume
f. Addition of CO

4. How will each change affect the reaction?

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = -9.48 kJ$

a. Addition of H_2
b. Removal of H_2
c. Increasing temperature
d. Decreasing temperature
e. Increasing volume
f. Decreasing volume

AnswerS

1.

a. shift right
b. shift left
c. shift right
d. shift right
e. shift left

f. shift left

2.

a. shift left
b. shift left
c. no effect
d. no effect
e. shift right
f. shift right

3.

a. shift right
b. shift left
c. shift right
d. shift left
e. shift right
f. shift left

4.

a. shift right
b. shift left
c. shift left
d. shift right
e. no effect
f. no effect

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4.3: Ionic Equations - A Review

Learning Objectives

- Write ionic equations for chemical reactions between ionic compounds.
- Write net ionic equations for chemical reactions between ionic compounds.

For single-replacement and double-replacement reactions, many of the reactions included ionic compounds: compounds between metals and nonmetals or compounds that contained recognizable polyatomic ions. Now, we take a closer look at reactions that include ionic compounds.

One important aspect about ionic compounds that differs from molecular compounds has to do with dissolution in a liquid, such as water. When molecular compounds, such as sugar, dissolve in water, the individual molecules drift apart from each other. When ionic compounds dissolve, *the ions physically separate from each other*. We can use a chemical equation to represent this process—for example, with NaCl:

$$\mathrm{NaCl(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq) + Cl^-(aq)}$$

When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure **4.3.1**). This process is called **dissociation;** we say that the ions *dissociate*.

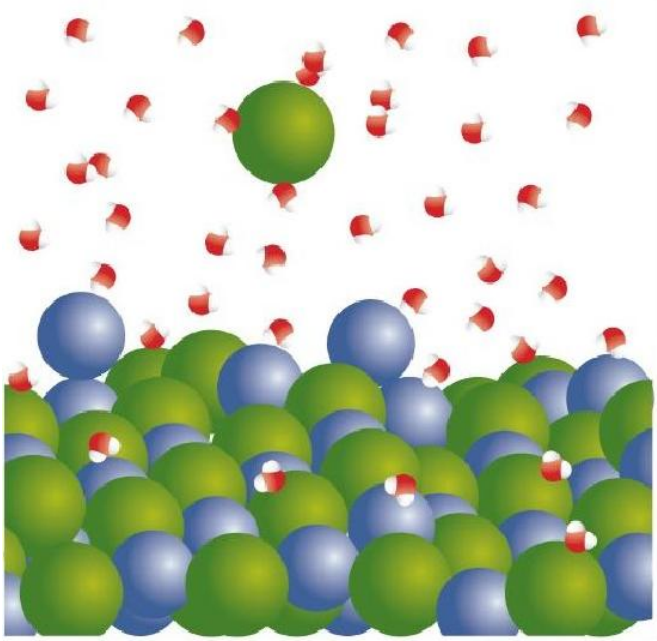


Figure **4.3.1** Ionic Solutions. When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.

All ionic compounds that dissolve behave this way. (This behavior was first suggested by the Swedish chemist Svante August Arrhenius [1859–1927] as part of his PhD dissertation in 1884. Interestingly, his PhD examination team had a hard time believing that ionic compounds would behave like this, so they gave Arrhenius a barely passing grade. Later, this work was cited when Arrhenius was awarded the Nobel Prize in Chemistry.) Keep in mind that when the ions separate, *all* the ions separate. Thus, when $CaCl_2$ dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from each other:

$$\mathrm{CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)}$$

$$\mathrm{CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq)}$$

That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions), and they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. Polyatomic ions also retain their overall identity when they are dissolved.

Example 4.3.1:

Write the chemical equation that represents the dissociation of each ionic compound.

1. KBr
2. Na_2SO_4

Solution

1. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$
2. Not only do the two sodium ions go their own way, but the sulfate ion stays together as the sulfate ion. The dissolving equation is $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

Exercise 4.3.1

Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Answer

$(NH_4)_2S(s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$

When chemicals in solution react, the proper way of writing the chemical formulas of the dissolved ionic compounds is in terms of the dissociated ions, not the complete ionic formula. A **complete ionic equation** is a chemical equation in which the dissolved ionic compounds are written as separated ions. Solubility rules are very useful in determining which ionic compounds are dissolved and which are not. For example, when NaCl(aq) reacts with $AgNO_3$(aq) in a double-replacement reaction to precipitate AgCl(s) and form $NaNO_3$(aq), the complete ionic equation includes NaCl, $AgNO_3$, and $NaNO_3$ written as separated ions:

$$\mathrm{Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)}$$

This is more representative of what is occurring in the solution.

Example 4.3.1:

Write the complete ionic equation for each chemical reaction.

1. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$
2. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

1. The complete ionic equation is $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. The complete ionic equation is $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Exercise 4.3.1

Write the complete ionic equation for

$$\mathrm{CaCl_2(aq) + Pb(NO_3)_2(aq) \longrightarrow Ca(NO_3)_2(aq) + PbCl_2(s)}$$

Answer

$Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$

You may notice that in a complete ionic equation, some ions do not change their chemical form; they stay exactly the same on the reactant and product sides of the equation. For example, in

$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

the $Ag^+(aq)$ and $Cl^-(aq)$ ions become $AgCl(s)$, but the $Na^+(aq)$ ions and the $NO_3^-(aq)$ ions stay as $Na^+(aq)$ ions and $NO_3^-(aq)$ ions. These two ions are examples of spectator ions—ions that do nothing in the overall course of a chemical reaction. They are present, but they do not participate in the overall chemistry. It is common to cancel spectator ions (something also done with algebraic quantities) on the opposite sides of a chemical equation:

$$\cancel{Na^+(aq)} + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-(aq)} \rightarrow AgCl(s) + \cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}$$

What remains when the spectator ions are removed is called the **net ionic equation**, which represents the actual chemical change occurring between the ionic compounds:

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

It is important to reiterate that the spectator ions are still present in solution, but they do not experience any net chemical change, so they are not written in a net ionic equation.

Example 4.3.1:

Write the net ionic equation for each chemical reaction.

1. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Solution

1. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{K^+(aq)} + Br^-(aq) + Ag^+(aq) + \cancel{C_2H_3O_2^-(aq)} \rightarrow K^+(aq) + \cancel{C_2H_3O_2^-(aq)} + AgBr(s)$$

The net ionic equation is

$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$$

2. In the second equation, the $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{Mg^{2+}(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + \cancel{2NO_3^-(aq)} \rightarrow Mg^{2+}(aq) + \cancel{2NO_3^-(aq)} + BaSo_4(s)$$

The net ionic equation is

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Exercise 4.3.1

Write the net ionic equation for

$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

Chemistry is Everywhere: Soluble and Insoluble Ionic Compounds

The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound that can be dissolved in a sample of water. For example, you can dissolve a maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water. We consider **NaCl** soluble but **AgCl** insoluble.

One place where solubility is important is in the tank-type water heater found in many homes in the United States. Domestic water frequently contains small amounts of dissolved ionic compounds, including calcium carbonate ($CaCO_3$). However, $CaCO_3$ has the relatively unusual property of being less soluble in hot water than in cold water. So as the water heater operates by heating water, $CaCO_3$ can precipitate if there is enough of it in the water. This precipitate, called *limescale*, can also contain magnesium compounds, hydrogen carbonate compounds, and phosphate compounds. The problem is that too much limescale can impede the function of a water heater, requiring more energy to heat water to a specific temperature or even blocking water pipes into or out of the water heater, causing dysfunction.



Figure 4.3.2 Tank water heater © Thinkstock. Most homes in the United States have a tank-type water heater like this one.

Another place where solubility versus insolubility is an issue is the Grand Canyon. We usually think of rock as insoluble. But it is actually ever so slightly soluble. This means that over a period of about two billion years, the Colorado River carved rock from the surface by slowly dissolving it, eventually generating a spectacular series of gorges and canyons. And all because of solubility!



Figure **4.3.3**: The Grand Canyon was formed by water running through rock for billions of years, very slowly dissolving it. Note the Colorado River is still present in the lower part of the photo. (Sonaal Bangera via unsplash)

Key Takeaways

- Ionic compounds that dissolve separate into individual ions.
- Complete ionic equations show dissolved ionic solids as separated ions.
- Net ionic equations show only the ions and other substances that change in a chemical reaction.

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CHAPTER OVERVIEW

5: Acids and Bases

5.1: Acids Nomenclature
5.2: Hydronium Ions
5.3: Strong Acids and Bases
5.4: Weak Acids
5.5: Weak Bases
5.6: Brønsted-Lowry Definition of Acids and Bases
5.7: Acid Strength and the Acid Dissociation Constant (Ka)
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5.10: Buffers
5.11: Neutralization Reactions

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5.1: Acids Nomenclature

Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydronium ions (H_3O^+) when dissolved in water.



Figure 5.1.1: (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like $NaCl$. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, creating a positively-charged hydronium ion and an anion. This can be symbolized in a chemical equation:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \tag{5.1.1}$$

The H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic.

Naming Binary acids (in aqueous form)

A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. The acid name begins with the prefix *hydro-*. followed by the base name of the anion, followed by the suffix *-ic*.

Hydro- and Base name of Non metal and *-ic + acid*

Example: $HCl_{(aq)}$

Cl^-, chloride ion

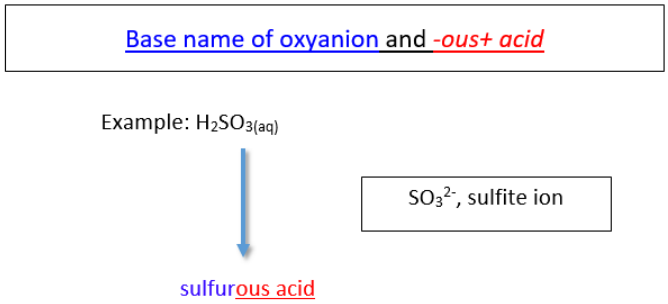
hydrochloric acid

Naming Oxyacids

An **oxyacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

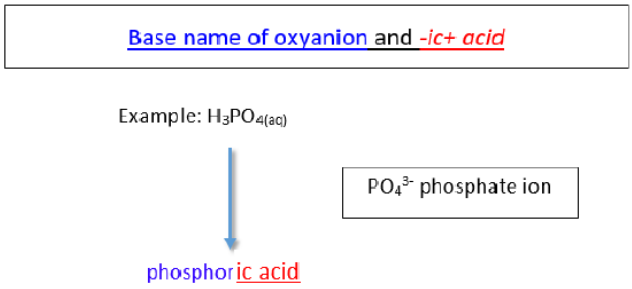
a. Oxyanions with ***-ite*** ending.

The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.



b. Oxyanions with ***-ate*** ending.

The name of the acid is the root of the anion followed by the suffix ***-ic***. There is no prefix.

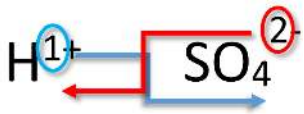


Note

The base name for sulfur containing oxyacid is ***sulfur-*** instead of just ***sulf-***. The same is true for a phosphorus containing oxyacid. The base name is ***phosphor-*** instead of simply ***phosph-***.

Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the $\mathbf{H^+}$ ions. Another way to think about writing the correct formula is to utilize the crisscross method, shown below for sulfuric acid.



Formula: H_2SO_4

***Figure* 5.1.2:** *Crisscross approach to writing formula for sulfuric acid.*

Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxyacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.

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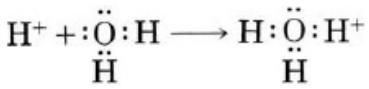
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5.2: Hydronium Ions

A hydrogen ion, H^+, is a hydrogen atom which has lost its single electron; that is, a hydrogen ion is just a proton. It does not, however, readily exist in an aqueous solution. Because a proton is only about one ten-thousandth as big as an average atom or ion, water dipoles can approach very close to a hydrogen ion in solution. Consequently the proton can exert a very strong attractive force on a lone pair of electrons in a water molecule—strong enough to form a coordinate covalent bond:



The H_3O^+ formed in this way is called a **hydronium ion** (on the left in the figure below). All three of its O—H bonds are exactly the same, and the ion has a pyramidal structure as predicted by VSEPR theory (1*a*). To emphasize the fact that a proton cannot exist by itself in aqueous solution, Eq. (1*a*) is often rewritten as

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{5.2.1}$$



Figure **5.2.1** Hydrogen and hydroxide ions in aqueous solution. (a) Hydronium ion, H_3O^+; (b) hydroxide ion, OH^-;

Like other ions in aqueous solution, both hydronium and hydroxide ions are hydrated. Moreover, hydrogen bonds are involved in attracting water molecules to hydronium and hydroxide ions. In both cases three water molecules appear to be rather tightly held, giving formulas $H_3O(H_2O)_3^+$ (or $H_9O_4^+$) and $HO(H_2O)_3^-$ (or $H_7O_4^-$). Possible structures for the hydrated hydronium and hydroxide ions are shown in Figure **5.2.1**.

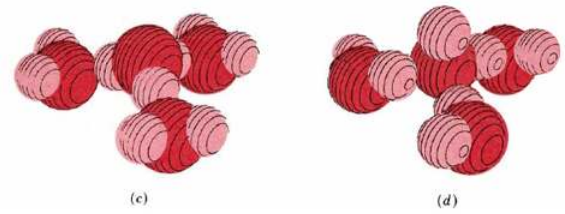


Figure **5.2.1** (c) hydrated Hydronium ion, $H_9O_4^+$; (d) hydrated hydroxide ion, $H_7O_4^-$.

Contributors

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5.3: Strong Acids and Bases

The most straight-forward examples involving acids and bases deal with *strong* acids and bases. **Strong acids**, like HCl or HNO_3, are strong electrolytes. All HCl molecules, for example, transfer their protons to H_2O molecules in an aqueous solution. The solution contains no HCl molecules, only $H_3O^+(aq)$ and $Cl^-(aq)$ ions. Similarly, **strong bases** are strong electrolytes and dissociate completely into hydroxide ions and the appropriate cation. All soluble hydroxides are strong bases. In an aqueous solution of barium hydroxide, for example, the base has completely dissociated into $Ba^{2+}(aq)$ and $OH^-(aq)$ ions.

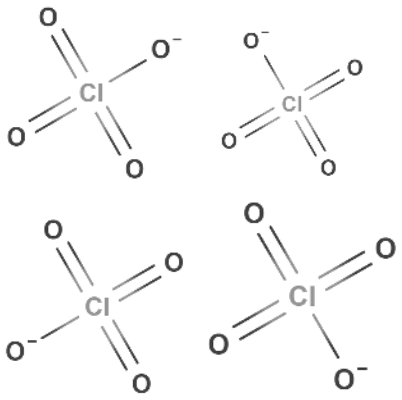
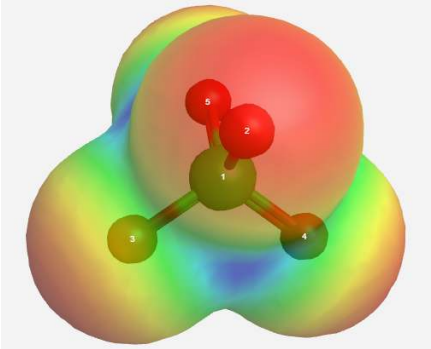
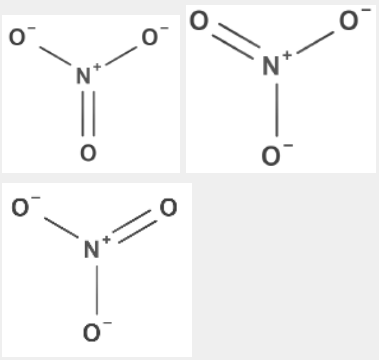
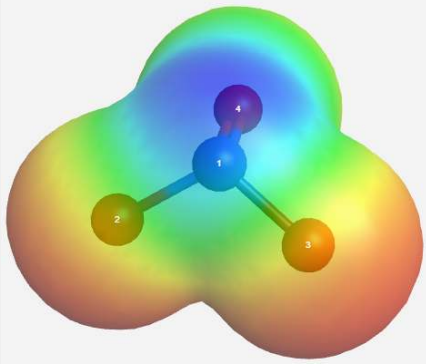
Table **5.3.1** lists molecules and ions which act as strong acids and bases in aqueous solution. Note that the strength of an acid refers only to its ability to donate protons to H_2O molecules and the strength of a base to its ability to accept protons from H_2O molecules. The acidity or basicity of a solution, on the other hand, depends on the concentration as well as the strength of the dissolved acid or base.

TABLE **5.3.1** Species Which Are Strong Acids and Bases in Aqueous Solution.

Strong Acids	Strong Bases
HCl, HBr, HI $HClO_4$, HNO_3, H_2SO_4	Soluble Hydroxides: LiOH, NaOH, KOH, RbOH, CsOH, $Sr(OH)_2$ and $Ba(OH)_2$

As a general rule, strong proton donors are molecules in which a hydrogen is attached to a rather electronegative atom, such as oxygen or a halogen. Considerable electron density is shifted away from hydrogen in such a molecule, making it possible for hydrogen ions to depart without taking along any electrons. The strong acids in Table **5.3.1** fit this rule nicely. They are either hydrogen halides (HCl, HBr, HI) or oxyacids (whose general formula is H_nXO_m).

Below are the resonance structures for oxoacids after they donate a proton. The reason for the strength of the following acids is the stability of the anion, which is shown by the number of resonance structures and the distribution of the negative charge amongst all of the oxygen atoms. The distribution of the negative charge can be visualized in the 3D structure, with red being representing negative charge and blue representing positive charge. The 3D structure represents the average of the resonance structures shown to the left.

Name	Lewis Structure (Resonance)	3D Structure
Perchloric Acid		
Nitric Acid		

The Lewis structures indicate a proton bonded to oxygen in each of the oxyacids, hence their general name. Note that for a strong oxyacid the number of oxygens is always larger by two or more than the number of hydrogens. That is, in the general formula H_nXO_m, $m \geq n + 2$.

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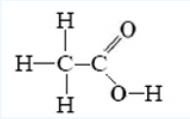
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5.4: Weak Acids

Not all molecules which contain hydrogen are capable of donating protons. For example, methane (CH_4) and other hydrocarbons show no acidic properties at all. Carbon is not highly electronegative, and so electron density is fairly evenly shared in a C—H bond, and the hydrogen atom is unlikely to depart without at least one electron. Even when it is bonded to highly electronegative atoms like oxygen or fluorine, a hydrogen atom is not *always* strongly acidic.

Example 5.4.1 : Proton Transfer

Acetic acid has the projection formula



Write an equation for transfer of a proton from acetic acid to water.

Solution

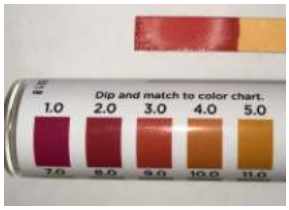
By the electronegativity rule given above, only the hydrogen attached to oxygen should be acidic. The equation is

$$\mathbf{CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-} \qquad (5.4.1)$$

Note: To emphasize that only one hydrogen atom is acidic, the formula acetic acid is often written $HC_2H_3O_2$. You may also find the formulas HA*c* or HOA*c* for acetic acid, where A*c*$^-$ or OA*c*$^-$ represents the acetate ion, CH_3COO^-.

The equation for the proton transfer between acetic acid and water is written with a double arrow because it occurs to only a limited extent. Like $HgCl_2$, acetic acid is a weak electrolyte. According to Table 1 in Ions in Solution (Electrolytes), 0.001 *M* $HC_2H_3O_2$ conducts slightly more than one-tenth as much current as the same concentration of the strong acids HCl or HNO_3. Therefore we can conclude that at a given instant only a little over 10 percent of the acetic acid molecules have donated protons to water molecules according to Eq. 5.4.1. Nearly 90 percent are in molecular form as CH_3COOH (or $HC_2H_3O_2$) and make no contribution to the current. Because acetic acid is not a strong enough proton donor to be entirely converted to hydronium ions in aqueous solution, it is called a **weak acid**. A given concentration of a weak acid produces fewer hydronium ions per unit volume and therefore less acidity than the same concentration of a strong acid.

For those of you in laboratory, you can identify a weak acid using litmus paper. Below is an image of litmus paper after the addition of the weak acid acetic acid (CH_3COOH). Notice the red hue, which indicates a weak acid. If HCl of the same molarity were tested, the color would be darker, more purple than red.



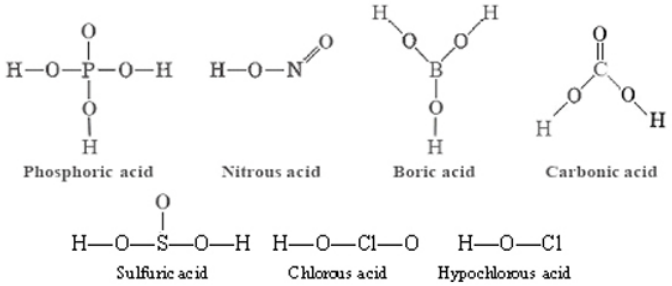
There are a large number of weak acids, but fortunately they fall into a few well-defined categories:

Carboxylic acids

These compounds have the general formula RCOOH. All react with water in the same way as acetic acid [Eq. 5.4.1]. The strength of carboxylic acids is dependent on the electronegative strength of the atoms in the "R" group. Consider the compounds F_3COOH and H_3COOH. Fluorine is the most electronegative element, while hydrogen is comparable to carbon in electronegativity. Thus, the fluorines pull electron density away from the carboxyl group. This removes electron density from the acidic oxygen-hydrogen bond, which weakens it. This weaker bond means that the hydrogen can be removed more easily, which creates a stronger acid. This concept can be applied to any R group. The more electronegative the R group, the stronger the carboxylic acid will be.

Weak oxyacids

These have the same general formula H_nXO_m as strong oxyacids, but the number of hydrogens is equal to or one less than the number of oxygens. For a weak oxyacid, in other words, $m \le n + 1$. Some examples are:



Some of the weak oxyacids, H_2CO_3 for example, are very unstable and cannot be separated in pure form from aqueous solution.

Other molecules containing acidic hydrogen atoms

Hydrogen fluoride (HF) has a very strong bond and does not donate its proton as readily as other hydrogen halides. Other molecules in this category are hydrogen sulfide (H_2S) and hydrogen cyanide (HCN). In the latter case, even though H is bonded to C, the electronegative N atom pulls some electron density away, and the HCN molecule is a very weak proton donor.

