CEEG 445: ENVIRONMENTAL ENGINEERING CHEMISTRY (FALL 2020)

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Licensing

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CHAPTER OVERVIEW

1: Chemistry Basics

1.1: The Structure of Atoms

An **atom** consists of a positively charged **nucleus**, surrounded by one or more negatively charged particles called **electrons**. The positive charges equal the negative charges, so the atom has no overall charge; it is electrically neutral. Most of an atom's mass is in its nucleus; the mass of an electron is only 1/1836 the mass of the lightest nucleus, that of hydrogen. Although the nucleus is heavy, it is quite small compared with the overall size of an atom. The radius of a typical atom is around 0.1 to 0.25 nanometres (nm), whereas the radius of a nucleus is about 10^{-6} nm. ***** If an atom were enlarged to the size of the earth, its nucleus would be only 200 feet in diameter and could easily rest inside a small football stadium.

Table 1-1. Fundamental Particles of Matter

Particle	Charge	Mass (amu)
Proton	+1	1.00728
Neutron	0	1.00867
Electron	-1	0.000549

The nucleus of an atom contains **protons** and **neutrons**. Protons and neutrons have