Ions having acidic protons

Certain other ions can donate protons. One example is the ammonium ion, NH_4^+:

$$\mathbf{NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+} \tag{5.4.2}$$

Anions formed when some acids donate protons can lose yet another H^+. An example of this is the hydrogen sulfate ion formed when sulfuric acid donates a proton:

$$\mathbf{H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-} \tag{5.4.3}$$

$$\mathbf{HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}} \tag{5.4.4}$$

Although sulfuric acid is strong, the negative charge on the hydrogen sulfate ion holds the proton tighter, and so the ion is a considerably weaker acid. Acids such as H_2SO_4, H_2S, H_2SO_3, and H_2CO_3 are called **diprotic** because they can donate two protons. Phosphoric acid, H_3PO_4, is **triprotic**—it can donate three protons.

Contributors

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5.5: Weak Bases

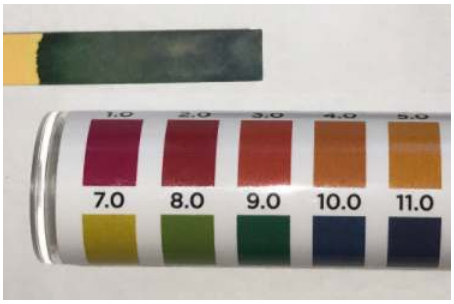
By analogy with weak acids, **weak bases** are not strong enough proton acceptors to react completely with water. A typical example is ammonia, which reacts only to a limited extent:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{5.5.1}$$



As in the case of acetic acid, the current conducted by 0.001 *M* NH_3 (Table 1 from Ions in Solution) is slightly above 10 percent that of 0.001 *M* NaOH or KOH, indicating that somewhat more than one-tenth of the NH_3 molecules have been converted to NH_4^+ and OH^- ions.

To verify that NH_3 is a weak base, a litmus test can be done. The NH_3 is added to litmus paper, which indicates it's pH based on the color of the litmus paper. In the image below you can see the litmus paper turns a greenish blue when exposed to NH_3 (pH 9-10). For comparison, a strong base of the same molarity like NaOH or KOH would have a darker blue coloring.



Weak bases fall into two main categories.

Ammonia and amines

Amines may be derived from ammonia by replacing one or more hydrogens with carbon chains. They react with water in the same way as ammonia. Trimethyl amine behaves as follows:

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^- \tag{5.5.2}$$

Anions of weak acids

The fact that the molecules of a weak acid are not entirely converted into hydronium ions and anions implies that those anions must have considerable affinity for protons. For example, the anion of acetic acid, acetate ion, can accept protons as follows:

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \tag{5.5.3}$$

Thus when a compound like sodium acetate,dissolves, some hydroxide ions are produced and the solution becomes slightly basic. (Sodium ions do not react with water at all, and so they have no effect on acidity or basicity.) Other examples of weak bases which are anions of weak acids are CN^-, CO_3^{2-}, PO_4^{3-}.

Contributors

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5.6: Brønsted-Lowry Definition of Acids and Bases

Learning Objectives

1. Recognize a compound as a Brønsted-Lowry acid or a Brønsted-Lowry base.
2. Illustrate the proton transfer process that defines a Brønsted-Lowry acid-base reaction.

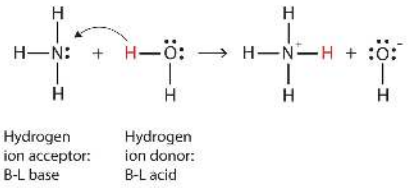
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

In 1923, the Danish scientist Johannes Brønsted and the English scientist Thomas Lowry independently proposed new definitions for acids and bases. Rather than considering both hydrogen and hydroxide ions, they focused on the hydrogen ion only. A Brønsted-Lowry acid is a compound that supplies a hydrogen ion in a reaction. A Brønsted-Lowry base, conversely, is a compound that accepts a hydrogen ion in a reaction. Thus, the Brønsted-Lowry definitions of an acid and a base focus on the movement of hydrogen ions in a reaction, rather than on the production of hydrogen ions and hydroxide ions in an aqueous solution.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_{3(aq)} + H_2O_{(\ell)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)} \tag{5.6.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

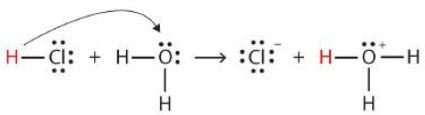
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

> A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl_{(g)} + H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{5.6.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, **HCl acts as a Brønsted-Lowry acid**; as a hydrogen ion acceptor, **H_2O is a Brønsted-Lowry base**. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

> All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Example 5.6.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightarrow C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise 5.6.1

Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffees and teas. When dissolved in water, it can accept a proton from a water molecule. Write the chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_8H_{10}N_4O_2(aq) + H_2O(\ell) \rightarrow C_8H_{11}N_4O_2^+(aq) + OH^-(aq)$

B-L base B-L acid

Application in Everyday Life

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure **5.6.1**). 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.



$CH_3COOH + NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow CH_3COO^- + NH_3^+CH_2CH_2CH_2CH_2NH_2$

Acetic acid + Putrescine → Acetate ion + Putrescinium ion

Figure 5.6.1: A neutralization reaction takes place between citric acid or acetic acid (proton donors) in lemons or vinegar and putrescine (proton acceptor) in the flesh of fish.

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.

To Your Health: Brønsted-Lowry Acid-Base Reactions in Pharmaceuticals

There are many interesting applications of Brønsted-Lowry acid-base reactions in the pharmaceutical industry. For example, drugs often need to be water soluble for maximum effectiveness. However, many complex organic compounds are not soluble or are only slightly soluble in water. Fortunately, those drugs that contain proton-accepting nitrogen atoms (and there are a lot of them) can be reacted with dilute hydrochloric acid [HCl(aq)]. The nitrogen atoms—acting as Brønsted-Lowry bases—accept the hydrogen ions from the acid to make an ion, which is usually much more soluble in water. The modified drug molecules can then be isolated as chloride salts:

$$\mathrm{RN(sl\ aq) + H^+(aq) \rightarrow RNH^+(aq) \xrightarrow{Cl^-(aq)} RNHCl(s)} \tag{5.6.3}$$

where RN represents some organic compound containing nitrogen. The label *(sl aq)* means “slightly aqueous,” indicating that the compound RN is only slightly soluble. Drugs that are modified in this way are called *hydrochloride salts*. Examples include the powerful painkiller codeine, which is commonly administered as codeine hydrochloride. Acids other than hydrochloric acid are also used. Hydrobromic acid, for example, gives *hydrobromide salts*. Dextromethorphan, an ingredient in many cough medicines, is dispensed as dextromethorphan hydrobromide. The accompanying figure shows another medication (lidocaine) as a hydrochloride salt.



Figure used with permission from Wikipedia.

Conjugate Acid-Base Pairs

According to the Bronsted-Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Once an acid has given up a proton, the part that remains is called the acid's **conjugate base**. This species is a base because it can accept a proton (to re-form the acid). The conjugate base of HF (first example below) is fluoride ion, F^-.

$$\text{Acid} = H^+ + \text{Conjugate base of Acid}^-$$

$$HF \rightleftharpoons H^+ + F^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3$$

Similarly, the part of the base that remains after a base accepts a proton is called the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base). The conjugate acid of fluoride ion, F^- (first example below) is HF.

$$H^+ + \text{Base} = \text{Conjugate acid of Base}^+$$

$$H^+ + F^- \rightleftharpoons HF$$

$$H^+ + OH^- \rightleftharpoons H_2O$$

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

To summarize, the conjugate base of HF is fluoride ion, F^-, and the conjugate acid of fluoride ion, F^-, is HF. The HF/F- pair is referred to as a conjugate acid-base pair. The difference in the formulas of a conjugate acid-base pair (example: HF and F^-) is H^+. The table below lists conjugate acid-base pairs for your reference so that you can figure out the strategy of identifying them. For any given acid or base, you should be able to give its conjugate base or conjugate acid. The formula of an acid's conjugate base is generated by **removing a proton** (H^+) from the acid formula. The formula of the base's conjugate acid is formed by **adding a proton** (H^+) to the formula of the base.

Table **5.6.1**. Conjugate acid-base pairs.

Conjugate Acid	Conjugate Base
H_3O^+	H_2O
H_2O	OH^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3
NH_3	NH_2^-
CH_3COOH	CH_3COO^-
$CH_3NH_3^+$	CH_3NH_2

Example 5.6.3 : Conjugate Pairs

Write the formula of the conjugate base of (a) HCl and (b) HCO_3^-.

Write the formula of the conjugate acid of (c) CH_3NH_2 and (d) OH^-.

Solution:

A conjugate base is formed by removing a proton (H^+). A conjugate acid is formed by accepting a proton (H^+).

a. After HCl donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.
b. After hydrogen carbonate ion, HCO_3^-, donates a proton, its conjugate base, CO_3^{2-} is produced.
c. After accepting a proton (H^+), CH_3NH_2 is converted to $CH_3NH_3^+$, its conjugate acid.
d. After accepting a proton (H^+), OH^- is converted to H_2O, its conjugate acid.

Exercise 5.6.3: Conjugate Pairs

Write the formula of the conjugate base of (a) HNO_2 and (b) H_2CO_3.

Write the formula of the conjugate acid of (c) C_6H5NH_2 and (d) HCO_3^-.

Answer

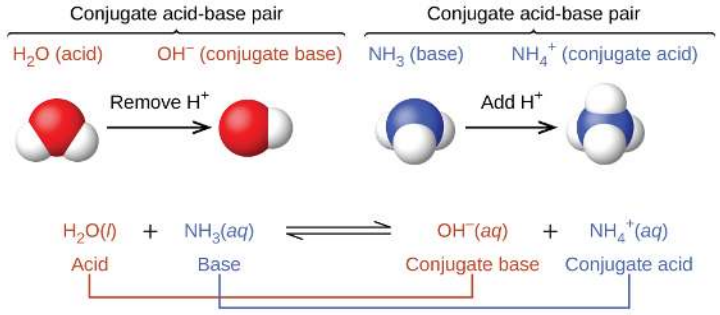
a. NO_2^- is the conjugate base of HNO_2.

b. HCO_3^- is the conjugate base of H_2CO_3

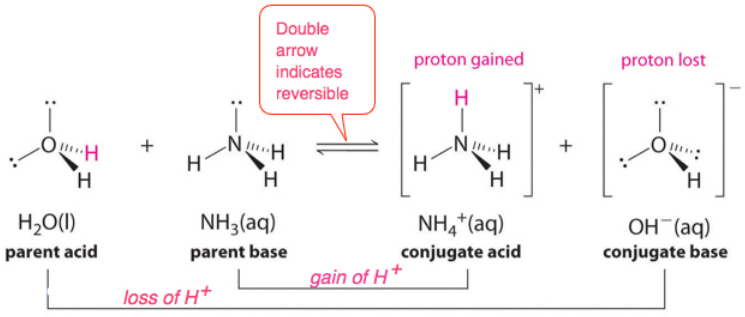
c. $C_6H5NH_3^+$ is the conjugate acid of C_6H5NH_2.

d. H_2CO_3 is the conjugate acid of HCO_3^-

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The **conjugate acid–base pairs** for this reaction are $\boldsymbol{NH_4^+/NH_3}$ and $\boldsymbol{H_2O/OH^-}$. This means that the conjugate acid of the base NH_3 is NH_4^+ while the conjugate base of the acid NH_4^+ is NH_3. Similarly, the conjugate base of the acid H_2O is OH^-, and the conjugate acid of the base OH^- is H_2O.



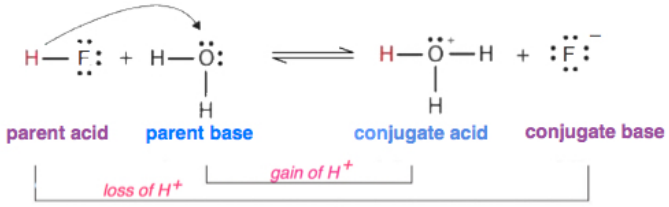
In the **forward** reaction, the parent acid is H_2O and and the parent base is NH_3 (shown in the illustration below). The acid H_2O loses a proton (H^+) to form its conjugate base OH^-. The base NH_3 gains a proton, to produce its conjugate acid NH_4^+. In the **reverse** reaction, the acid NH_4^+ loses a proton (H^+) to form its conjugate base NH_3. The base OH^- gains a proton, to produce its conjugate acid H_2O.



When hydrogen fluoride (HF) dissolves in water and ionizes, protons are transferred from hydrogen fluoride (parent acid) molecules to water (parent base) molecules, yielding hydronium ions (conjugate acid of water) and fluoride ions (conjugate base of

HF):

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$



Example 5.6.3

Identify the conjugate acid-base pairs in this equilibrium.

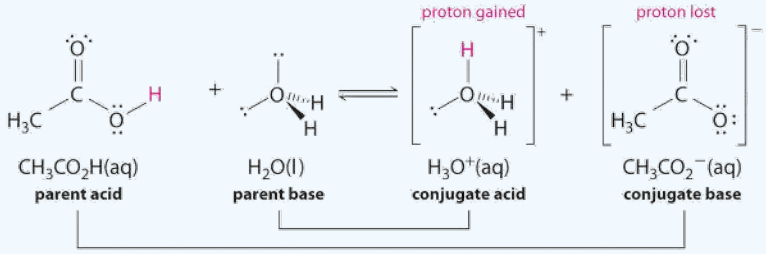
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid–base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 5.6.4

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 5.6.4

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer:

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base*, and, conversely, *the stronger a base, the weaker its conjugate acid.*

Concept Review Exercise

1. Give the definitions of a Brønsted-Lowry acid and a Brønsted-Lowry base.

Answer

1. A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

Key Takeaways

- A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.
- Brønsted-Lowry acid-base reactions are essentially proton transfer reactions.

Exercises

1. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

2. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $H_2O(\ell) + N_2H_4(aq) \rightarrow N_2H_5^+(aq) + OH^-(aq)$

3. Explain why a Brønsted-Lowry acid can be called a proton donor.
4. Explain why a Brønsted-Lowry base can be called a proton acceptor.
5. Write the chemical equation of the reaction of ammonia in water and label the Brønsted-Lowry acid and base.
6. Write the chemical equation of the reaction of methylamine (CH_3NH_2) in water and label the Brønsted-Lowry acid and base.
7. Demonstrate that the dissolution of HNO_3 in water is actually a Brønsted-Lowry acid-base reaction by describing it with a chemical equation and labeling the Brønsted-Lowry acid and base.
8. Identify the Brønsted-Lowry acid and base in the following chemical equation:

   $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$

9. Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in each of the following equations

   1. $\mathbf{NO_2^- + H_2O \longrightarrow HNO_2 + OH^-}$
   2. $\mathbf{HBr + H_2O \longrightarrow H_3O^+ + Br^-}$
   3. $\mathbf{HS^- + H_2O \longrightarrow H_2S + OH^-}$
   4. $\mathbf{H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O}$
   5. $\mathbf{H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-}$

10. Write the chemical equation for the reaction that occurs when cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) dissolves in water and donates a proton to a water molecule. (When hydrochlorides dissolve in water, they separate into chloride ions and the appropriate cation.)

11. If codeine hydrobromide has the formula $C_{18}H_{22}BrNO_3$, what is the formula of the parent compound codeine?

Answers

1. HCl: Brønsted-Lowry acid; NH_3: Brønsted-Lowry base
2. H_2O: Brønsted-Lowry acid; N_2H_4: Brønsted-Lowry base
3. A Brønsted-Lowry acid gives away an H^+ ion—nominally, a proton—in an acid-base reaction.
4. A Brønsted-Lowry base accepts an H^+ ion (a proton) in an acid-base reaction.
5. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (here NH_3 = Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
6. $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$ (here CH_3NH_2 = Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
7. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ (here HNO_3 = Brønsted-Lowry acid; H_2O = Brønsted-Lowry base)

8. $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$ (here H_3O^+ = Brønsted-Lowry acid; $C_3H_7NH_2$ = Brønsted-Lowry base)
9.
    1. NO_2^- (base) + H_2O (acid)
    2. HBr (acid) + H_2O (base)
    3. HS^- (base) + H_2O (acid)
    4. $H_2PO_4^-$ (acid) + OH^- (base)
    5. $H_2PO_4^-$ (base) + HCl (acid)
10. cocaine hydrochloride dissolves in water: $C_{17}H_{22}ClNO_4 \rightarrow Cl^- + C_{17}H_{22}NO_4^+$

cation donates a proton to a water molecule: $C_{17}H_{22}NO_4^+ + H_2O \rightarrow H_3O^+ + C_{17}H_{21}NO_4$

11. $C_{18}H_{21}NO_3$

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5.7: Acid Strength and the Acid Dissociation Constant (Ka)

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{5.7.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{5.7.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 5.7.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 5.7.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{5.7.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 5.7.1.

Table 5.7.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^{9}	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^{2}	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^{1}	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{5.7.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{5.7.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 5.7.2.

Table 5.7.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00

*As in Table 5.7.1.

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{5.7.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{5.7.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{5.7.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{5.7.9}$$

If we add Equations 5.7.6 and 5.7.7, we obtain the following:

add Equations 5.7.6 and 5.7.7, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,\cancel{[CN^-]} / \cancel{[HCN]}$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,\cancel{[HCN]} / \cancel{[CN^-]}$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{5.7.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{5.7.11}$$

$$K_a = 10^{-pK_a} \tag{5.7.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{5.7.13}$$

$$K_b = 10^{-pK_b} \tag{5.7.14}$$

Similarly, Equation 5.7.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{5.7.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{5.7.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 5.7.1 and 5.7.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

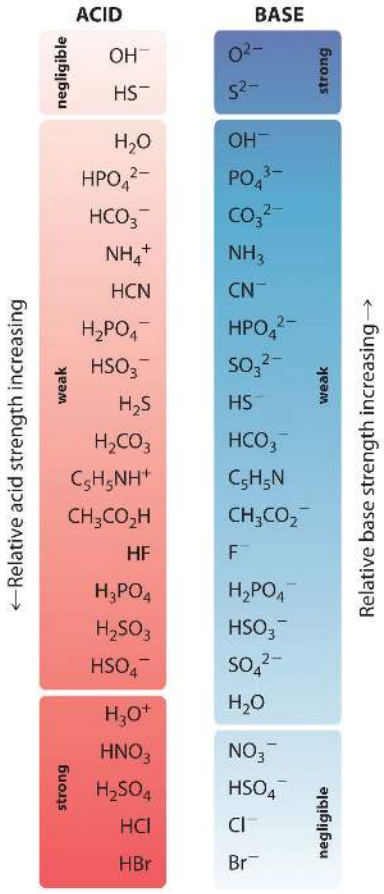


Figure 5.7.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 5.7.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This

order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 5.7.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\textbf{stronger acid} + \textbf{stronger base} \rightleftharpoons \textbf{weaker acid} + \textbf{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{5.7.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 5.7.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 5.7.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 5.7.15 and 5.7.16. Use the relationships pK = −log K and K = 10^{-pK} (Equations 5.7.11 and 5.7.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 5.7.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 5.7.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

? Exercise 5.7.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 5.7.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a

greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 5.7.1 were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 5.7.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{5.7.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{5.7.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{5.7.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO_{4(aq)}^{2-} + H_2O_{(aq)} \rightleftharpoons HSO_{4(aq)}^{-} + OH_{(aq)}^{-}$$

$$HSO_{4(aq)}^{-} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH_{(aq)}^{-} \tag{5.7.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by pK_a + pK_b = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table 5.7.1, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 5.7.21 lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

Example 5.7.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH_{4(aq)}^{+} + PO_{4(aq)}^{3-} \rightleftharpoons NH_{3(aq)} + HPO_{4(aq)}^{2-}$
- $CH_3CH_2CO_2H_{(aq)} + CN_{(aq)}^{-} \rightleftharpoons CH_3CH_2CO_{2(aq)}^{-} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 5.7.1and5.7.2 and Figure 5.7.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables 5.7.1 and 5.7.2, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH_{4(aq)}^{+}} + \underset{\text{stronger base}}{PO_{4(aq)}^{3-}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO_{4(aq)}^{2-}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table 5.7.1, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 5.7.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN_{(aq)}^{-}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO_{2(aq)}^{-}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise 5.7.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

a. $H_2O_{(l)} + HS_{(aq)}^{-} \rightleftharpoons OH_{(aq)}^{-} + H_2S_{(aq)}$
b. $HCO_{2(aq)}^{-} + HSO_{4(aq)}^{-} \rightleftharpoons HCO_2H_{(aq)} + SO_{4(aq)}^{2-}$

Answer a

left

Answer b

left



A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25°C$$

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5.8: Autoionization of Water

Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of H_3O^+ and OH^- in aqueous solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:

$$\underbrace{NH_3}_{\text{base}} + \underbrace{H_2O}_{\text{acid}} \rightleftharpoons NH_4^+ + OH^- \tag{5.8.1}$$

where H_2O acts as an acid (in red).

$$\underbrace{HCl}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \longrightarrow H_3O^+ + Cl^- \tag{5.8.2}$$

where H_2O acts as an base (in blue).

It may not surprise you to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{5.8.3}$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**.

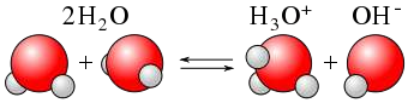


Figure 5.8.1: Autoionization of water, giving hydroxide and hydronium ions.

At this level, the concentration of both $H_3O^+(aq)$ and $OH^-(aq)$ in a sample of pure H_2O is about $1.0 \times 10^{-7}\ M$ (at room temperature). If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H_3O^+]=[OH^-] = 1.0 \times 10^{-7} \tag{5.8.4}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H_3O^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14} \tag{5.8.5}$$

- For acids, the concentration of $H_3O^+(aq)$ (i.e., $[H_3O^+]$) is greater than $1.0 \times 10^{-7}\ M$.
- For bases the concentration of $OH^-(aq)$ (i.e., $[OH^-]$) is greater than $1.0 \times 10^{-7}\ M$.

However, the *product* of the two concentrations—$[H_3O^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{5.8.6}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_w:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{5.8.7}$$

This means that if you know $[H_3O^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$), you can calculate $[H_3O^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

Warning: Temperature Matters

The degree of autoionization of water (Equation 5.8.3) and hence the value of K_w changes with temperature, so Equations 5.8.4 - 5.8.7 are accurate only at room temperature.

Example 5.8.1: Hydroxide ConCentration

What is $[OH^-]$) of an aqueous solution if $[H_3O^+]$ is $1.0 \times 10^{-4} M$?

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $[H_3O^+] = 1.0 \times 10^{-4}\ M$ Find: $[OH^-]$ = ? M
List other known quantities	none
Plan the problem	Using the expression for K_w, (Equation 5.8.7), rearrange the equation algebraically to solve for $[OH^-]$. $$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$
Calculate	Now substitute the known quantities into the equation and solve. $$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$ It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.
Think about your result.	The concentration of the acid is high (> 1 x 10^{-7} M) so $[OH^-]$ should be low.

Exercise 5.8.1

What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4?

Hint

Assume **both** protons ionize from the molecule.. although this is not the case.

Answer

$3.1 \times 10^{-11}\ M$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H_3O^+ or OH^- ions in the formula unit because $[H_3O^+]$ or $[OH^-]$) may not be the same as the concentration of the acid or base itself.

Example 5.8.2: Hydronium Concentration

What is $[H_3O^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: $[Ca(OH)_2] = 0.0044\,M$ Find: $[H_3O^+]$ = ? M
List other known quantities	We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this, $$[OH^-] = 2 \times 0.0044\ \text{M} = 0.0088\,\text{M}\cdot$$
Plan the problem	Use the expression for K_w (Equation 5.8.7) and rearrange the equation algebraically to solve for $[H_3O^+]$. $$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
Calculate	Now substitute the known quantities into the equation and solve. $$[H_3O^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} M$$ $[H_3O^+]$ has decreased significantly in this basic solution.
Think about your result.	The concentration of the base is high (> 1 x 10^{-7} M) so Extra close brace or missing open brace should be low.

Exercise 5.8.2

What is $[H_3O^+]$ of an aqueous solution if $[OH^-]$ is $1.0 \times 10^{-9}\,M$?

Answer

1.0×10^{-5} M

In any aqueous solution, the product of $[H_3O^+]$ and $[OH^-]$ equals 1.0×10^{-14} (at room temperature).

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5.9: The pH and pOH Scales

Learning Objectives

- Define pH and pOH
- Determine the pH of acidic and basic solutions.
- Determine the hydronium ion concentration and pOH from pH.

As we have seen, $[H_3O^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of $[H_3O^+]$:

$$pH = -\log[H_3O^+] \tag{5.9.1}$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H_3O^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale. The range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral. Figure **5.9.1** illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative log of*** $[H_3O^+]$, which will give a positive value for pH.

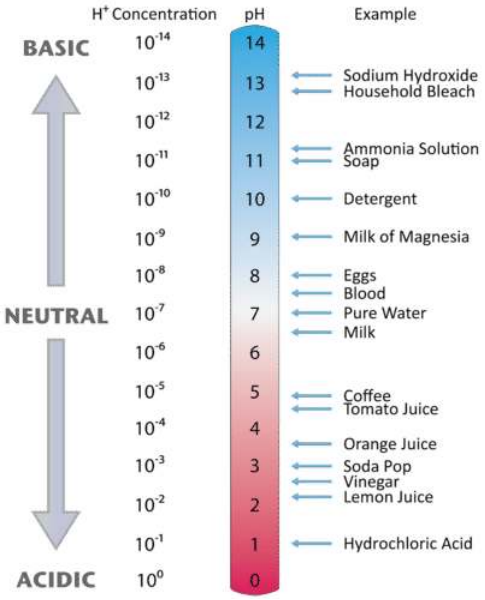


Figure **5.9.1**: The pH *values for several common materials.*

Warning: The Ph scale has no limits

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H_3O^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale. The range of values from 0 to 14 that describes the acidity or basicity of a solution.. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

Example 5.9.1

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Answer

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

Exercise 5.9.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer a

basic

Answer b

basic

Answer c

acidic

Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the pH of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

Logarithms

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x 10^{-5} (for $[H_3O^+]$ = 1.0 x 10^{-5} M) you should get an answer of "-5"

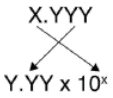
If you get a different answer, or an error, try pressing the LOG key before you enter the number.

Example 5.9.2: Converting Ph to Hydronium Concentration

Find the pH, given the $[H_3O^+]$ of the following:

a. 1 ×10^{-3} M
b. 2.5 ×10^{-11} M
c. 4.7 ×10^{-9} M

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: a. $[H_3O^+] = 1 \times 10^{-3}$ M b. $[H_3O^+] = 2.5 \times 10^{-11}$ M c. $[H_3O^+] = 4.7 \times 10^{-9}$ M Find: ? pH
Plan the problem	Need to use the expression for pH (Equation 5.9.1) $pH = - \log [H_3O^+]$
Calculate	Now substitute the known quantity into the equation and solve. a. $pH = - \log [1 \times 10^{-3}] = 3.0$ (1 decimal places since 1 has 1 significant figure) b. $pH = - \log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures) c. $pH = - \log [4.7 \times 10^{-9}] = 8.30$ (2 decimal places since 4.7 has 2 significant figures) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 5.9.2

Find the pH, given $[H_3O^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7}

Answer a

3.22

Answer b

7.00

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards" - you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation 5.9.1 for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[H_3O^+] = \text{antilog}(-pH) \tag{5.9.2}$$

or

$$[H_3O^+] = 10^{-pH} \tag{5.9.3}$$

As mentioned above, different calculators work slightly differently - make sure you can do the following calculations using ***your*** calculator.

Calculator Skills

We have a solution with a pH = 8.3. What is $[H_3O^+]$?

With some calculators you will do things in the following order:

1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key)
2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be 10^x.
3. You should get the answer **5.0×10^{-9}**

Other calculators require you to enter keys in the order they appear in the equation.

1. Use the Shift or second function to key in the 10^x function.
2. Use the +/- key to type in a negative number, then type in 8.3
3. You should get the answer **5.0×10^{-9}**

If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up - you must master your calculator!

Example 5.9.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem	Need to use the expression for $[H_3O^+]$ (Equation 5.9.3) $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$
Calculate	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.60) = 2.5 x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: X.YYY Y.YY x 10^x

Exercise 5.9.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5×10^{-8} M

The pOH scale

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^-\right] \tag{5.9.4}$$

The relation between the hydronium and hydroxide ion concentrations expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH}^-] \tag{5.9.5}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH}^-]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH}^-] \tag{5.9.6}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{5.9.7}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{5.9.8}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{5.9.9}$$

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{5.9.10}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (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 $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Example 5.9.4:

Find the pOH of a solution with a pH of 4.42.

Solution

Steps for Problem Solving	
Identify the "given"information and what the problem is asking you to "find."	Given: pH =4.42 Find: ? pOH
Plan the problem	Need to use the expression pOH = 14 - pH
Calculate	Now substitute the known quantity into the equation and solve. pOH=14−4.42=9.58
Think about your result	The pH is that of an acidic solution, and the resulting pOH is the difference after subtracting from 14. The answer has two significant figures because the given pH has two decimal places.

Exercise 5.9.4

The pH of a solution is 8.22. What is the pOH?

Answer

5.78

The diagram below shows all of the interrelationships between [H3O+][H3O+], [OH−][OH−], pH, and pOH.

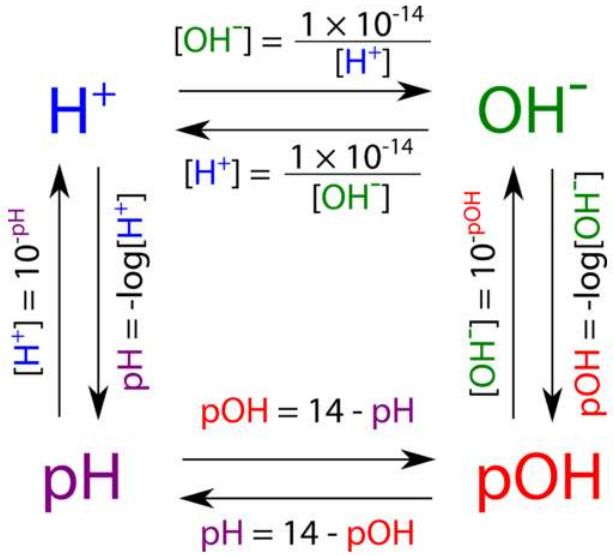


Figure 5.9.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

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5.10: Buffers

So far in discussing pH we have dealt only with solutions obtained by adding a single acid, such as acetic acid, or a single base, such as the acetate ion, to water. We must now turn to a consideration of solutions to which both an acid and a base have been added. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also present in comparable amounts. Solutions of this special kind are called **buffer solutions** because, as we shall shortly see in the video below, it is difficult to change their pH even when an appreciable amount of strong acid or strong base is added.



As a typical example of a buffer solution, let us consider the solution obtained when 3.00 mol acetic acid ($HC_2H_3O_2$) and 2.00 mol sodium acetate ($Na\ C_2H_3O_2$) are added to sufficient water to produce a solution of total volume 1 L. The stoichiometric concentration of acetic acid, namely, c_a, is then 3.00 mol L^{-1}, while the stoichiometric concentration of sodium acetate, c_b, is 2.00 mol L^{-1}. As a result of mixing the two components, some of the acetic acid, say x mol L^{-1}, is converted to acetate ion and hydronium ion. We can now draw up a table in order to find the equilibrium concentrations in the usual way.

Species	Initial Concentration (mol L^{-1})	Change in Concentration (mol L^{-1})	Equilibrium Concentration (mol L^{-1})
H_3O^+	10^{-7} (negligible)	x	x
CH_3COO^-	2.00	x	2.00 + x
CH_2COOH	3.00	(-x)	3.00 - x

We can now substitute concentrations in the equilibrium expression

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \tag{5.10.1}$$

from which we obtain

$$1.8 \times 10^{-5}\ \text{mol}\ L^{-1} = \frac{(2.00 + x)x}{3.00 - x}\ \text{mol}\ L^{-1} \tag{5.10.2}$$

In order to solve this equation, we make the approximation that x is negligibly small compared with both 2.00 and 3.00, that is, that only a minute fraction of acetic acid has converted to acetate ion. We then have

$$\frac{2.00x}{3.00} = 1.8 \times 10^{-5} \tag{5.10.3}$$

or

$$x = \frac{3.00}{2.00} \times 1.8 \times 10^{-5} \tag{5.10.4}$$

$$= 2.7 \times 10^{-5} \tag{5.10.5}$$

Obviously, our approximation is a very good one. Since x is only 0.001 percent of 2.00 or 3.00, there really is no point in obtaining a second approximation by feeding x back into Eq. 5.10.2. We can thus safely conclude that

$$[H_3O^+] = 2.7 \times 10^{-5} \text{mol L}^{-1}$$

and

$$pH = 4.57$$

The example we have just considered demonstrates two obvious features:

1. When the acid and its conjugate base are mixed, very little of the acid is converted to base, or vice versa. (x was small compared with 2.00 and 3.00.)
2. In a buffer mixture, the hydronium-ion concentration and the hydroxide-ion concentration are small compared with the concentrations of acid and conjugate base. ($[H_3O^+] = 2.7 \times 10^{-5}$ mol L^{-1}; $[HO^-] = 3.7 \times 10^{-10}$ mol L^{-1} as compared with $[CH_3COO^-] = 2.00$ mol L^{-1} and $[CH_3COOH] = 3.00$ mol L^{-1})

By assuming that these features are common to all buffer solutions, we make it very easy to handle them from a mathematical standpoint.

Let us now consider the general problem of finding the pH of a buffer solution which is a mixture of a weak acid HA, of stoichiometric concentration c_a, and its conjugate base A^-, of stoichiom

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \tag{5.10.6}$$

Taking negative logarithms of both sides, we obtain

$$-\log [H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \tag{5.10.7}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{5.10.8}$$

Equation 5.10.8 is called the **Henderson-Hasselbalch equation** and is often used by chemists and biologists to calculate the pH of a buffer.

As we saw in the case of the acetic acid—sodium acetate buffer described earlier, the equilibrium concentrations of HA and A^- are usually almost identical to the stoichiometric concentrations. That is,

$[HA] \approx c_a$ and $[A^-] \approx c_b$

We can substitute these values into Eqs. 5.10.6 and 5.10.8 to obtain the very useful approximations

$$[H_3O^+] \approx K_a \times \frac{c_a}{c_b} \tag{5.10.9}$$

and

$$pH \approx pK_a + \log \frac{c_b}{c_a} \tag{5.10.10}$$

Example 5.10.1: pH of Solution

Find the pH of the solution obtained when 1.00 mol NH_3 and 0.40 mol NH_4Cl are mixed to give 1 L of solution. $K_b(NH_3) = 1.8 \times 10^{-5}$ mol L^{-1}.

Solution

In order to use Eq. 5.10.9,we need first to have the value of

$$K_a\left(NH_4^+\right) = \frac{K_w}{K_b\left(NH_3\right)} \tag{5.10.11}$$

$$= \frac{1.00 \times 10^{-14}\ \text{mol}^2\ \text{L}^2}{1.8 \times 10^{-5}\ \text{mol L}^{-1}} \tag{5.10.12}$$

$$= 5.56 \times 10^{-10}\ \text{mol L}^{-1} \tag{5.10.13}$$

We also have c_a = 0.40 mol L^{-1} and c_b = 1.00 mol L^{-1}. Thus

$$\left[H_3O^+\right] = K_a \times \frac{c_a}{c_b} \tag{5.10.14}$$

$$= 5.56 \times 10^{-10}\ \text{mol L}^{-1} \times \frac{0.4\ \text{mol L}^{-1}}{1.0\ \text{mol L}^{-1}} \tag{5.10.15}$$

$$= 2.22 \times 10^{-10}\ \text{mol L}^{-1} \tag{5.10.16}$$

from which

and $\mathbf{pH = 9.65}$

To see why a mixture of an acid and its conjugate base is resistant to a change in pH, let us go back to our first example: a mixture of acetic acid (3 mol L^{-1})and sodium acetate (2 mol L^{-1}). What would happen if we now added 0.50 mol sodium hydroxide to 1 L of this mixture? The added hydroxide ion will attack both the acids present, namely, the hydronium ion and acetic acid. Since the hydronium-ion concentration is so small, very little hydroxide ion will be consumed by reaction with the hydronium ion. Most will be consumed by reaction with acetic acid. Further, since the hydroxide ion is such a strong base, the reaction

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \tag{5.10.17}$$



will go virtually to completion, and 0.50 mol acetic acid will be consumed. The same amount of acetate ion will be produced. In tabular form:

Species	Initial Concentration mol L^{-1}	Change in Concentration mol L^{-1}	Equilibrium Concentration mol L^{-1}
H_3O^+	2.7 x 10^{-5}	Small	approx. 2.7 x 10^{-5}
CH_3COO^-	2.00	0.50	2.50 + 2.7 x 10^{-5} = 2.50
CH_2COOH	nbsp; 3.00	(-0.50)	2.50 - 2.7 x 10^{-5} = 2.50

Substituting the equilibrium concentrations of base (acetate ion) and conjugate acid (acetic acid) into the Henderson-Hasselbalch equation, Eq. 5.10.8, we have

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]} \tag{5.10.18}$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{(2.50\ \text{mol L}^{-1})}{(2.50\ \text{mol L}^{-1})} \tag{5.10.19}$$

$$= -(0.25 - 5) + \log(1) \tag{5.10.20}$$

$$= 4.74 + 0 = 4.74 \tag{5.10.21}$$

The addition of 0.5 mol sodium hydroxide to buffer mixture has thus succeeded in raising its pH from 4.57 to only 4.74. If the same 0.5 mol had been added to a cubic decimeter of pure water, the pH would have jumped all the way from 7.00 up to 13.7! The buffer is extremely effective at resisting a change in pH because the added hydroxide ion attacks the *weak acid* (in very high concentration) rather than the hydronium ion (in very low concentration). The major effect of the addition of the hydroxide ion is thus to change the ratio of acid to conjugate base, i.e., to change the value of

$$\frac{[CH_3COOH]}{[CH_3COO^-]} \tag{5.10.22}$$

As long as the amount of weak acid is much larger than the amount of base added, this ratio is not altered by very much. Since the hydronium-ion concentration is governed by

$$[H_3O^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} \tag{5.10.23}$$

the hydronium-ion concentration and pH are also altered to only a small extent.

The ability of a buffer solution to resist large changes in pH has a great many chemical applications, but perhaps the most obvious examples of buffer action are to be found in living matter. If the pH of human blood, for instance, gets outside the range 7.2 to 7.6, the results are usually fatal. The pH of blood is controlled by the buffering action of several conjugate acid-base pairs. The most important of these is undoubtedly the H_2CO_3/HCO_3^- pair, but side chains of the amino acid histidine in the hemoglobin molecule also play a part. (Hemoglobin, a protein, is the red substance in the blood. It is responsible for carrying oxygen away from the lungs.) Most enzymes (biological catalysts) can only function inside a rather limited pH range and must therefore operate in a buffered environment. The enzymes which start the process of digestion in the mouth at a pH of around 7 become inoperative in the stomach at a pH of 1.4. The stomach enzymes in turn cannot function in the slightly basic environment of the intestines.

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5.11: Neutralization Reactions

Learning Objectives

- Identify an acid and a base.
- Identify a neutralization reaction and predict its products.

In Chapter 3, we defined an acid as an ionic compound that contains H^+ as the cation. This is slightly incorrect, but until additional concepts were developed, a better definition needed to wait. Now we can redefine an acid: an **acid** is any compound that increases the amount of hydrogen ion (H^+) in an aqueous solution. The chemical opposite of an acid is a base. The equivalent definition of a base is that a **base** is a compound that increases the amount of hydroxide ion (OH^-) in an aqueous solution. These original definitions were proposed by Arrhenius (the same person who proposed ion dissociation) in 1884, so they are referred to as the **Arrhenius definition** of an acid and a base, respectively.

You may recognize that, based on the description of a hydrogen atom, an H^+ ion is a hydrogen atom that has lost its lone electron; that is, H^+ is simply a proton. Do we really have bare protons moving about in aqueous solution? No. What is more likely is that the H^+ ion has attached itself to one (or more) water molecule(s). To represent this chemically, we define the **hydronium ion** as H_3O^+, which represents an additional proton attached to a water molecule. We use the hydronium ion as the more logical way that a hydrogen ion appears in an aqueous solution, although in many chemical reactions H^+ and H_3O^+ are treated equivalently.

The reaction of an acid and a base is called a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base cancel each other's chemistry to produce a rather innocuous substance—water. In fact, the general reaction between an acid and a base is:

$$\textbf{acid} + \textbf{base} \longrightarrow \textbf{water} + \textbf{salt}$$

where the term **salt** is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is

$$\mathrm{HCl\,(aq) + KOH\,(aq) \longrightarrow H_2O(\ell) + KCl\,(aq)}$$

where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between HCl(aq) and $Mg(OH)_2$(aq), additional molecules of HCl and H_2O are required to balance the chemical equation:

$$\mathrm{2\,HCl\,(aq) + Mg(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + MgCl_2\,(aq)}$$

Here, the salt is $MgCl_2$. (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)

Example 5.11.1:

Write the neutralization reactions between each acid and base.

a. HNO_3(aq) and $Ba(OH)_2$(aq)
b. H_3PO_4(aq) and $Ca(OH)_2$(aq)

Solution

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

a. The expected products are water and barium nitrate, so the initial chemical reaction is

$$\mathrm{HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow H_2O(\ell) + Ba(NO_3)_2\,(aq)}$$

To balance the equation, we need to realize that there will be two H_2O molecules, so two HNO_3 molecules are required:

$$\mathrm{2\,HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + Ba(NO_3)_2\,(aq)}$$

This chemical equation is now balanced.

b. The expected products are water and calcium phosphate, so the initial chemical equation is

$$H_3PO_4(aq) + Ca(OH)_2(aq) \longrightarrow H_2O(\ell) + Ca_3(PO_4)_2(s)$$

According to the solubility rules, $Ca_3(PO_4)_2$ is insoluble, so it has an (s) phase label. To balance this equation, we need two phosphate ions and three calcium ions. We end up with six water molecules to balance the equation:

$$2\,H_3PO_4(aq) + 3\,Ca(OH)_2(aq) \longrightarrow 6\,H_2O(\ell) + Ca_3(PO_4)_2(s)$$

This chemical equation is now balanced.

Exercise 5.11.1

Write the neutralization reaction between $H_2SO_4(aq)$ and $Sr(OH)_2(aq)$.

Answer

$$H_2SO_4(aq) + Sr(OH)_2(aq) \longrightarrow 2\,H_2O(\ell) + SrSO_4(aq)$$

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between HCl(aq) and $Fe(OH)_3(s)$ still proceeds according to the equation:

$$3\,HCl(aq) + Fe(OH)_3(s) \longrightarrow 3\,H_2O(\ell) + FeCl_3(aq)$$

even though $Fe(OH)_3$ is not soluble. When one realizes that $Fe(OH)_3(s)$ is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!)

Complete and net ionic reactions for neutralization reactions will depend on whether the reactants and products are soluble, even if the acid and base react. For example, in the reaction of HCl(aq) and NaOH(aq),

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

the complete ionic reaction is

$$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(\ell) + Na^+(aq) + Cl^-(aq)$$

The extra water molecule needs to be added to balance the hydronium ion on the reactant side of the equation. The $Na^+(aq)$ and $Cl^-(aq)$ ions are spectator ions, so we can remove them to have

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(\ell)$$

as the net ionic equation.

However, for the reaction between HCl(aq) and $Cr(OH)_2(s)$, because chromium(II) hydroxide is insoluble, we cannot separate it into ions for the complete ionic equation:

$$2\,H_3O^+(aq) + 2\,Cl^-(aq) + Cr(OH)_2(s) \longrightarrow 4\,H_2O(\ell) + Cr^{2+}(aq) + 2\,Cl^-(aq)$$

The chloride ions are the only spectator ions here, so the net ionic equation is

$$2\,H_3O^+(aq) + Cr(OH)_2(s) \longrightarrow 4\,H_2O(\ell) + Cr^{2+}(aq)$$

Example 5.11.2

Oxalic acid, $H_2C_2O_4(s)$, and $Ca(OH)_2(s)$ react very slowly. What is the net ionic equation between these two substances if the salt formed is insoluble? (The anion in oxalic acid is the oxalate ion, $C_2O_4^{2-}$.)

Solution

The products of the neutralization reaction will be water and calcium oxalate:

$H_2C_2O_4(s) + Ca(OH)_2(s) \rightarrow 2H_2O(\ell) + CaC_2O_4(s)$

Because nothing is dissolved, there are no substances to separate into ions, so the net ionic equation is the equation of the three solids and one liquid.

Exercise 5.11.2

What is the net ionic equation between $HNO_3(aq)$ and $Ti(OH)_4(s)$?

Answer

$4H_3O^+(aq) + Ti(OH)_4(s) \rightarrow 8H_2O(\ell) + Ti^{4+}(aq)$

Key Takeaways

- The Arrhenius definition of an acid is a substance that increases the amount of H^+ in an aqueous solution.
- The Arrhenius definition of a base is a substance that increases the amount of OH^- in an aqueous solution.
- Neutralization is the reaction of an acid and a base, which forms water and a salt.
- Net ionic equations for neutralization reactions may include solid acids, solid bases, solid salts, and water.

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CHAPTER OVERVIEW

6: Redox Reactions

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6.2: Oxidation Numbers
6.3: Half-Reactions and Balancing Redox Equations
6.4: The Activity Series
6.5: Batteries
6.6: Redox Reactions in Organic Chemistry and Biochemistry

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6.1: Oxidation and Reduction

"Redox" is short for "oxidation and reduction", two complimentary types of chemical reactions. The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion. **Reduction** originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.

These two terms have broader meanings now. In all oxidation-reduction reactions an exchange of electrons occurs - one substance loses electrons while something else gains them. That is the key to understanding redox reactions. We'll define these terms below.



Figure **6.1.1:** *Reaction of copper wire in a silver nitrate solution.*

A simple demonstration of a redox reaction involves placing a solid piece of copper wire in a silver nitrate solution. Within minutes the wire begins to look fuzzy or furry, as small silver crystals begin to form on the wire. Meanwhile, the originally clear silver nitrate solution begins to take on a pale bluish tint. Furthermore, if the crystals are shaken off of the wire we see that the wire partially disintegrated.

The overall equation for our demonstration describes the events:

$$\mathrm{Cu\,(s) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,Ag\,(s)} \tag{6.1.1}$$

Remember that when we have aqueous solutions of ionic compounds, the ions are really present as separate ions, not as bonded particles. So we can write an expanded equation:

$$\mathrm{Cu\,(s) + 2\,Ag^+\,(aq) + 2\,NO_3^-\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2\,NO_3^-\,(aq) + 2\,Ag\,(s)} \tag{6.1.2}$$

Finally we remove spectator ions from the equation. Remember that spectator ions are ions that undergo no change during a reaction. Notice the nitrate ions, NO_3^- – they start as aqueous ions and end up exactly the same.

Removing the spectator ions gives us our **net ionic equation:**

$$\mathrm{Cu\,(s) + 2\,Ag^+\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2\,Ag\,(s)} \tag{6.1.3}$$

We can now see a bit more clearly what changes are occurring with this reaction.

Oxidation of Copper Metal to Make Copper Ions

Copper began as a neutral atom with no charge, but changed into an ion with a charge of +2. An atom becomes a positive ion by losing electrons:

$$\mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq) + 2\,e^-} \tag{6.1.4}$$

Notice that copper began as a solid but is converted into aqueous ions - this is why the copper wire disintegrates. We say that copper was **oxidized** because is has lost electrons (i.e., electrons appear on the product side of the Equation 6.1.4).

Reduction of Silver Ions to Make Silver Metal

Silver was converted from an ion with a charge of +1, Ag+, to a neutral atom, Ag. The only way an ion can undergo this change is to gain an electron:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \quad (6.1.5)$$

Notice that solid silver is formed - this is what causes the fuzzy appearance to begin appearing on the wire - solid silver crystals. Silver has gained electrons - it has been reduced (i.e., electrons appear on the reactant side of Equation 6.1.5).

The electrons that silver gained had to come from somewhere - they came from copper. Conversely, a substance such as copper can only lose electrons if there is something else that will take them up, the silver ions. **One cannot occur without the other**. This exchange of electrons is what defines an **oxidation - reduction reaction**.

Definition: Oxidation

oxidation is the **loss** of electrons.

Definition: Reduction

Reduction the **gain** of electrons

You will be learning several new terms in this unit and it is important that you learn them very quickly. You may find it useful to have some tricks to help you remember these terms including the LEO/GER.

LEO the Lion Says GER

- LEO: Loss of Electrons is Oxidation
- GER: Gain of Electrons is Reduction



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6.2: Oxidation Numbers

Redox reactions are all about electrons being transferred from one substance to another, so it would be useful if we had a system for keeping track of what gains and what loses electrons, and how many electrons are involved. We do - our record-keeping system is called **Oxidation Numbers.** You may remember from earlier chemistry classes something called **electronegativity.**

Electronegativity

The ability of a bonded atom to attract shared electrons towards itself

When two atoms of different elements are bonded together by a covalent bond (sharing electrons), the electrons are generally not shared equally between the two atoms due to differences in their electronegativity. Think of this as a tug-of-war for electrons. Sometimes both atoms pull with equal strength on shared electrons; other times there is a clearly stronger player who will pull the electrons closer to itself.

Consider the bond between a hydrogen atom (with one valence electron) and an oxygen atom (with its six valence electrons):



Because oxygen has a higher electronegativity than hydrogen, the shared electrons are closer to the oxygen atom than to the hydrogen atom. This is not the total transfer of electrons that would create an ion, but partial charges do form - the hydrogen end of the bond is partially positive (+1) because it has partially lost one electron, and the oxygen end of the H–O is partially negative (-1) because it has partially gained the one electron from hydrogen:



Our molecule is incomplete however, because there is a lone electron around oxygen. Let's add one more hydrogen to complete our water molecule:



We see that each of the two hydrogen has "lost" one electron to oxygen. Oxygen has "gained" two electrons - one from each hydrogen. Again, these are not true ions but it is useful to think of them in the same way.

Charges given to atoms in a molecule in this way are called **oxidation numbers**. We can use oxidation numbers to keep track of where electrons are in a molecule, and how they move during a reaction. In our water example, hydrogen is assigned an oxidation number of +1 because each individual hydrogen has "lost" one electron. Oxygen has an oxidation number of +2 because the single oxygen atom has "gained" a total of two electrons, one from each hydrogen.

Here is another molecule involving hydrogen and oxygen - hydrogen peroxide, H_2O_2:



In hydrogen peroxide, each hydrogen still has an oxidation number of +1 because each hydrogen "gives up" a single electron to oxygen. Oxygen, however, now has an oxidation number of -1 because each oxygen gains just one electron from its neighboring hydrogen. The electrons between the two identical oxygen atoms are shared equally, so there is no partial charge resulting from that bond.

Oxidation Numbers

A positive or negative number assigned to an atom in a molecule or ion that reflects a partial gain or loss of electrons

Knowing the oxidation number of each individual element in a molecule will be a key step in our understanding of redox reactions. Fortunately it will not usually involve drawing electron dot

diagrams. Instead there are a series of rules that we can use to determine oxidation numbers. Here are the main rules:

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

2. The oxidation number of a monatomic ion (by itself or as part of an ionic compound) is equal to its charge.
Alkali metals - elements in the first column of the periodic table - will always have an oxidation number of +1; Alkali metals (column 2) are almost always +2

Ionic Compound	Ions	Charge
NaCl	Na^+	+1
	Cl^-	-1
Mg_3N_2	Mg^{+2}	+2
	N^{-3}	-3

3. The oxidation number of hydrogen is almost always +1 when it is in a compound.

Compound	element	O: N
HCl	H	
	Cl	
H_2S	H	
	S	

4. The oxidation number of oxygen is almost always -2 when it is in a compound
The exceptions:
- peroxides, such as hydrogen peroxide. In peroxides oxygen has an oxidation number of -1.
- when oxygen is combined with fluorine it's oxidation number is +2

Compound	element	O: N
MgO magnesium oxide	Mg	
	O	
Na_2O sodium oxide	Na	
	O	
Na_2O_2 sodium peroxide	Na	
	O	

5. The sum of the oxidation numbers in a compound is zero.
To determine the oxidation number of Mn in Mn_2O_7 we must work backwards:
- We know each oxygen is -2 (Rule 4)
- 7 oxygen gives a total of:

-2 × 7 atoms = -14 total

Since the sum of oxidation numbers must be zero, the total oxidation number of Mn must be +14 to cancel out oxygen's -14, but since there are 2 Mn atoms, each **individual atom** will have an oxidation number of +7:

$$\frac{+14 \text{ total}}{2 \text{ Mn atoms}} = +7$$

Compound	element	Oxidation Number	Number atoms
Mg_3N_2	Mg	+2	3
	N	-3	2
			SUM
Mn_2O_7	Mn	+7	2
	O	-2	7
			SUM
Cl_2O_3	Cl	+3	2
	O	-2	3
			SUM

6. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on that ion.
Again, work backwards to determine the oxidation number of any non-oxygen or non-hydrogen atom.
To determine the oxidation number of Cr in $Cr_2O_7^{2-}$:
- Oxygen will be -2 (Rule 4), for a total of:

Compound	element	Oxidation Number	Number atoms
NO_3^-	N	+5	1

-2 × 7 = -14

- Since the sum of the oxidation numbers will be -2 (the charge on the entire ion), the total for all Cr must be +12 because:

+12 + (-14) = -2

- Since there is are two Cr, each Cr will have an oxidation number of +6

= +7

$$\frac{+12}{2} = +6$$

	O	-2	3	
			SUM	
$Cr_2O_7^{2-}$	Cr	+6	2	
	O	-2	7	
			SUM	
SO_4^{2-}	S	+6	1	
	O	-2	4	
			SUM	

It is important to note that oxidation number always refers to ***each individual atom*** in the compound, not to the total for that element.

For example in H_2O - the total positive "charge" for both hydrogen atoms will be +2 (which balances with the -2 from oxygen), but EACH HYDROGEN has an oxidation number of +1.

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6.3: Half-Reactions and Balancing Redox Equations

Balancing Redox Equations using Half-reactions

Another way to balance redox reactions is by the half-reaction method. This technique involves breaking an equation into its two separate components - the oxidation reaction and the reduction reaction. Since neither oxidation nor reduction can actually occur without the other, we refer to the separate equations as **half-reactions**.

The general technique involves the following:

- The overall equation is broken down into **two** half-reactions. If there are any spectator ions, they are removed from the equations.
- Each half-reaction is balanced separately - first for atoms and then for charge. Electrons are added to one side of the equation or the other in order to balance charge. For example, if the reactant side of the equation has a total charge of +3, the product side must also equal +3.
- Next the two equations are compared to make sure electrons lost equal electrons gained. One of the half reactions will be an oxidation reaction, the other will be a reduction reaction.
- Finally the two half-reactions are added together, and any spectator ions that were removed are placed back into the equation

Consider the following reaction:

$$Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)} \tag{6.3.1}$$

In this reaction, Mg is oxidized and Cl is reduced. You may find it useful to use oxidation numbers to help you determine this. Mg changes from 0 to +2; Cl changes from 0 to -1.

When we write the half-reactions,we break apart compounds that contain either of the key elements (elements undergoing oxidation or reduction). Oxidation numbers are written as if they were ion charges. Notice that the chlorine from $MgCl_2$ is written as two separate ions, not combined as is Cl_2. Balance the two reactions for atoms.

$Mg \rightarrow Mg^{+2}$	$Cl_2 \rightarrow 2\ Cl^-$

Next balance the equations for charge by adding electrons. Remember - one half-reaction will be an oxidation reaction (electrons on the product side) and the other will be reduction (electrons will be on the reactant side)

$Mg \rightarrow Mg^{+2} + 2\ e^-$	$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$
oxidation	**reduction**

In this example, balancing for charge results in both sides, of both equations, having net charges of 0. That won't always be the case. Be sure you see in this example how charges are balanced.

We then compare the two equations for numbers of electrons. We see that both equations have 2 electrons so we do not need to make any adjustments for that. Finally, add the two equations together:

$$Mg + Cl_2 \rightarrow Mg^{+2} + 2Cl^- \tag{6.3.2}$$

and reform any compounds broken apart in the earlier steps:

$$Mg + Cl_2 \rightarrow MgCl_2 \tag{6.3.3}$$

We see that the original equation was already balanced, not just for atoms but for electrons as well.

Example 2

$$Cu_{(s)} + AgNO_{3(aq)} \rightarrow Cu(NO_3)2(aq) + Ag_{(s)} \tag{6.3.4}$$

Solution

Identify the elements undergoing oxidation (Cu) and reduction (Ag). The nitrate group (NO_3) is a spectator ion which we will not include in our half-reactions.

$Cu \rightarrow Cu^{+2} + 2\ e^-$	$Ag^+ + 1\ e^- \rightarrow Ag$
oxidation	**reduction**

After balancing for atoms and for charge, we see that the two equations do not have the same number of electrons - there are 2 in the copper reaction but only one in the silver reaction. Multiply everything in the silver reaction by 2, then we will add the equations together:

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions	**Balance electrons**	**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2\ e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2\ e^-}$
$Ag + 1\ e^- \rightarrow Ag^-$	$\times 2$	$2\ Ag^+ + \cancel{2e^-} \rightarrow 2\ Ag$
Add equations together		$Cu + 2\ Ag^+ \rightarrow Cu^{+2} + 2\ Ag$
Reform compound/return spectator ions		$\mathbf{Cu + 2\ AgNO_3 \rightarrow Cu(NO_3)_2 + 2\ Ag}$

Here is a reaction occurring in an acid solution, which accounts for the presence of the H^+ions. This example adds a little more complexity to our problem.

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

In this example, spectator ions have already been removed. Even though hydrogen and oxygen do not undergo changes in oxidation number they are not spectators and we need to work with them in our half-reactions.

We determine that Mn undergoes reduction (+7 to +2) while Fe undergoes oxidation (+2 to +3). The iron half-reaction is straight forward, but the manganese reaction is more complex - we must include hydrogen and oxygen in its half-reaction:

$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$
oxidation	**reduction**

To balance the manganese half-reaction - first balance for Mn and O atoms. Next balance the H atoms, and finally add enough electrons to balance the charge on both sides of the equation. Be sure you see what has been done so you can do it on your own.

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions		**Add half-reactions**
$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	× 5	$5Fe^{2+} \rightarrow 5Fe^{+3} + \cancel{5e^-}$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		$MnO_4^- + 8\ H^+ + \cancel{5e^-} \rightarrow Mn^{2+} + 4\ H_2O$
Add equations together		**$MnO_4^- + 5\ Fe^{2+} + 8\ H^+ \rightarrow Mn^{2+} + 5\ Fe^{3+} + 4H_2O$**

Example 3

$$HNO_3 + Cu + H^+ \rightarrow NO_2 + Cu^{2+} + H_2O \tag{6.3.5}$$

Solution

1. Determine what is oxidized, what is reduced, and write the two **balanced** half-reactions (Step 1)
2. Balance for electrons lost = electrons gained (Step 2)
3. Add equations together

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions		**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2e^-}$
$HNO_3 + H^+ + 1\ e^- \rightarrow NO_2 + H_2O$	× 2	$2HNO_3 + 2H^+ + \cancel{2e^-} \rightarrow 2NO_2 + 2H_2O$
Add equations together		**$2HNO_3 + Cu + 2H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O$**

When balancing redox reactions, either the oxidation number method or the half-reaction method may be used. Often you'll find that one method works best for some equations, while the other method is more suited for other reactions. Or you may find one method just easier to use. The practice exercises and assignments tell you which method to use for a reaction, but as you get get more experience you'll be able to make your own decision as to which method to use.

Writing half-reactions, however, is a skill you will need for our final topic in this course - Electrochemistry - so be sure you can write balanced half-reactions.

Check your understanding with the practice questions, set 3 , then complete Assignment 2 .

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6.4: The Activity Series

Learning Objectives

- Use the activity series to predict if a reaction will occur.

We see below two metals that can be exposed to water. The picture on the left is of sodium, which gives a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels.



Figure 6.4.1: On the left, sodium reacts with water. On the right, silver in the form of cups do not react with water.

The Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivities. The **activity series** is a list of elements in decreasing order of their reactivity. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The table below is an activity series of most common metals and of the halogens.

Table 6.4.1: Activity Series of Metals in Aqueous Solutions

most active (easily oxidized – readily lose electrons))		
lithium	Li	These metals displace hydrogen from water $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_2 + H_{2\ (g)}$ These elements are very reactive and react readily to form compounds
potassium	K	
barium	Ba	
calcium	Ca	
sodium	Na	
magnesium	Mg	These metals displace hydrogen from acids $Zn_{(s)} + HCl_{(aq)} \rightarrow ZnCl_2 + H_{2(g)}$
aluminum	A	
zinc	Zn	
chromium	Cr	
iron	Fe	
cadmium	Cd	
nickel	Ni	
tin	Sn	
lead	Pb	
hydrogen	H	
copper	Cu	These metals do not displace hydrogen from acids or water These elements are more stable, and form compounds less readily than do those higher in the table.
silver	Ag	
mercury	Hg	
platinum	Pt	
gold	Au	
least active		

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron (III) nitrate and one of lead (II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$\mathrm{Ni}\,(s) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow \mathrm{Ni(NO_3)_2}\,(aq) + \mathrm{Pb}\,(s) \tag{6.4.1}$$

$$\mathrm{Ni}\,(s) + \mathrm{Fe(NO_3)_3}\,(aq) \rightarrow \mathrm{NR\ (no\ reaction)} \tag{6.4.2}$$

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and with acids, since that requires a lower degree of reactivity.

Steps for Problem Solving	**Example 6.4.1** Use the activity series to predict if the reaction below will occur. If not, write **NR**. If the reaction does occur, write the products of the reaction and balance the equation. $\mathbf{Al\,(s) + Zn(NO_3)_2\,(aq) \rightarrow}$	**Example 6.4.2** Use the activity series to predict if the reaction below will occur. If not, write **NR**. If the reaction does occur, write the products of the reaction and balance the equation. $\mathbf{Ag\,(s) + HCl\,(aq) \rightarrow}$
Plan the problem.	Compare the placements of aluminum (the element doing the replacing) and zinc (the element being replaced) on the activity series.	Compare the placements of silver (the element doing the replacing) and hydrogen (the element being replaced) on the activity series.
Solve	Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a $+3$ charge in an ionic compound, so the formula for aluminum nitrate is $\mathbf{Al(NO_3)_3}$. The balanced equation is: $$\mathbf{2Al\,(s) + 3Zn(NO_3)_2\,(aq) \rightarrow 2Al(NO_3)_3\,(aq) + 3Zn\,(s)} \quad (6.4.3)$$	Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid. $$\mathbf{Ag\,(s) + HCl\,(aq) \rightarrow NR} \quad (6.4.4)$$

Exercise 6.4.1

Use the activity series to predict if the following reactions will occur. If not, write **NR**. If the reaction does occur, write the products of the reaction and balance the equation.

a. Would it be possible to store a silver spoon in a zinc nitrate solution? That is, will the following reaction occur:

$$\Ag_{(s)} + Zn(NO_3)_{2\,(aq)} \rightarrow$$

b. Would it be possible to store a silver nitrate solution in a copper container? That is, will the following reaction occur:

$$\[Cu_{(s)} + AgNO_{3\,(aq)} \rightarrow$$

Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the series.

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6.5: Batteries

Learning Objectives

- Identify the substance being oxidized and the substance being reduced in an oxidation-reduction reaction.
- Identify the anode and the cathode given a diagram of an electrolysis apparatus that includes the compound being electrolyzed.
- Describe how batteries can produce electrical energy.

Electricity is an important form of energy that you use every day. It runs your calculators, cell phones, dishwashers, and watches. This form of energy involves moving electrons through a wire and using the energy of these electrons. Electrochemical cells used for power generation are called batteries. Although batteries come in many different shapes and sizes there are a few basic types. You won't be required to remember details of the batteries, but some general information and features of each type is presented here. Batteries are one way of producing this type of energy. Many important chemical reactions involve the exchange of one or more electrons, and, therefore we can use this movement of electrons as electricity. These reactions are called oxidation-reduction (or "redox") reactions.

Oxidation and Reduction

Reactions in which electrons are transferred are called oxidation-reduction (or "redox") reactions. There are two parts to these changes: one atom must lose electrons and another atom must gain them. These two parts are described by the terms "oxidation" and "reduction".

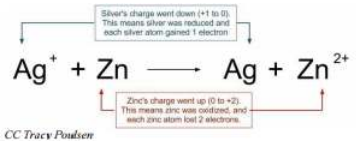
Originally, a substance was said to be oxidized when it reacted with oxygen. Today, the word "oxidized" is still used for those situations, but now we have a much broader second meaning for these words. Today, the broader sense of the word **oxidation** is defined as losing electrons. When a substance loses electrons, its charge will increase. This may feel a bit backwards, but remember that electrons are negative. If an atom loses electrons, it is losing negative particles so its charge will increase.

The other half of this process, the gaining of electrons, also needs a name. When an atom or an ion gains electrons, the charge on the particle goes down. For example, if a sulfur atom whose charge is zero (0) gains two electrons, its charge becomes (-2) and if an $\mathrm{Fe^{3+}}$ ion gains an electron, its charge changes from $+3$ to $+2$. In both cases the charge on the particle is reduced by the gain of electrons. Remember that electrons have a negative charge, so gaining electrons will result in the charge decreasing. The word **reduction** is defined to mean gaining electrons and the reduction of charge.

In chemical systems, these two processes (oxidation and reduction) must occur simultaneously and the number of electrons lost in the oxidation must be the same as the number of electrons gained in the reduction. In oxidation-reduction reactions, electrons are transferred from one substance to another. Here's an example of an oxidation-reduction reaction.

$$\mathrm{2Ag^{+}\,(\mathit{aq})+Cu\,(\mathit{s})\rightarrow 2Ag\,(\mathit{s})+Cu^{2+}\,(\mathit{aq})} \tag{6.5.1}$$

In this reaction, the silver ions are gaining electrons to become silver atoms. Therefore, the silver ions are being reduced and the charge of silver is decreasing. The copper atoms are losing electrons to become copper $+2$ ions and are therefore, being oxidized and the charge of copper is increasing. Whenever a chemical reaction involves electrons being transferred from one substance to another, the reaction is an **oxidation-reduction reaction** (or a redox reaction).



Half-equations are very helpful in discussing and analyzing processes but half-reactions cannot occur as they appear. The half-reactions for the reaction above would be:

$$\mathrm{2Ag^{+}\,(\mathit{aq})+2e^{-}\rightarrow 2Ag\,(\mathit{s})} \tag{6.5.2}$$

$$\mathrm{Cu\,(\mathit{s})\rightarrow Cu^{2+}\,(\mathit{aq})+2e^{-}} \tag{6.5.3}$$

Both oxidation and reduction must occur at the same time so the electrons are donated and absorbed nearly simultaneously. The two half-reactions may be added together to represent a complete reaction. In order to add the half-reactions, the number of electrons donated and the number of electrons accepted must be equal.

Example 9.3.1

For each reaction, identify what is oxidized and what is reduced.

a) $\mathbf{Zn + HCl \rightarrow H_2 + ZnCl_2}$

b) $\mathbf{Fe + O_2 \rightarrow Fe_2O_3}$

c) $\mathbf{NaBr + I_2 \rightarrow NaI + Br_2}$

Solution

In order to determine what is being oxidized and reduced, we must look at charges of atoms and see if they increase or decrease. (Remember, elements have no charge. In a compound, we can use our periodic table and what we learned in Chapter 4 to assign charges.) If the charge increases, the atom was oxidized. If the charge decreases, the atom was reduced.

a) This reaction written with charges is:

$$\mathbf{Zn^0 + H^+Cl^- \rightarrow H_2{}^0 + Zn^{2+}Cl_2{}^-} \tag{6.5.4}$$

Zn is oxidized because it went from **0** to **+2**. **H** is reduced because it went from **+1** to **0**. **Cl** was neither oxidized nor reduced.

b) This reaction written with charges is:

$$\mathbf{Fe^0 + O_2{}^0 \rightarrow Fe_2{}^{3+}O_3{}^{2-}} \tag{6.5.5}$$

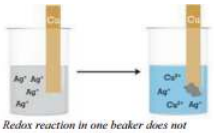
Fe is oxidized because it went from **0** to **+3**. **O** is reduced because it went from **0** to **−2**.

c) This reaction written with charges is:

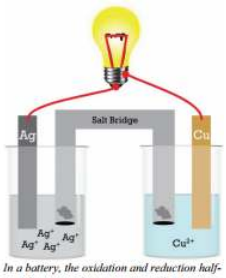
$$\mathbf{Na^+Br^- + I_2{}^0 \rightarrow Na^+I^- + Br_2{}^0} \tag{6.5.6}$$

Br is oxidized because it went from **−2** to **0**. **I** is reduced because it went from **0** to **−1**. **Na** was neither oxidized nor reduced as it stayed **+1** the whole time.

Batteries


Redox reaction in one beaker does not produce electricity. (Source: Richard Parsons. CC-BY-SA)

Batteries are devices that use chemical reactions to produce electrical energy. These reactions occur because the produces contain less potential energy in their bonds than the reactants. The energy produced from excess potential energy not only allows the reaction to occur but also often gives off energy to the surroundings. Some of these reactions can be physically arranged so the energy given off is given off in the form of an electric current. These are the type of reactions that occur inside batteries. When a reaction is arranged to produce an electric current as it runs, the arrangement is called an **electrochemical cell** or a **Galvanic Cell.**



In a battery, the oxidation and reduction half-reactions occur in separate containers, allowing the electrons to flow through a wire producing electricity.

If a strip of copper is placed in a solution of silver nitrate, the following reaction takes place:

$$\mathbf{2Ag^+ (aq) + Cu (s) \rightarrow 2Ag (s) + Cu^{2+} (aq)} \tag{6.5.7}$$

In this reaction, copper atoms are donating electrons to silver ions so the silver ions are reduced to silver atoms and copper atoms are oxidized to copper (II) ions.

As the reaction occurs, an observer would see the solution slowly turn blue ($\mathbf{Cu^{2+}}$ ions are blue in solution) and a mass of solid silver atoms would build up on the copper strip.

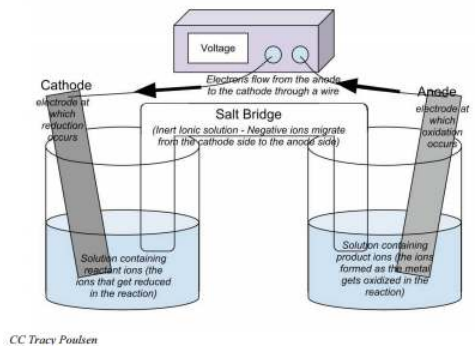
The reaction we just described is not set up in such a way as to produce electricity. It is true that electrons are being transferred, but to produce electricity we need electrons flowing through a wire so we can use the energy of these electrons. This reactions, $\mathbf{2Ag^+ (aq) + Cu (s) \rightarrow 2Ag (s) + Cu^{2+} (aq)}$, is one that could be arranged to produce electricity. To do this, the two half-reactions (oxidation and reduction) must occur in separate compartments and the separate compartments must remain in contact through an ionic solution and an external wire.

In this electrochemical cell, the copper metal must be separated from the silver ions to avoid a direct reaction. Each electrode in its solution could be represented by a half-reaction.

$$\mathrm{Cu \rightarrow Cu^{2+} + 2e^-} \tag{6.5.8}$$

$$\mathrm{2Ag^+ + 2e^- \rightarrow 2Ag} \tag{6.5.9}$$

The wire connects the two halves of the reaction, allowing electrons to flow from one metal strip to the other. In this particular example, electrons will flow from the copper electrode (which is losing electrons) into the silver electrode (which is where the silver ions gain the electrons). The cell produce electricity through the wire and will continue to do so as long as there are sufficient reactants ($\mathrm{Ag^+}$ and Cu) to continue the reaction.



Electrochemical cells will always have two electrodes, the pieces of metal where electrons are gained or lost. (In this example, the strip of Ag metal and Cu metal are the electrodes.) The electrode where reduction occurs and electrons are gained is called the **cathode**. The electrode where oxidation occurs and electrons are lost is called the **anode**. Electrons will always move from the anode to the cathode. The electrons that pass through the external circuit can do useful work such as lighting lights, running cell phones, and so forth.

If the light bulb is removed from the circuit with the electrochemical cell and replaced with a voltmeter, the voltmeter will measure the voltage (electrical potential energy per unit charge) of the combination of half-cells. The size of the voltage produced by a cell depends on the temperature, the metals used for electrodes, and the concentrations of the ions in the solutions. If you increase the concentration of the reactant ion (not the produce ion), the reaction rate will increase and so will the voltage.

It may seem complicated to construct an electrochemical cell because of all their complexities. Electrochemical cells are actually easy to make and sometimes even occur accidentally. If you take two coins of different denomination and push them part way through the peel of a whole lemon and then connect the two coins with a wire, a small electric current will flow.

1. Primary batteries - (dry cell batteries)

- non-rechargeable
- electrolytes are present as a paste rather than as a liquid
- general purpose battery used for flashlights, transistor radios, toys, etc.
- The basic dry cell battery consists of: zinc case as the anode (oxidation); a graphite rod is the cathode (reduction) surrounded by a moist past of either MnO_2, NH_4Cl, and $ZnCl_2$ or in alkaline dry cells a KOH electrolytic paste.
- General reactions for the battery - manganese(IV) oxide-zinc cell (different batteries have different reactions - you don't need to remember any of these reactions)

cathode	$2MnO_{2(s)} + 2\ NH_4^+{}_{(aq)} + 2e^- \rightarrow Mn_2O_{3\ (s)} + H_2O_{(l)} + 2NH_{3\ (aq)}$
anode	$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$

- - Maximum voltage 1.5V. By connecting several cells in series 90V can be achieved.
  - Advantages of alkaline batteries - consistent voltage, increased capacity, longer shelf-life, and reliable operation at temperatures as low as -40°C
  - Disadvantage - higher cost

2. Secondary Batteries (storage batteries)

- rechargeable
- an example - lead-acid battery used in cars. Anode is grid of lead-antimony or lead-calcium alloy packed with spongy lead; Cathode is lead(IV) oxide. Electrolyte is aqueous sulfuric acid. Consists of numerous small cells connected in parallel (anode to anode; cathode to cathode).
- General reaction:

cathode	$PbO_{2(s)} + 4H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4\,(s)} + 2H_2O_{(l)} + 2NH_{3\,(aq)}$
anode	$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4\,(s)} + 2e^-$

- - Secondary batteries are recharged by passing a current through the battery in the opposite direction. In a car battery this occurs when the engine is running.
  - Other examples include the nickel-iron alkaline battery, nickel-zinc batter, nickel-cadmium alkaline battery, silver-zinc, silver-cadmium

3. Fuel Cells

- fuel cells are electrochemical cells that convert energy of a redox combustion reaction directly into electrical energy. Requires a continuous supply of reactants and a constant removal of products.
- Cathode reactant usually air or pure oxygen; anode fuel is a gas such as hydrogen, methane, or propane. Carbon electrodes typically contain a catalyst. The electrolyte is typically KOH.
- General reaction:

cathode	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$
anode	$2H_{2\,(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
net	$2H_{2\,(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

- - Advantages - no toxic waste products (water is the only product); very efficient energy conversion (70-80% efficient)
  - Disadvantage - too expensive for large-scale use.

Summary

- Reactions in which there is a transfer of electrons is said to be an oxidation-reduction reaction or a redox reaction.
- A substance that loses electrons is said to be oxidized, and the substance that gains electrons is said to be reduced.
- Redox reactions can be used in electrochemical cells to produce electricity.
- Electrochemical cells are composed of an anode and cathode in two separate solutions. These solutions are connected by a salt bridge and a conductive wire.
- An electric current consists of a flow of charged particles.
- The electrode where oxidation occurs is called the anode and the electrode where reduction occurs is called the cathode.

Vocabulary

- Electrochemical cell: An arrangement of electrodes and ionic solutions in which a redox reaction is used to make electricity (a.k.a., a battery)
- Electrolysis: A chemical reaction brought about by an electric current.
- Electroplating: A process in which electrolysis is used as a means of coating an object with a layer of metal.

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6.6: Redox Reactions in Organic Chemistry and Biochemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure **6.6.1**: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. from Wikipedia.

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure **6.6.1**).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{6.6.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($\mathrm{C_6H_{12}O_6}$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{6.6.2}$$

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\mathrm{K_2Cr_2O_7}$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal *carbonyl group* (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol ($\mathrm{CH_3CH_2OH}$) in a person's breath:

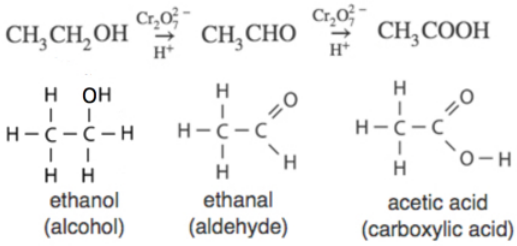
$$\mathrm{3\,CH_3CH_2OH + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O} \tag{6.6.3}$$

If the product acetaldehyde ($\mathrm{CH_3CHO}$) is not removed as it forms, it is further oxidized to acetic acid ($\mathrm{CH_3COOH}$). In this case, the overall reaction is as follows:

$$\mathrm{3\,CH_3CH_2OH + 2\,Cr_2O_7^{2-} + 16\,H^+ \rightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11\,H_2O} \tag{6.6.4}$$

In this reaction, the chromium atom is reduced because it lost oxygen atoms from $Cr_2O_7^{2-}$ to Cr^{3+}. On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol (CH_3CH_2OH, a.k.a. ethanol) to form acetaldehayde (CH_3CHO, a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.



When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol ($\mathbf{CH_3CHOHCH_3}$). It is the common solvent acetone [$\mathbf{(CH_3)_2CO}$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$\mathbf{3\,CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,(CH_3)_2CO + 2\,Cr^{3+} + 7\,H_2O} \tag{6.6.5}$$

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($\mathbf{CH_3COCOOH}$) is reduced to lactic acid ($\mathbf{CH_3CHOHCOOH}$) in the muscles.

$$\mathbf{CH_3COCOOH \rightarrow CH_3CHOHCOOH} \tag{6.6.6}$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $\mathbf{C_6H_8O_6}$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($\mathbf{C_6H_6O_6}$). In the stomach, ascorbic acid reduces the nitrite ion ($\mathbf{NO_2^-}$) to nitric oxide ($\mathbf{NO}$):

$$\mathbf{C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO} \tag{6.6.7}$$

> *If reaction in Equation 6.6.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure **6.6.2**).



Figure **6.6.2**: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($\mathbf{C_6H_{12}O_6}$). The synthesis

of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure **6.6.3**). The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{6.6.8}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure **6.6.3**: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

Concept Review Exercise

1. Give some biochemical examples of oxidation and reduction reactions.

Answer

1. photosynthesis and antioxidants in foods (answers will vary)

Exercises

1. A typical respiratory reaction discussed in the text is the oxidation of glucose ($C_6H_{12}O_6$):

   $$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

   Is this a redox reaction? If so, what are the oxidizing and reducing agents?

2. The major net reaction in photosynthesis is as follows:

   $$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

   Is this a redox reaction? If so, what are the oxidizing and reducing agents?

3. What would be the ultimate organic product if $CH_3CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?
4. What would be the ultimate organic product if $CH_3CH_2CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?
5. What would be the final organic product if $CH_3CH_2CHOHCH_3$ were to react with a solution of $K_2Cr_2O_7$?
6. What would be the major organic product if $CH_3CH_2CHOHCH_2CH_3$ were to react with a solution of $K_2Cr_2O_7$?
7. What alcohol is produced in the reduction of acetone [$(CH_3)_2CO$]?
8. What alcohol is produced in the reduction of propanal (CH_3CH_2CHO)?

Answers

1. yes; oxidizing agent: O_2; reducing agent: $C_6H_{12}O_6$
2. yes; oxidizing agent: CO_2; reducing agent: H_2O

3. CH_3CH_2COOH
4. $CH_3CH_2CH_2COOH$
5. $CH_3CH_2C(O)CH_3$, where the carbon is double bonded to the oxygen
6. $CH_3CH_2C(O)CH_2CH_3$, carbon #3 is double bonded to the oxygen
7. $CH_3CHOHCH_3$, or isopropyl alcohol
8. $CH_3CH_2CH_2OH$

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CHAPTER OVERVIEW

7: Nuclear Chemistry

7.1: Nuclear Reactions
7.2: Stable and Unstable Isotopes
7.3: Spontaneous Nuclear Decay
7.4: Ionizing Radiation
7.5: Nuclear Fission and Nuclear Fusion
7.6: Half-Life and Nuclear Decay Kinetics
7.7: Radiation Units

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7.1: Nuclear Reactions

Learning Objectives

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Identify a nuclear reaction
- Identify the key characteristics separating nuclear and chemical reactions

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:

$$ {}^{A}_{Z}\mathrm{X} \tag{7.1.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

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." The element in this example, represented by the symbol *C*, is carbon. Its atomic number, 6, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 14, which means that the number of neutrons in the atom is 14 − 6 = 8 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen, $^{2}\mathrm{H}$ and $^{3}\mathrm{H}$, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Nuclear reactions are very different from chemical reactions. In chemical reactions, atoms become more stable by participating in a transfer of electrons or by sharing electrons with other atoms. In nuclear reactions, it is the nucleus of the atom that gains stability by undergoing a change of some kind. The energies that are released in nuclear reactions are many orders of magnitude greater than the energies involved in chemical reactions. Unlike chemical reactions, nuclear reactions are not noticeably affected by changes in environmental conditions, such as temperature or pressure.

As the following Sections will discuss, there are three main forms of radioactive emissions. The first is called an alpha particle,which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use ${}^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a **nuclear equation**—for example, the alpha-particle emission of uranium-235 is as follows:

$$ {}^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{7.1.2}$$

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example, ${}^{235}_{92}\mathrm{U}$ is the parent isotope, and ${}^{231}_{90}\mathrm{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Major Differences between Nuclear and Chemical Reactions

1. Nuclear reactions involve a change in an atom's nucleus, usually producing a different element. Chemical reactions, on the other hand, involve only a rearrangement of electrons and do not involve changes in the nuclei.
2. Different isotopes of an element normally behave similarly in chemical reactions. The nuclear chemistry of different isotopes vary greatly from each other.
3. Rates of chemical reactions are influenced by temperature and catalysts. Rates of nuclear reactions are unaffected by such factors.
4. Nuclear reactions are independent of the chemical form of the element.
5. Energy changes accompanying nuclear reactions are much larger. This energy comes from destruction of mass.
6. In a nuclear reaction, mass is not strictly conserved. Some of the mass is converted into energy.

Contributors and Attributions

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7.2: Stable and Unstable Isotopes

Learning Objectives

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or decay, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

Each element can be represented by the notation ${}^{A}_{Z}\mathrm{X}$, where A, the mass number, is the sum of the number of protons and the number of neutrons, and Z, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called **nucleons**, and an atom with a particular number of protons and neutrons is called a **nuclide**. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

${}^{A}_{Z}\mathrm{X}$	${}^{16}_{8}\mathrm{O}$	${}^{17}_{8}\mathrm{O}$	${}^{18}_{8}\mathrm{O}$
${}^{A}\mathrm{X}$	${}^{16}\mathrm{O}$	${}^{17}\mathrm{O}$	${}^{18}\mathrm{O}$
element-A:	oxygen-16	oxygen-17	oxygen-18

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17. Any nucleus that is unstable and decays spontaneously is said to be **radioactive**, emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called **radioisotopes**.

Nuclear Stability

The nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the **strong nuclear force**, an extremely powerful but very short-range attractive force between nucleons (Figure **7.2.1**). All stable nuclei except the hydrogen-1 nucleus (${}^{1}\mathrm{H}$) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

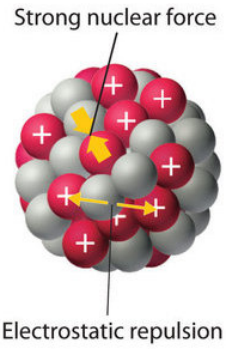


Figure 7.2.1: Competing Interactions within the Atomic Nucleus. Electrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 7.2.2. The stable isotopes form a "peninsula of stability" in a "sea of instability." Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., $^{4}_{2}He$, $^{10}_{5}B$, and $^{40}_{20}Ca$). All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with Z > 83 are unstable and radioactive.

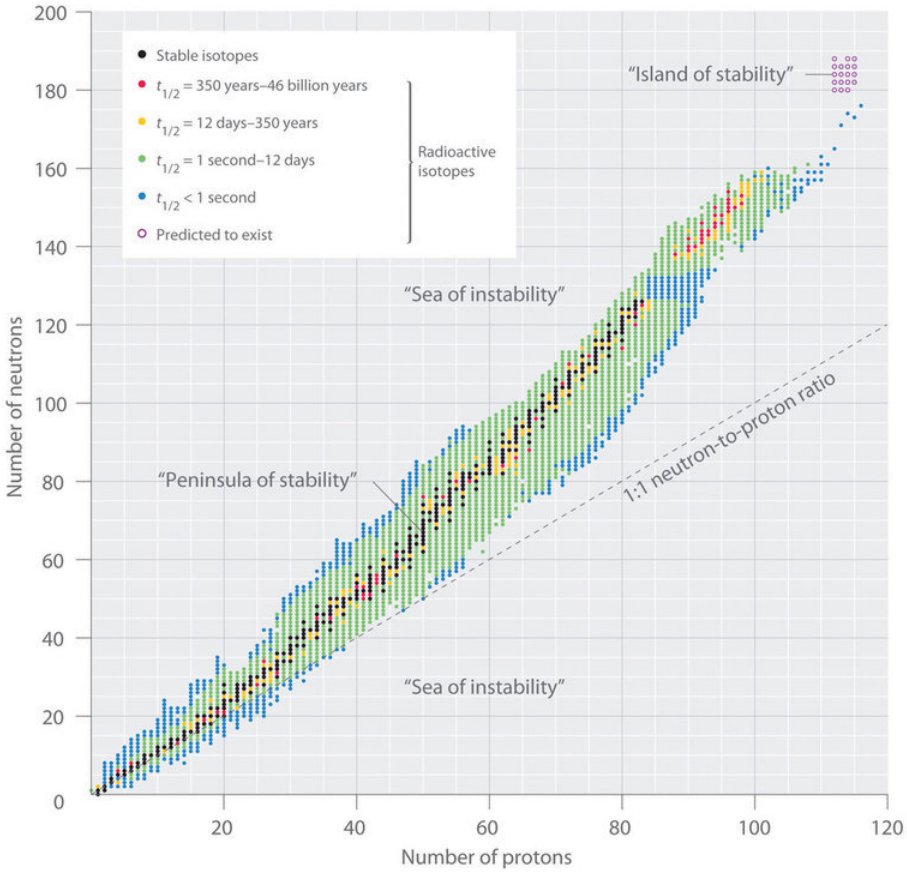


Figure **7.2.2**: The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio. In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized. Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

As shown in Figure **7.2.3**, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be "doubly magic" and are even more stable. Examples of elements with doubly magic nuclei are $^{4}_{2}\mathrm{He}$, with 2 protons and 2 neutrons, and $^{208}_{82}\mathrm{Pb}$, with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

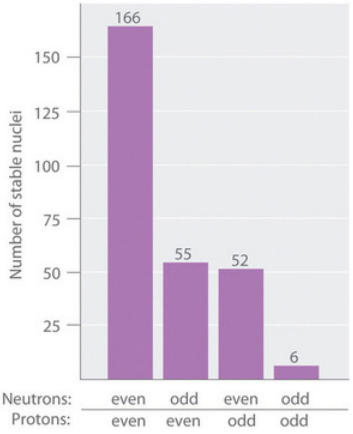


Figure **7.2.3**: The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability.

> *Most stable nuclei contain **even** numbers of both neutrons and protons*

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure **7.2.2**, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Origin of the Magic Numbers

Multiple models have been formulated to explain the origin of the magic numbers and two popular ones are the Nuclear Shell Model and the Liquid Drop Model. Unfortuneatly, both require advanced quantum mechanics to fully understand and are beyond the scope of this text.

Example 7.2.1

Classify each nuclide as stable or radioactive.

a. $^{30}_{15}\mathrm{P}$
b. $^{98}_{43}\mathrm{Tc}$
c. tin-118
d. $^{239}_{94}\mathrm{Pu}$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

a. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 7.2.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}\mathrm{P}$ is predicted to be radioactive, and it is.

b. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}\mathrm{Tc}$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are

unstable. These facts suggest that $^{98}_{43}\text{Tc}$ might be stable. However, $^{98}_{43}\text{Tc}$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}\text{Tc}$ is predicted to be radioactive, and it is.

c. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an even number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}\text{Sn}$should be particularly stable.

d. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}\text{Pu}$ must be radioactive.

Exercise 7.2.1

Classify each nuclide as stable or radioactive.

a. $^{232}_{90}\text{Th}$
b. $^{40}_{20}\text{Ca}$
c. $^{15}_{8}\text{O}$
d. $^{139}_{57}\text{La}$

Answer a

radioactive

Answer b

stable

Answer c

radioactive

Answer d

stable

Superheavy Elements

In addition to the “peninsula of stability” there is a small “island of stability” that is predicted to exist in the upper right corner. This island corresponds to the **superheavy elements**, with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with Z = 114 and Z = 116 have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an “eternity” by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with A = 292 that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with Z = 122. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

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7.3: Spontaneous Nuclear Decay

Learning Objectives

- Write and balance nuclear equations
- To know the different kinds of radioactive decay.
- To balance a nuclear reaction.

Unstable nuclei spontaneously emit radiation in the form of particles and energy. This generally changes the number of protons and/or neutrons in the nucleus, resulting in a more stable nuclide. One type of a nuclear reaction is **radioactive decay**, *a reaction in which a nucleus spontaneously disintegrates into a slightly lighter nucleus, accompanied by the emission of particles, energy, or both*. An example is shown below, in which the nucleus of a polonium atom radioactively decays into a lead nucleus.

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{7.3.1}$$

Note that in a balanced nuclear equation, the sum of the atomic numbers (subscripts) and the sum of the mass numbers (superscripts) must be equal on both sides of the equation. How do we know that a product of the reaction is $^{231}_{90}\mathrm{Th}$? We use a modified type of the **law of conservation of matter**, which says that we must have the same number of protons and neutrons on both sides of the chemical equation. If our uranium nucleus loses 2 protons from the alpha particle, then there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom—in this case, $^{231}_{90}\mathrm{Th}$.

Because the number of protons changes as a result of this nuclear reaction, the identity of the element changes. **Transmutation** *is a change in the identity of a nucleus as a result of a change in the number of protons*. There are several different types of naturally occurring radioactive decay, and we will examine each separately.

Alpha Decay

An **alpha particle** (α) *is a helium nucleus with two protons and two neutrons.* Alpha particles are emitted during some types of radioactive decay. The net charge of an alpha particle is $2+$, and its mass is approximately $4\ \mathrm{amu}$. The symbol for an alpha particle in a nuclear equation is usually $^{4}_{2}\mathrm{He}$, though sometimes α is used. Alpha decay typically occurs for very heavy nuclei in which the nuclei are unstable due to large numbers of nucleons. For nuclei that undergo alpha decay, their stability is increased by the subtraction of two protons and two neutrons. For example, uranium-238 decays into thorium-234 by the emission of an alpha particle (see figure below).

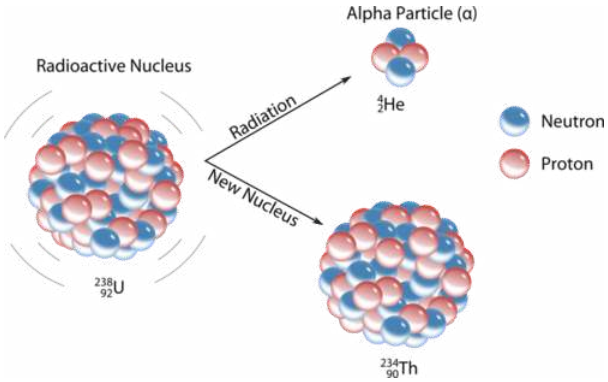


Figure **7.3.3**: The unstable uranium-238 nucleus spontaneously decays into a thorium-234 nucleus by emitting an alpha particle.

Example 7.3.1: Radon-222

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\text{Rn}$. We represent the alpha particle as $^{4}_{2}\text{He}$ and use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\text{Po}$:

$$^{222}_{86}\text{Rn} \rightarrow \ ^{4}_{2}\text{He} + \ ^{218}_{84}\text{Po}$$

Exercise 7.3.1: Polonium-209

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

Answer

$$^{209}_{84}\text{Po} \rightarrow \ ^{4}_{2}\text{He} + \ ^{205}_{82}\text{Pb}$$

Beta Decay

Nuclei above the band of stability are unstable because their neutron to proton ratio is too high. To decrease that ratio, a neutron in the nucleus is capable of turning into a proton and an electron. The electron is immediately ejected at a high speed from the nucleus. A **beta particle** (β) *is a high-speed electron emitted from the nucleus of an atom during some kinds of radioactive decay* (see figure below). The symbol for a beta particle in an equation is either β or $^{0}_{-1}\text{e}$. Carbon-14 undergoes beta decay, transmutating into a nitrogen-14 nucleus.

$$^{14}_{6}\text{C} \rightarrow \ ^{14}_{7}\text{N} + \ ^{0}_{-1}\text{e} \tag{7.3.2}$$

Note that beta decay increases the atomic number by one, but the mass number remains the same.

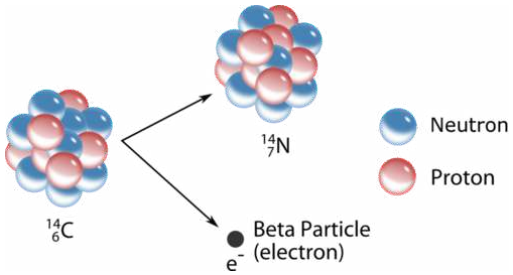


Figure 7.3.4: The beta decay of a carbon-14 nuclide involves the conversion of a neutron to a proton and an electron, with the electron being emitted from the nucleus.

Example 7.3.2: Boron-12

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{12}_{5}\text{B}$ while one of the products is an electron, $^{0}_{-1}\text{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$$^{12}_{5}\text{B} \rightarrow \ ^{12}_{6}\text{C} + \ ^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is $^{12}_{6}\text{C}$.

Exercise 7.3.2: Iodine-131

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$$^{131}_{53}\text{I} \rightarrow {}^{131}_{54}\text{Xe} + {}^{0}_{-1}\text{e} + \gamma$$

Positron Emission

Nuclei below the band of stability are unstable because their neutron to proton ratio is too low. One way to increase that ratio is for a proton in the nucleus to turn into a neutron and another particle called a positron. A **positron** *is a particle with the same mass as an electron, but with a positive charge*. Like the beta particle, a positron is immediately ejected from the nucleus upon its formation. The symbol for a positron in an equation is $^{0}_{+1}\text{e}$. For example, potassium-38 emits a positron, becoming argon-38.

$$^{38}_{19}\text{K} \rightarrow {}^{38}_{18}\text{Ar} + {}^{0}_{1}\text{e} \tag{7.3.3}$$

Positron emission decreases the atomic number by one, but the mass number remains the same.

Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called electron capture. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$^{106}_{47}\text{Ag} + {}^{0}_{-1}\text{e} \rightarrow {}^{106}_{46}\text{Pd} \tag{7.3.4}$$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the mass number remains the same.

Gamma Ray Emission

Gamma rays (γ) *are very high energy electromagnetic waves emitted from a nucleus.* Gamma rays are emitted by a nucleus when nuclear particles undergo transitions between nuclear energy levels. This is analogous to the electromagnetic radiation emitted when excited electrons drop from higher to lower energy levels; the only difference is that nuclear transitions release much more energetic radiation. Gamma ray emission often accompanies the decay of a nuclide by other means.

$$^{230}_{90}\text{Th} \rightarrow {}^{226}_{88}\text{Ra} + {}^{4}_{2}\text{He} + \gamma \tag{7.3.5}$$

The emission of gamma radiation has no effect on the atomic number or mass number of the products, but it reduces their energy.

Summary of Nuclear Radiation

The table below summarizes the main types of nuclear radiation, including charge, mass, symbol, and penetrating power. Penetrating power refers to the relative ability of the radiation to pass through common materials. Radiation with high penetrating power is potentially more dangerous because it can pass through skin and do cellular damage.

Table **7.3.1** *Summary of types of nuclear radiation.*

Type	Symbol	Mass number	Charge	Penetration Power	Shielding
Alpha particle	$^{4}_{2}\text{He}$ or α	4	2+	Low	Paper, skin
Beta particle	$^{0}_{-1}\text{e}$ or β	0	1−	Moderate	Heavy cloth, plastic
Positron	$^{0}_{1}\text{e}$ or β^{+}	0	1+	Moderate	Heavy cloth, plastic
Gamma ray	γ or $^{0}_{0}\gamma$	0	0	High	Lead, concrete
Neutron	$^{1}_{0}\text{n}$	1	0	High	Water, lead

Example 7.3.3

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of $^{35}_{16}\text{S}$
b. the decay of $^{201}_{80}\text{Hg}$ by electron capture

c. the decay of $^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as $^{A}_{Z}\mathrm{X}$:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta$$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta$$

b.

A We know the identities of both reactants: $^{201}_{80}\mathrm{Hg}$ and an inner electron, $^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X}$$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta$$

Exercise 7.3.3

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\mathrm{W}$

Answer a

$$^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$$

Answer d

$$^{99}_{42}\mathrm{Mo} \rightarrow {}^{99m}_{43}\mathrm{Tc} + {}^{0}_{-1}\beta$$

Answer c

$^{185}_{74}\mathrm{W} \rightarrow {}^{181}_{72}\mathrm{Hf} + {}^{4}_{2}\alpha + {}^{0}_{0}\gamma$

Example 7.3.4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.
c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 7.3.4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer a

beta decay

Answer d

positron emission or electron capture

Answer c

alpha decay

Contributors and Attributions

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7.4: Ionizing Radiation

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle can act as a powerful oxidant.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{7.4.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 7.4.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1\ \text{MeV/particle} = 96\ \text{billion J/mol.} \tag{7.4.2}$$



Figure 7.4.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue.

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table **7.4.1**.

Table **7.4.1**: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m

*Distance at which half of the radiation has been absorbed.

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure. Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{7.4.3}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays.

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation.

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7.5: Nuclear Fission and Nuclear Fusion

Learning Objectives

- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions

Nuclear fusion and **nuclear fission** are two different types of energy-releasing reactions in which energy is released from high-powered atomic bonds between the particles within the nucleus. The main difference between these two processes is that fission is the splitting of an atom into two or more smaller ones while fusion is the fusing of two or more smaller atoms into a larger one.

Protons and neutrons make up a nucleus, which is the foundation of nuclear science. Fission and fusion involves the dispersal and combination of elemental nucleus and isotopes, and part of nuclear science is to understand the process behind this phenomenon. Adding up the individual masses of each of these subatomic particles of any given element will always give you a greater mass than the mass of the nucleus as a whole. The missing idea in this observation is the concept called nuclear binding energy. **Nuclear binding energy** is the energy required to keep the protons and neutrons of a nucleus intact, and the energy that is released during a nuclear fission or fusion is nuclear power. There are some things to consider however. The mass of an element's nucleus as a whole is less than the total mass of its individual protons and neutrons.

To calculate the energy released during mass destruction in both nuclear fission and fusion, we use Einstein's equation that equates energy and mass:

$$E = mc^2 \tag{7.5.1}$$

with m is mass (kilograms), c is speed of light (meters/sec) and E is energy (Joules).

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. 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 **7.5.2**.

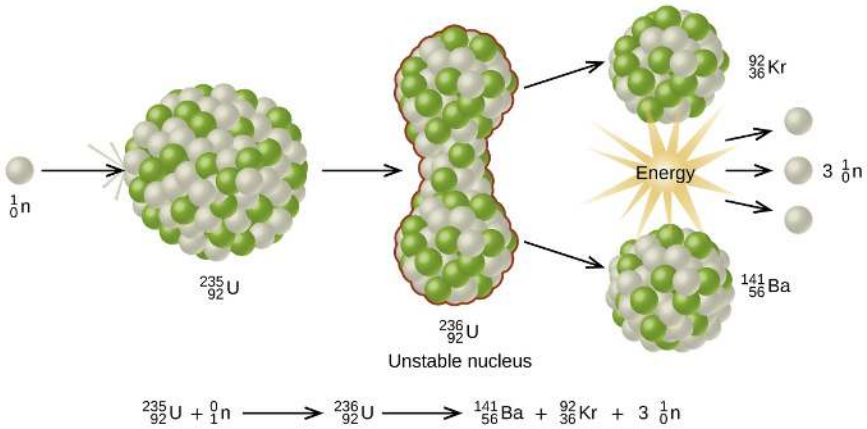


Figure **7.5.2**: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

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 **7.5.3**. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

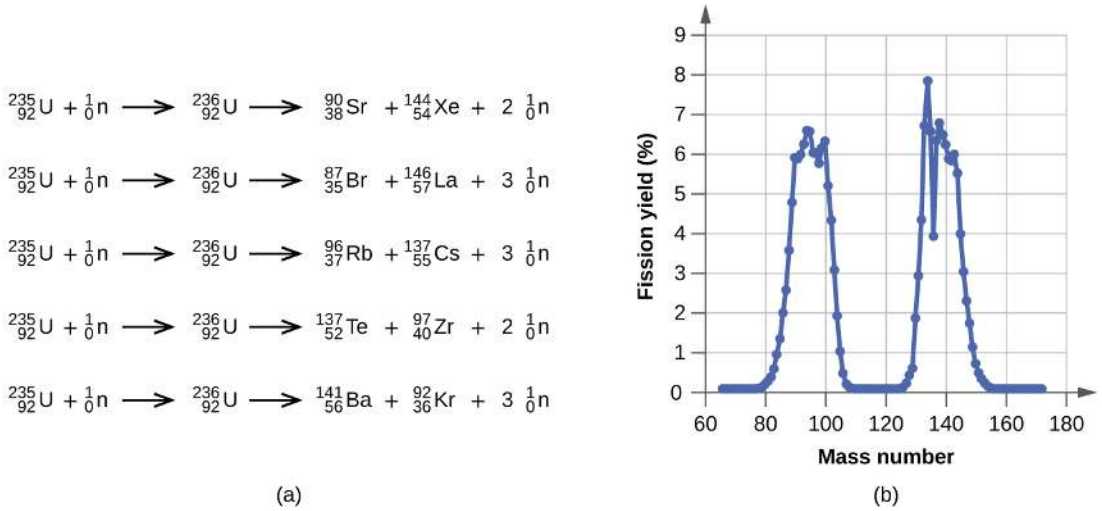


Figure **7.5.3**: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

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 (Figure **7.5.4**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

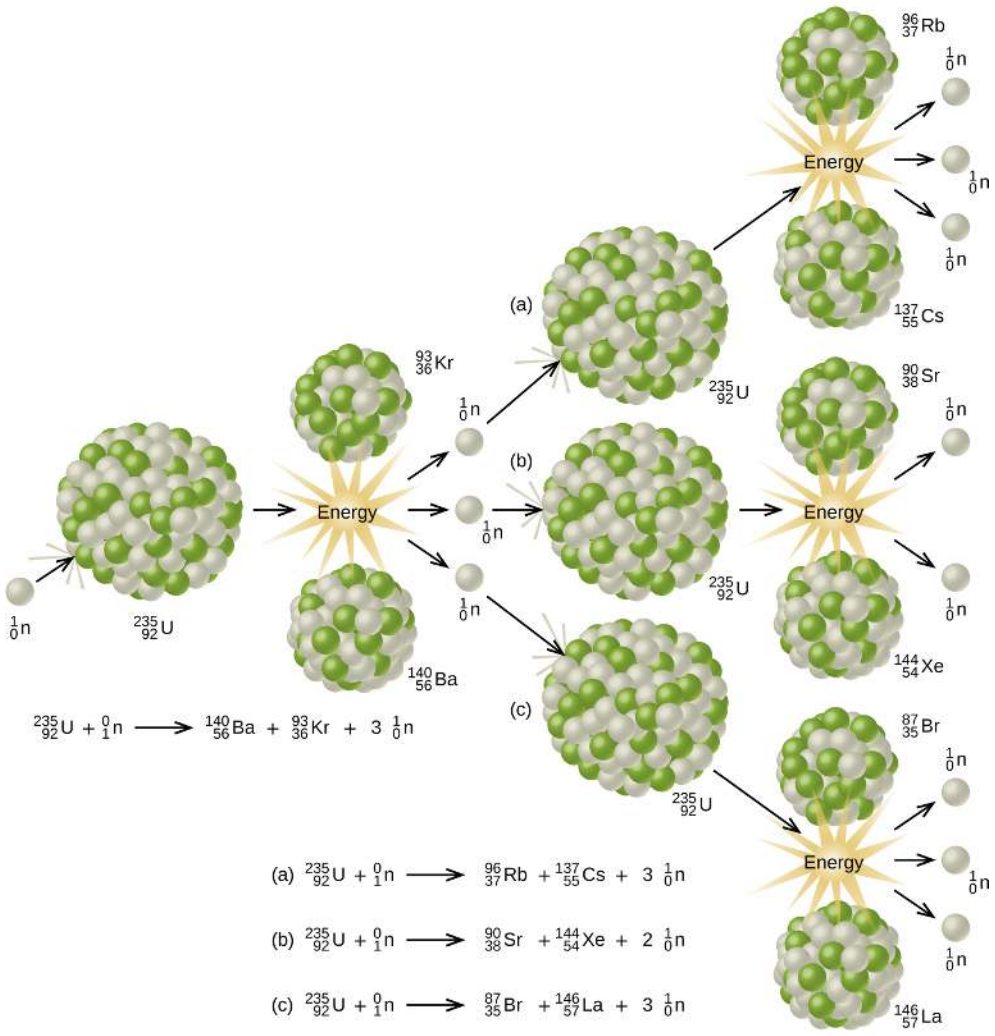


Figure **7.5.4**: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

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 **7.5.5**).

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.

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.

Nuclear Fusion

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:

$$4{}_1^1\mathrm{H} \longrightarrow {}_2^4\mathrm{He} + 2{}_{+1}^0 \tag{7.5.2}$$

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 ${}_2^4\mathrm{He}$ 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, ${}_1^2$ and a triton, ${}_1^3$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}_1^2\mathrm{H} + {}_1^3\mathrm{H} \longrightarrow {}_2^4\mathrm{He} + 2{}_0^1\mathrm{n} \tag{7.5.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^9 kilojoules per mole of ${}_2^4\mathrm{He}$ 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.

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7.6: Half-Life and Nuclear Decay Kinetics

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Describe common radiometric carbon-14 dating technique.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life**. which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

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 **7.6.1**). In a given cobalt-60 source, since half of the $^{60}_{27}\mathrm{Co}$ 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.) Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

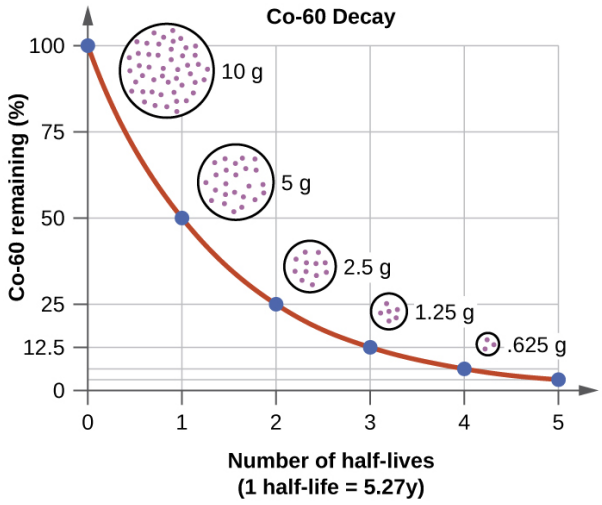


Figure **7.6.1**: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on. (CC BY 4.0; OpenStax)

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\textbf{amount remaining} = \textbf{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{7.6.1}$$

where n is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 7.6.1: Fluorine-20

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, $n = 4$. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\,g \times \left(\frac{1}{2}\right)^4 \\ &= 5.00\,g \times \left(\frac{1}{16}\right) \\ &= 0.313\,g\end{aligned}$$

Less than one-third of a gram of fluorine-20 remains.

Exercise 7.6.1: Titanium-44

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer

0.0375 g

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table **7.6.1** - Half-Lives of Various Isotopes, lists the half-lives of some isotopes.

Table **7.6.1** Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^{8} y
^{238}U	4.47×10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Chemistry Is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

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. 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 $^{14}_{6}\text{CO}_2$ to $^{12}_{6}\text{CO}_2$ depends on the ratio of $^{14}_{6}\text{CO}$ to $^{12}_{6}\text{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\text{CO}$ 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 $^{14}_{6}\text{C}$ $^{14}_{6}\text{CO}_2$ and $^{12}_{6}\text{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio found in a living plant is the same as the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\text{C}$ 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:

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

Thus, the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ 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 **7.6.2** visually depicts this process.

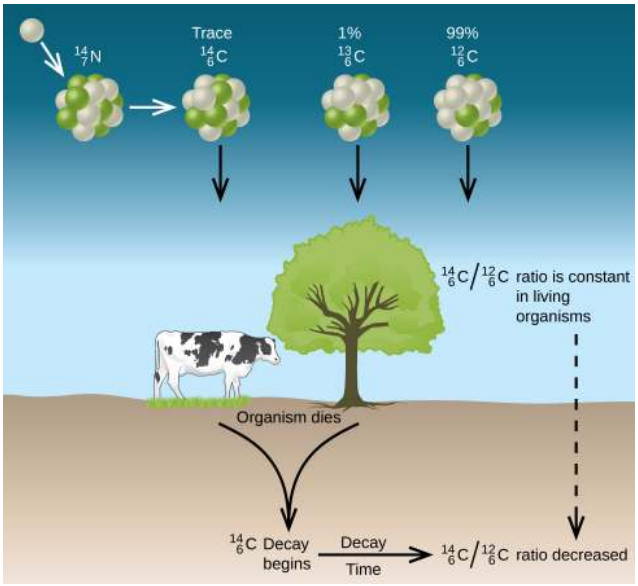


Figure **7.6.2**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC BY 4.0; OpenStax)

For example, with the half-life of $^{14}_{6}\text{C}$ being 5730 years, if the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ 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 $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

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7.7: Radiation Units

Learning Objectives

- Define units for measuring radiation exposure

We previously used mass to indicate the amount of radioactive substance present. However, this is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation. A variety of units are used to measure various aspects of radiation (Table **7.7.1**).

Table **7.7.1**: 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

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 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:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{7.7.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

The becquerel Unit

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one **becquerel (Bq).** Even in a small mass of radioactive material, however, there are thousands upon thousands of decays or disintegrations per second. The becquerel is named after Henri Becquerel, who discovered radioactivity in 1896.

The curie Unit

The **curie** (Ci) is one measure of the rate of decay (named after Pierre and Marie Curie). One curie is equivalent to 3.7×10^{10} disintegrations per second. Since this is obviously a large and unwieldy number, radiation is often expressed in millicuries or microcuries (still very large numbers). The curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena in the early 1900s. The curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 μCi.

The roentgen Unit

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation

needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air.

The rad Unit

The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\,rad = 0.010\,J/kg \quad 1\,Gy = 1\,J/kg \tag{7.7.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

The gray Unit

Another unit of radiation absorption is the **gray (Gy)**:

1 Gy = 100 rad

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

The rem Unit

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in man)** was devised to describe the actual amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor:

$$em = rad \times RBE \tag{7.7.3}$$

where RBE is the *relative biological effectiveness factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, RBE factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem.

The sievert Unit

A sievert (Sv) is related to the rem unit and is defined as 100 rem. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table **7.7.2**. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table **7.7.2**: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Which of the two is applicable to humans?

According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

Summary

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 = $\mathbf{3.7 \times 10^{10}}$ 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.

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CHAPTER OVERVIEW

8: Saturated Hydrocarbons

8.1: Introduction to Hydrocarbons
8.2: Linear Alkanes
8.3: Isomerism in Alkanes
8.4: Condensed Structural and Line-Angle Formulas
8.5: IUPAC Nomenclature
8.6: Physical Properties of Alkanes
8.7: Chemical Properties of Alkanes
8.8: Halogenated Hydrocarbons
8.9: Cycloalkanes

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8.1: Introduction to Hydrocarbons

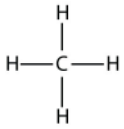
Learning Objectives

- To get an overview of hydrocarbons molecules and their four primary classifications

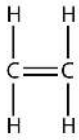
Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

The classifications for hydrocarbons, defined by IUPAC nomenclature of organic chemistry are as follows:

1. Saturated hydrocarbons (alkanes) are the simplest of the hydrocarbon species. They are composed entirely of single bonds and are saturated with hydrogen. The general formula for saturated hydrocarbons is C_nH_{2n+2} (assuming non-cyclic structures). Saturated hydrocarbons are the basis of petroleum fuels and are found as either linear or branched species.The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:



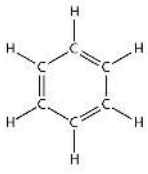
2. Unsaturated hydrocarbons have one or more double or triple bonds between carbon atoms. Those with double bond are called alkenes and those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures). Those containing triple bonds are called alkynes, with general formula C_nH_{2n-2}. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:



The smallest alkyne is ethyne, which is also known as acetylene:



3. Cycloalkanes are hydrocarbons containing one or more carbon rings to which hydrogen atoms are attached. The general formula for a saturated hydrocarbon containing one ring is C_nH_{2n}.
4. Aromatic hydrocarbons, also known as arenes, are hydrocarbons that have at least one aromatic ring. Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



Because of differences in molecular structure, the empirical formula remains different between hydrocarbons; in linear, or "straight-run" alkanes, alkenes and alkynes, the amount of bonded hydrogen lessens in alkenes and alkynes due to the "self-bonding" or catenation of carbon preventing entire saturation of the hydrocarbon by the formation of double or triple bonds.

The inherent ability of hydrocarbons to bond to themselves is known as catenation, and allows hydrocarbon to form more complex molecules, such as cyclohexane, and in rarer cases, arenes such as benzene. This ability comes from the fact that the bond character between carbon atoms is entirely non-polar, in that the distribution of electrons between the two elements is somewhat even due to the same electronegativity values of the elements (~0.30).

Contributors and Attributions

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8.2: Linear Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure **8.2.1**.

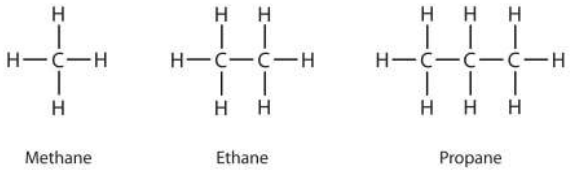


Figure **8.2.1**: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure **8.2.2**).

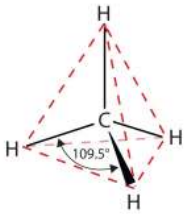


Figure **8.2.2**: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table **8.2.1**.

Table **8.2.1**: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure **8.2.3**. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

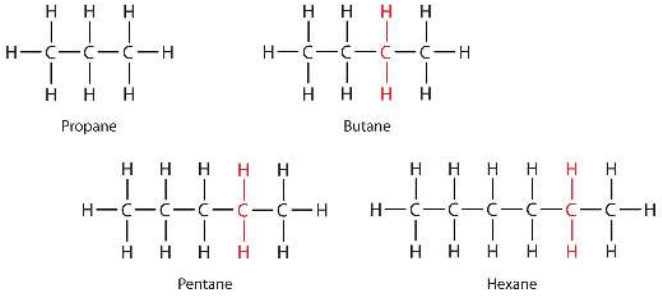


Figure **8.2.3**: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2\times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

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8.3: Isomerism in Alkanes

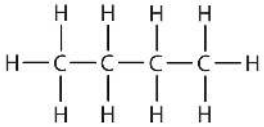
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

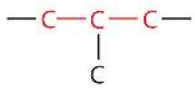
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

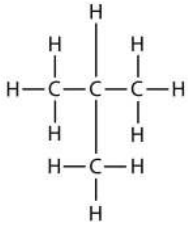


Figure **8.3.1**).

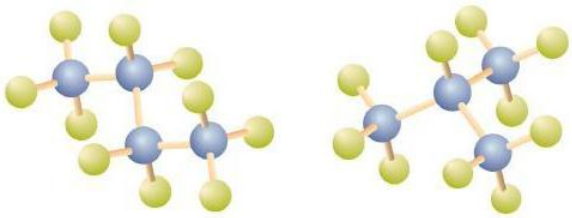
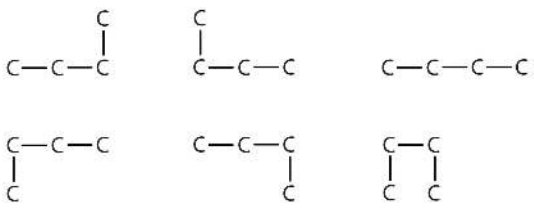


Figure **8.3.1**: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

Notice that C_4H_{10} is depicted with a bent chain in Figure **8.3.1**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:

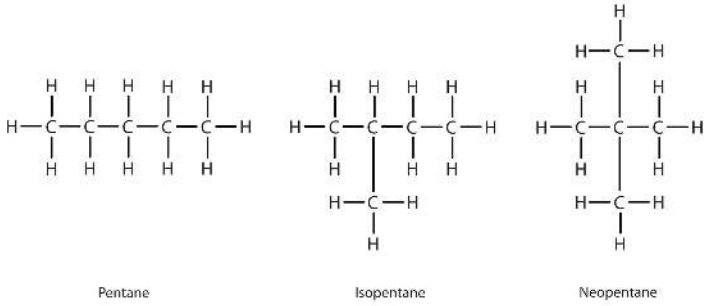


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The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure **8.3.1**.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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8.4: Condensed Structural and Line-Angle Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Pentane Isopentane

Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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8.5: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

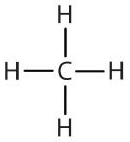
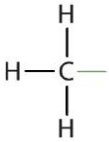
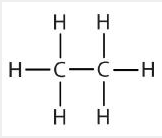
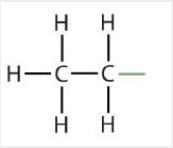
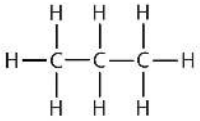
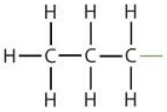
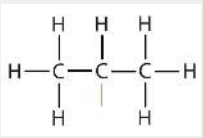
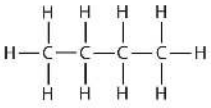
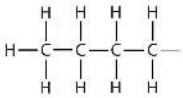
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table 8.5.1) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table 8.5.1: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the $-CH_3$ group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table 8.5.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 8.5.2: Common Alkyl Groups

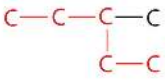
Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		$CH_3–$
ethane		ethyl		$CH_3CH_2–$
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl*		$CH_3CH_2CH_2CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example **8.5.1**).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.

2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

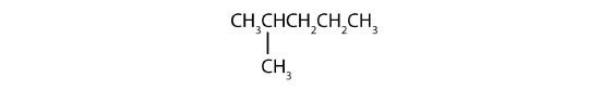
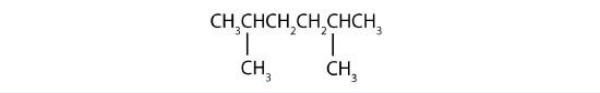
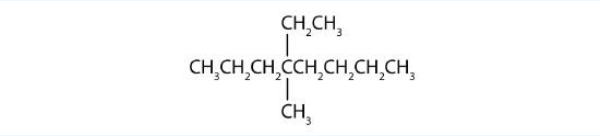


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 8.5.1

Name each compound.

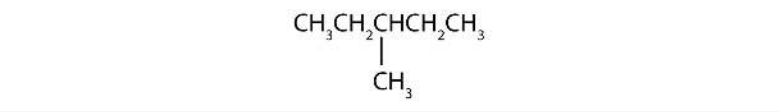
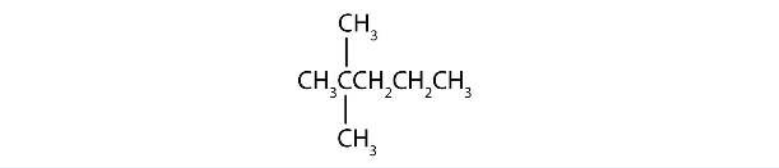
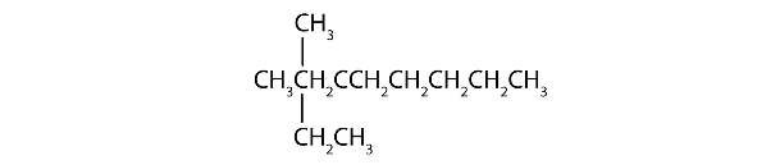
1. 
2. 
3. 

Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

Exercise 8.5.1

Name each compound.

1. 
2. 
3. 

Example 8.5.2

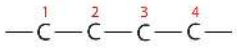
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-isopropyl-2-methylheptane

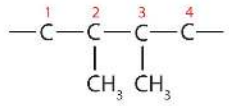
Solution

In drawing structures, always start with the parent chain.

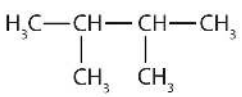
a. The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.

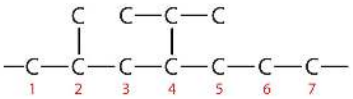


Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.

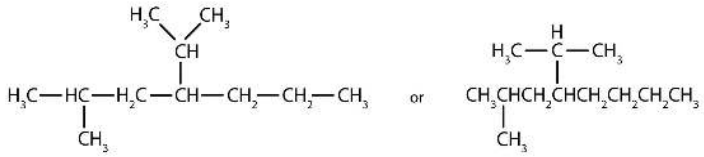


b. The parent chain is heptane in this case, indicating seven carbon atoms in the LCC. –C–C–C–C–C–C–C–

Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 8.5.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

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8.6: Physical Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table **8.6.1** describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table **8.6.1**: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure **8.6.1**: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, http://www.nasa.gov/topics/earth/features/oilspill/oil-20100519a.html.

Looking Closer: Gas Densities and Fire Hazards

Table **8.6.1** indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table **8.6.1** are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

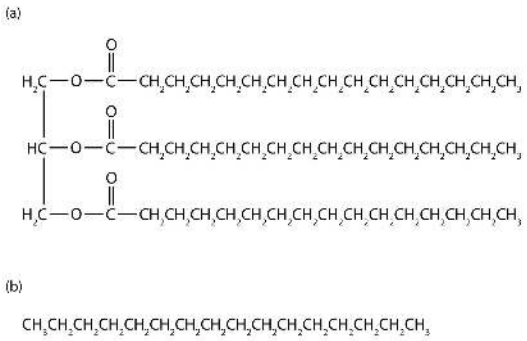


Figure **8.6.2**: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Concept Review Exercises

1. Without referring to a table, predict which has a higher boiling point—hexane or octane. Explain.
2. If 25 mL of hexane were added to 100 mL of water in a beaker, which of the following would you expect to happen? Explain.
   a. Hexane would dissolve in water.
   b. Hexane would not dissolve in water and would float on top.
   c. Hexane would not dissolve in water and would sink to the bottom of the container.

Answers

1. octane because of its greater molar mass
2. b; hexane is insoluble in water and less dense than water.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
   a. pentane or butane
   b. heptane or nonane
2. For which member of each pair is hexane a good solvent?
   a. pentane or water
   b. sodium chloride or soybean oil

Answer

1. a. pentane
   b. nonane

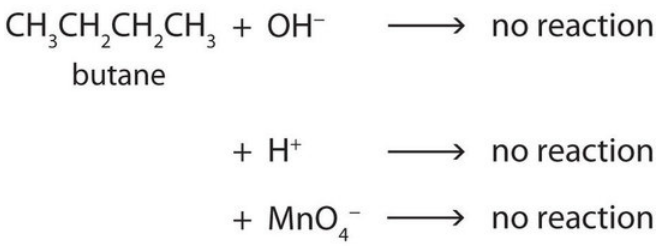
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8.7: Chemical Properties of Alkanes

Learning Objectives

- To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:



Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{8.7.1}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{8.7.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{8.7.3}$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

Concept Review Exercises

1. Why are alkanes sometimes called paraffins?
2. Which halogen reacts most readily with alkanes? Which reacts least readily?

Answers

1. Alkanes do not react with many common chemicals. They are sometimes called paraffins, from the Latin parum affinis, meaning "little affinity."
2. most readily: F_2; least readily: I_2

Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

Exercises

1. Why do alkanes usually not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents?
2. Write an equation for the complete combustion of methane (CH_4), the main component of natural gas).
3. What is the most important reaction of alkanes?
4. Name some substances other than oxygen that react readily with alkanes.

Answers

1. Alkanes are nonpolar; they do not attract ions.

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8.8: Halogenated Hydrocarbons

Learning Objectives

- To name halogenated hydrocarbons given formulas and write formulas for these compounds given names.

Many organic compounds are closely related to the alkanes. As we noted previously, alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce halogenated hydrocarbons, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:



The replacement of only one hydrogen atom gives an alkyl halide (or haloalkane). The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*. The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location. The prefixes are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. Thus CH_3CH_2Cl has the common name ethyl chloride and the IUPAC name chloroethane. Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 8.8.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2$–) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

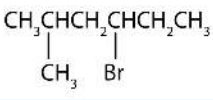
Exercise 8.8.1

Give common and IUPAC names for each compound.

a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

Example 8.8.2

Give the IUPAC name for each compound.

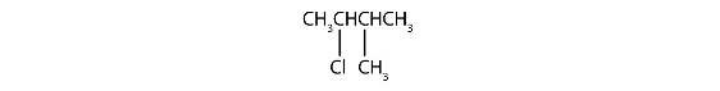
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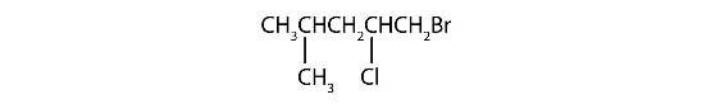
Solution

1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl (CH_3) and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

Exercise 8.8.2

Give the IUPAC name for each compound.

a. 

b. 

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table **8.8.1**, along with some of their uses.

Table **8.8.1**: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

To Your Health: Chlorofluorocarbons and the Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table 8.8.1.

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

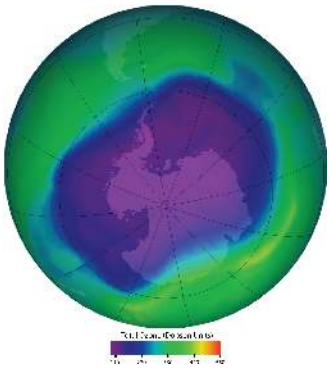


Figure 8.8.1: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24.

Concept Review Exercises

1. What is the IUPAC name for the HFC that has the formula CH_2FCF_3? (Hint: you must use a number to indicate the location of each substituent F atom.)
2. What is the IUPAC name for the HCFC that has the formula $CHCl_2CF_3$?

Answers

1. 1,1,1,2-tetrafluoroethane
2. 2,2-dichloro-1,1,1-trifluoroethane

Key Takeaway

- The replacement of an hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound.

Exercises

1. Write the condensed structural formula for each compound.
   a. methyl chloride
   b. chloroform
2. Write the condensed structural formula for each compound.
   a. ethyl bromide
   b. carbon tetrachloride
3. Write the condensed structural formulas for the two isomers that have the molecular formula C_3H_7Br. Give the common name and the IUPAC name of each.
4. Write the condensed structural formulas for the four isomers that have the molecular formula C_4H_9Br. Give the IUPAC name of each.
5. What is a CFC? How are CFCs involved in the destruction of the ozone layer?
6. Explain why each compound is less destructive to the ozone layer than are CFCs.
   a. fluorocarbons
   b. HCFCs

Answers

1. a. CH_3Cl
   b. $CHCl_3$

3. $CH_3CH_2CH_2Br$, propyl bromide, 1-bromopropane; $CH_3CHBrCH_3$, isopropyl bromide, 2-bromopropane

5. compounds containing Cl, F, and C; by releasing Cl atoms in the stratosphere

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8.9: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6. Each carbon atom has two hydrogen atoms attached (Figure **8.9.1**) and is called cyclopropane.

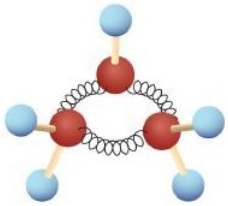
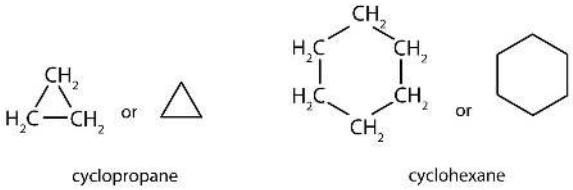


Figure **8.9.1**: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example **8.9.1** interprets the name of a cycloalkane with a single substituent group.

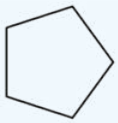
Example 8.9.1

Draw the structure for each compound.

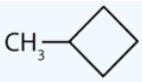
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



b. The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



Exercise 8.9.1

Draw the structure for each compound.

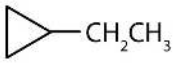
a. cycloheptane
b. ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure 8.9.1.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

Concept Review Exercises

1. What is the molecular formula of cyclooctane?
2. What is the IUPAC name for this compound?



Answers

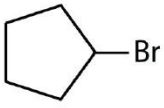
1. C_8H_{16}
2. ethylcyclopropane

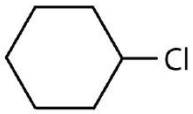
Key Takeaway

- Many organic compounds have cyclic structures.

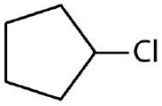
Exercises

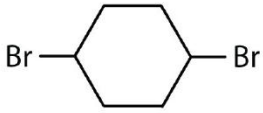
1. Draw the structure for each compound.
   a. ethylcyclobutane
   b. propylcyclopropane
2. Draw the structure for each compound.
   a. methylcyclohexane
   b. butylcyclobutane
3. Cycloalkyl groups can be derived from cycloalkanes in the same way that alkyl groups are derived from alkanes. These groups are named as cyclopropyl, cyclobutyl, and so on. Name each cycloalkyl halide.

   a. 

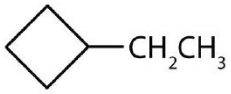
b. 

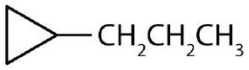
4. Halogenated cycloalkanes can be named by the IUPAC system. As with alkyl derivatives, monosubstituted derivatives need no number to indicate the position of the halogen. To name disubstituted derivatives, the carbon atoms are numbered starting at the position of one substituent (C1) and proceeding to the second substituted atom by the shortest route. Name each compound.

a. 

b. 

Answers

1. a. 

b. 

3. a. cyclopentyl bromide
   b. cyclohexyl chloride

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CHAPTER OVERVIEW

9: Unsaturated Hydrocarbons

9.1: Alkenes - Structures and Names
9.2: Cis-Trans Isomerism
9.3: Physical Properties of Alkenes
9.4: Chemical Properties of Alkenes
9.5: Polymers
9.6: Alkynes
9.7: Aromatic Compounds - Benzene
9.8: Structure and Nomenclature of Aromatic Compounds

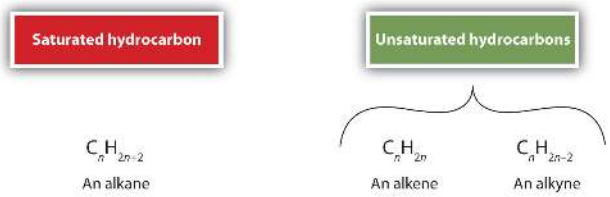
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9.1: Alkenes - Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

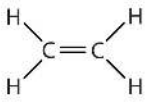


Some representative alkenes—their names, structures, and physical properties—are given in Table **9.1.1**.

Table **9.1.1**: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table **9.1.1**. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table **9.1.1**, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure **9.1.1**). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

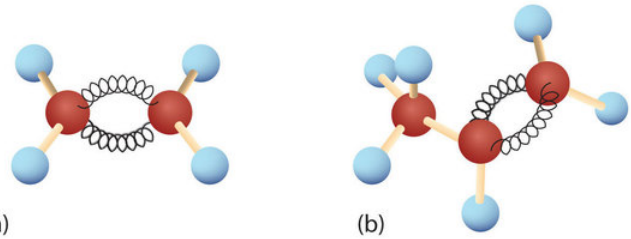
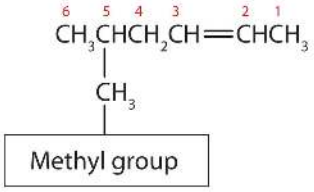


Figure **9.1.1**: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

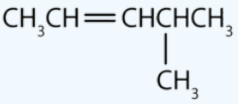
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

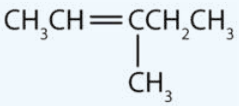
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



Example 9.1.1

Name each compound.

a. 

b. 

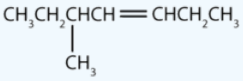
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.

b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 9.1.1

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$
2. 

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

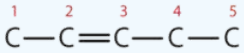
Example 9.1.2

Draw the structure for each compound.

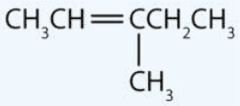
1. 3-methyl-2-pentene
2. cyclohexene

Solution

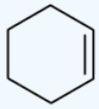
1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

   Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.

2. First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.

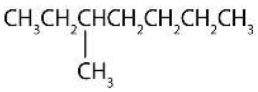
Exercise 9.1.2

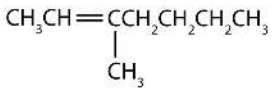
Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Concept Review Exercises

1. Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon.
2. Briefly identify the important distinctions between an alkene and an alkane.
3. Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne.

   a. 
   b. $CH_3CH_2C{\equiv}CCH_3$

c. 

Answers

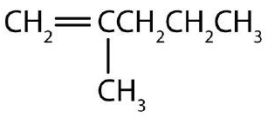
1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
2. An alkene has a double bond; an alkane has single bonds only.
3. a. saturated; alkane
   b. unsaturated; alkyne
   c. unsaturated; alkene

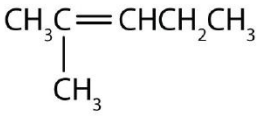
Key Takeaway

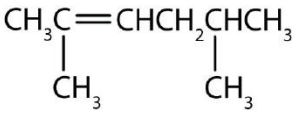
- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

Exercises

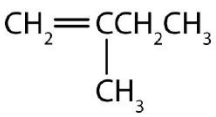
1. Draw the structure for each compound.
   a. 2-methyl-2-pentene
   b. 2,3-dimethyl-1-butene
   c. cyclohexene
2. Draw the structure for each compound.
   a. 5-methyl-1-hexene
   b. 3-ethyl-2-pentene
   c. 4-methyl-2-hexene
3. Name each compound according to the IUPAC system.

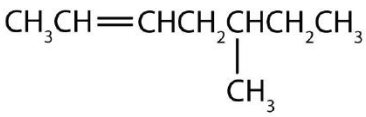
a. 

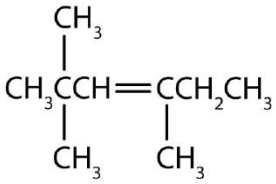
b. 

c. 

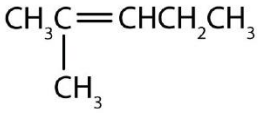
4. Name each compound according to the IUPAC system.

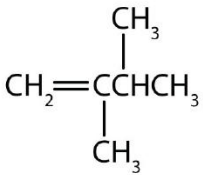
a. 

b. 

c. 

Answers

1. a. 

   b. 

   c. 

3. a. 2-methyl-1-pentene
   b. 2-methyl-2-pentene
   c. 2,5-dimethyl-2-hexene

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9.2: Cis-Trans Isomerism

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure **9.2.1**.

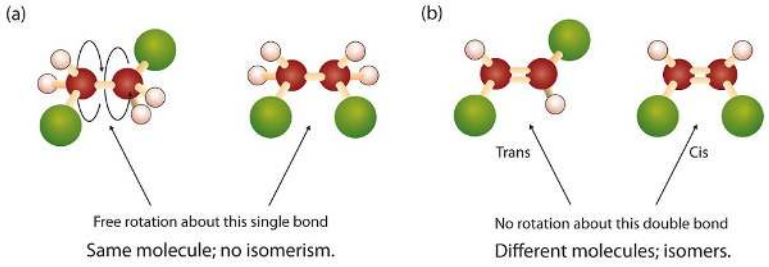


Table* 9.2.1: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure **9.2.1**), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (Figure **9.2.1***b*), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure **9.2.2**).

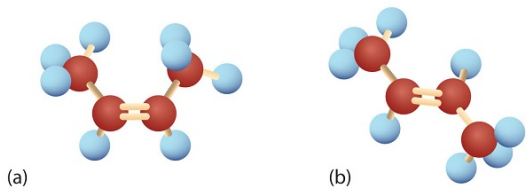


Figure **9.2.2**: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:



***Figure* 9.2.3**: *Models of (left) Cis-2-Butene and (right) Trans-2-Butene.*

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure **9.2.4**). We can draw two *seemingly* different propenes:



***Figure* 9.2.4**: *Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Advanced Note: E/Z Isomerization

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E/Z nomenclature discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



Example 9.2.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. CHCl=CHBr
2. CH_2=$CBrCH_3$
3. $(CH_3)_2C$=$CHCH_2CH_3$
4. CH_3CH=$CHCH_2CH_3$

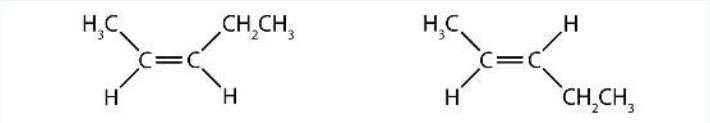
Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:

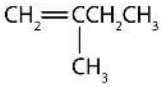


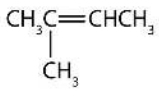
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



Exercise 9.2.1

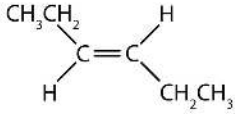
Which compounds can exist as cis-trans isomers? Draw them.

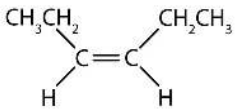
a. CH_2=$CHCH_2CH_2CH_3$
b. CH_3CH=$CHCH_2CH_3$
c. CH_3CH_2CH=$CHCH_2CH_3$
d. 

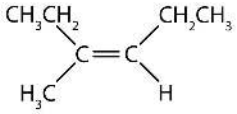
e. 

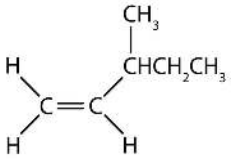
Concept Review Exercises

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.

a. 

b. 

c. 

d. 

Answers

1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.

2. a. trans (the two hydrogen atoms are on opposite sides)
   b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
   c. cis (the two ethyl groups are on the same side)
   d. neither (fliping the bond does not change the molecule. There are no isomers for this molecule)

Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

Exercises

1. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.

   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene
   d. 1,1-dibromo-1-butene
   e. 2-butenoic acid ($CH_3CH=CHCOOH$)

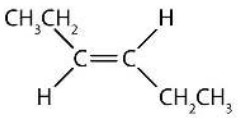
2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.

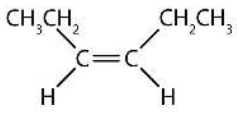
   a. 2,3-dimethyl-2-pentene
   b. 1,1-dimethyl-2-ethylcyclopropane
   c. 1,2-dimethylcyclohexane
   d. 5-methyl-2-hexene
   e. 1,2,3-trimethylcyclopropane

Answer

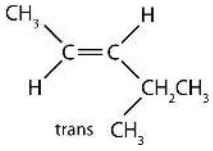
1. a: none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).

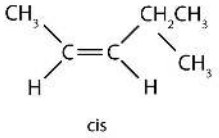
   b:


cis

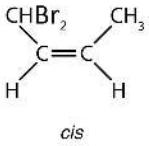

trans

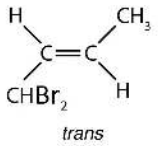
c:



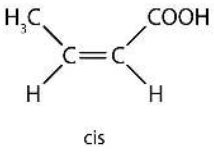


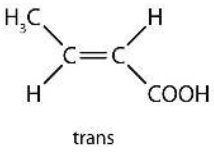
d:





e:





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9.3: Physical Properties of Alkenes

Learning Objectives

- To identify the physical properties of alkenes and describe trends in these properties.

The physical properties of alkenes are similar to those of the alkanes. The table at the start of the chapter shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.



The bright red color of tomatoes is due to lycopene—a polyene.

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene (CH_2=$CHCH$=CH_2) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

Concept Review Exercises

1. Briefly describe the physical properties of alkenes. How do these properties compare to those of the alkanes?
2. Without consulting tables, arrange the following alkenes in order of increasing boiling point: 1-butene, ethene, 1-hexene, and propene.

Answers

1. Alkenes have physical properties (low boiling points, insoluble in water) quite similar to those of their corresponding alkanes.
2. ethene < propene < 1-butene < 1-hexene

Key Takeaway

- The physical properties of alkenes are much like those of the alkanes: their boiling points increase with increasing molar mass, and they are insoluble in water.

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.

    a. 1-pentene or 1-butene
    b. 3-heptene or 3-nonene

2. Which is a good solvent for cyclohexene, pentane or water?

Answer

1. a. 1-pentene
    b. 3-nonene

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9.4: Chemical Properties of Alkenes

Learning Objectives

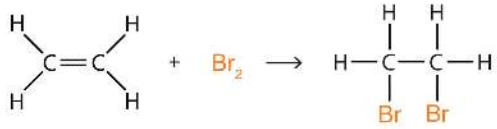
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen (H_2) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).

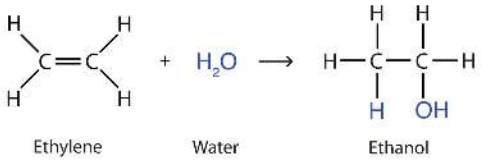


The product is an alkane having the same carbon skeleton as the alkene.

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine (Br_2) can be used to test for alkenes. Bromine solutions are brownish red. When we add a Br_2 solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:



Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):



The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

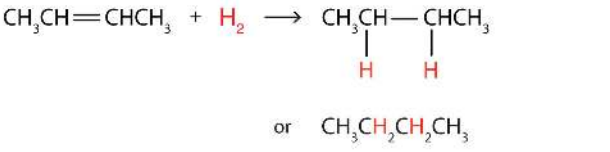
Example 9.4.1

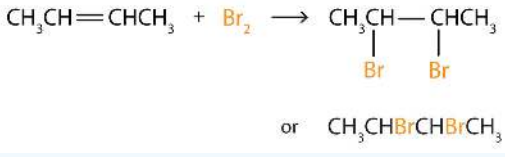
Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

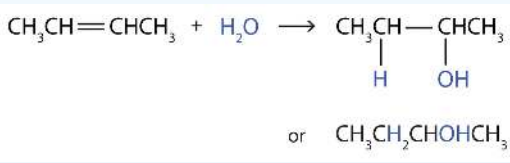
a. H_2 (Ni catalyst)
b. Br_2
c. H_2O (H_2SO_4 catalyst)

Solution

In each reaction, the reagent adds across the double bond.

a. 

b. 

c. 

Exercise 9.4.1

Write the equation for each reaction.

a. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)
b. $CH_3CH{=}CH_2$ with Cl_2
c. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

Concept Review Exercises

1. What is the principal difference in properties between alkenes and alkanes? How are they alike?
2. If $C_{12}H_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product?

Answers

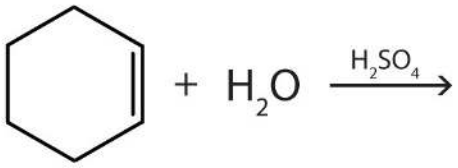
1. Alkenes undergo addition reactions; alkanes do not. Both burn.
2. $C_{12}H_{24}Br_2$

Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

Exercises

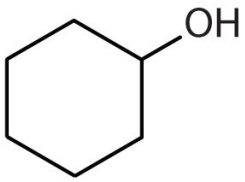
1. Complete each equation.

a. $(CH_3)_2C{=}CH_2 + Br_2 \rightarrow$
b. $\mathbf{CH_2{=}C(CH_3)CH_2CH_3 + H_2 \xrightarrow{Ni}}$
c. 

2. Complete each equation.

a. $\mathbf{CH_2{=}CHCH{=}CH_2 + 2H_2 \xrightarrow{Ni}}$
b. $\mathbf{(CH_3)_2C{=}C(CH_3)_2 + H_2O \xrightarrow{H_2SO_4}}$
c. 

Answer

1. a. $(CH_3)_2CBrCH_2Br$
   b. $CH_3CH(CH_3)CH_2CH_3$
   c. 

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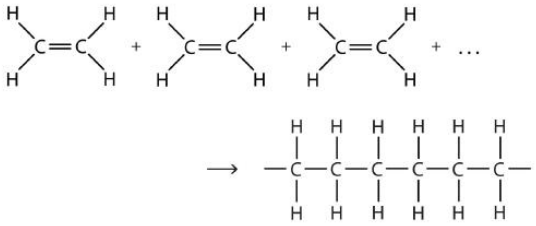
9.5: Polymers

Learning Objectives

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning “one,” and *meros*, meaning “parts”), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning “many,” and *meros*, meaning “parts”). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



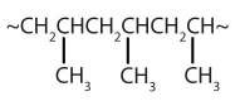
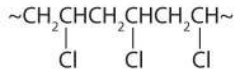
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \text{–}\mathrm{CH_2CH_2}\text{–}_n$$

Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table **9.5.1**. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table **9.5.1***: Some Addition Polymers*

Monomer	Polymer	Polymer Name	Some Uses
$CH_2=CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2=CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2=CHCl$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2=CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

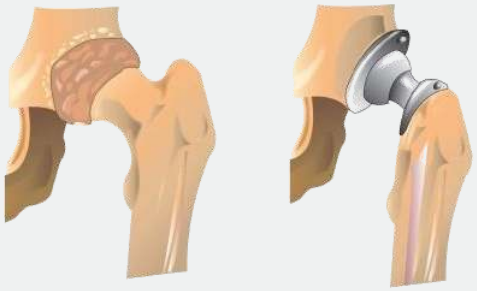


Figure **9.5.1**: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Concept Review Exercises

1. What is a monomer? What is a polymer? How do polymer molecules differ from the molecules we have discussed in earlier sections of this chapter?
2. What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?
3. What is the molecular formula of a polymer molecule formed by the addition polymerization of 175 molecules of vinyl chloride ($CH_2=CHCl$)?

Answers

1. Monomers are small molecules that can be assembled into giant molecules referred to as polymers, which are much larger than the molecules we discussed earlier in this chapter.
2. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers.
3. $C_{350}H_{525}Cl_{175}$

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

Exercises

1. Write the condensed structural formula of the monomer from which Saran is formed. A segment of the Saran molecule has the following structure: $CH_2CCl_2CH_2CCl_2CH_2CCl_2CH_2CCl_2$.
2. Write the condensed structural formula for the section of a molecule formed from four units of the monomer CH_2=CHF.

Answer

1. $H_2C=CCl_2$

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9.6: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure **9.6.1**). Its structure is H–C≡C–H.

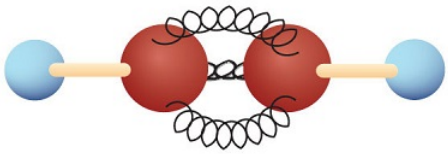


Figure **9.6.1**: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

Concept Review Exercises

1. Briefly identify the important differences between an alkene and an alkyne. How are they similar?
2. The alkene $(CH_3)_2CHCH_2CH{=}CH_2$ is named 4-methyl-1-pentene. What is the name of $(CH_3)_2CHCH_2C{\equiv}CH$?
3. Do alkynes show cis-trans isomerism? Explain.

Answers

1. Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.
2. 4-methyl-1-pentyne
3. No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

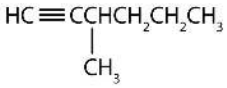
Exercises

1. Draw the structure for each compound.
   a. acetylene
   b. 3-methyl-1-hexyne
2. Draw the structure for each compound.
   a. 4-methyl-2-hexyne
   b. 3-octyne
3. Name each alkyne.
   a. $CH_3CH_2CH_2C{\equiv}CH$

b. $CH_3CH_2CH_2C{\equiv}CCH_3$

Answers

1. a. H–C≡C–H

   b. 

3. a. 1-pentyne

   b. 2-hexyne

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9.7: Aromatic Compounds - Benzene

Learning Objectives

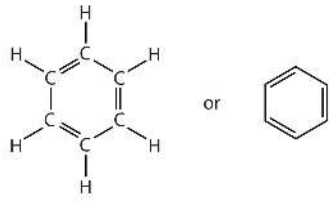
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or

heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Concept Review Exercises

1. How do the typical reactions of benzene differ from those of the alkenes?
2. Briefly describe the bonding in benzene.
3. What does the circle mean in the chemist's representation of benzene?

Answers

1. Benzene is rather unreactive toward addition reactions compared to an alkene.
2. Valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized).
3. The six electrons are shared equally by all six carbon atoms.

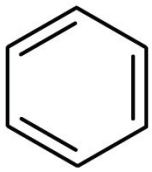
Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

Exercises

1. Draw the structure of benzene as if it had alternate single and double bonds.
2. Draw the structure of benzene as chemists usually represent it today.

Answer

1. 

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9.8: Structure and Nomenclature of Aromatic Compounds

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

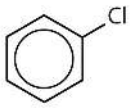
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 9.8.1, where the benzene ring is represented as C_6H_5.

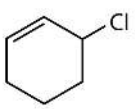
Table 9.8.1: *Some Representative Aromatic Compounds*

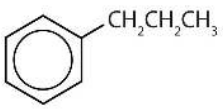
Name	Structure	Typical Uses
aniline	$C_6H_5–NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	$C_6H_5–COOH$	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	$C_6H_5–Br$	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5–NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	$C_6H_5–OH$	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5–CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

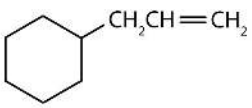
Example 9.8.1

Which compounds are aromatic?

1. 

2. 

3. 

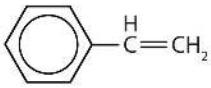
4. 

Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

Exercise 9.8.1

Which compounds are aromatic?

1. 
2. 
3. 

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure **9.8.1** shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

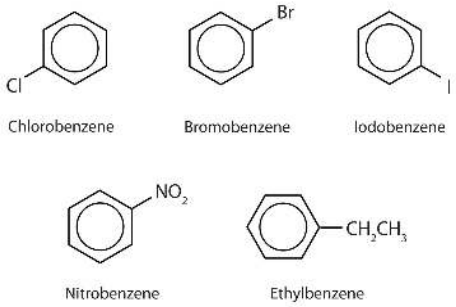


Figure **9.8.1**: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table **9.8.1**.



When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure **9.8.2**). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

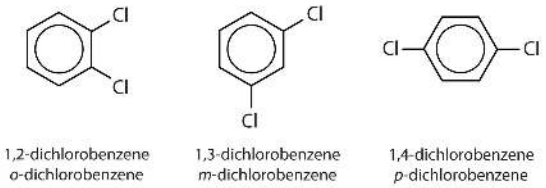
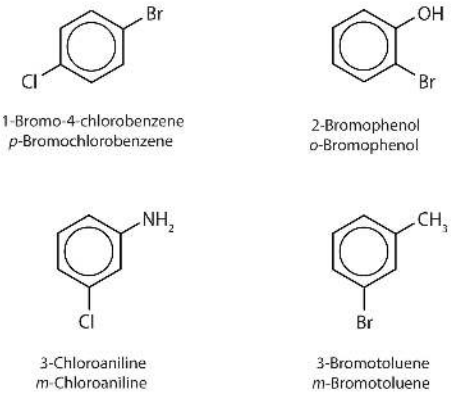


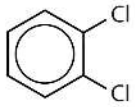
Figure **9.8.2**: The Three Isomeric Dichlorobenzenes

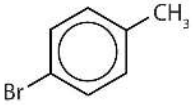
In Figure **9.8.2**, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:

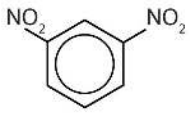


Example 9.8.2

Name each compound using both the common name and the IUPAC name.

1. 

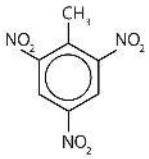
2. 

3. 

Solution

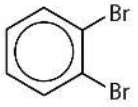
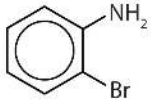
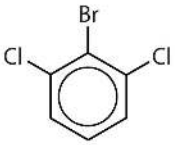
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).



Exercise 9.8.2

Name each compound using both the common name and the IUPAC name.

1. 
2. 
3. 

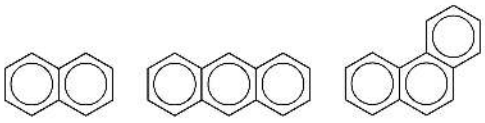
Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



Phenyl group 2-Phenylheptane

Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



Naphthalene Anthracene Phenanthrene

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are

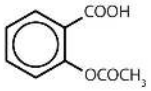
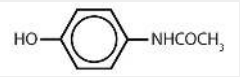
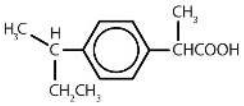
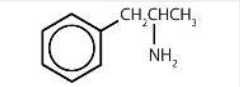
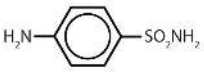
emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B_2 (riboflavin), and B_9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table **9.8.2**, also feature a benzene ring.

> So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table **9.8.2**: Some Drugs That Contain a Benzene Ring

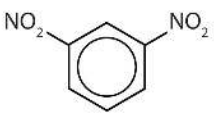
Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

Concept Review Exercises

1. Briefly identify the important characteristics of an aromatic compound.
2. What is meant by the prefixes *meta*, *ortho*, or *para*? Give the name and draw the structure for a compound that illustrates each.
3. What is a phenyl group? Give the structure for 3-phenyloctane.

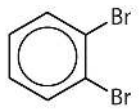
Answers

1. An aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties.
2. meta = 1,3 disubstitution; (answers will vary)



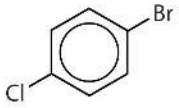
m-dinitrobenzene or 1,3-dinitrobenzene

ortho = 1,2 disubstitution



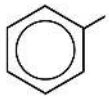
o-dibromobenzene or 1,2-dibromobenzene

para = 1,4 disubstitution or 1-bromo-4-chlorobenzene

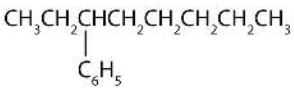


p-bromochlorobenzene or 1-bromo-2-chlorobenzene

3. phenyl group: C_6H_5 or



3-phenyloctane:

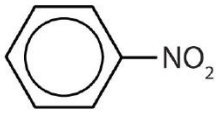


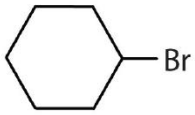
Key Takeaway

- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

Exercises

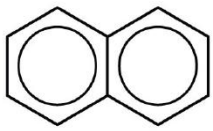
1. Is each compound aromatic?

a. 

b. 

2. Is each compound aromatic?

a. 

b. 

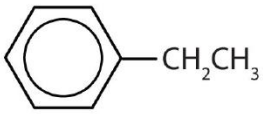
3. Draw the structure for each compound.

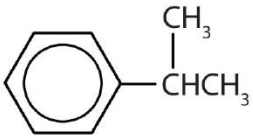
a. toluene
b. *m*-diethylbenzene
c. 3,5-dinitrotoluene

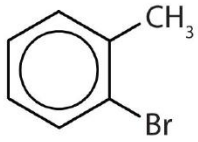
4. Draw the structure for each compound.

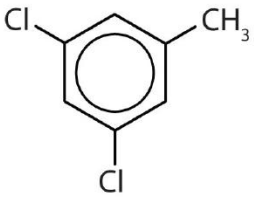
a. *p*-dichlorobenzene
b. naphthalene
c. 1,2,4-trimethylbenzene

5. Name each compound with its IUPAC name.

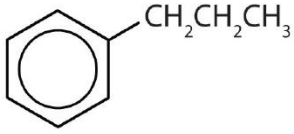
a. 

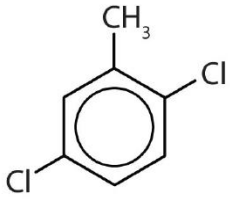
b. 

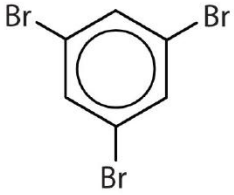
c. 

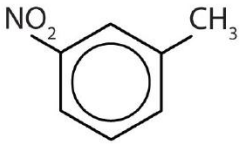
d. 

6. Name each compound with its IUPAC name.

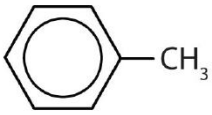
a. 

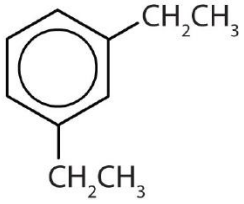
b. 

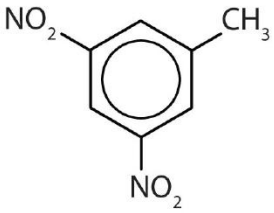
c. 

d. 

Answers

1. a. yes
   b. no
3. a. 

   b. 

   c. 

5. a. ethylbenzene
   b. isopropylbenzene
   c. *o*-bromotoluene
   d. 3,5-dichlorotoluene

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Glossary

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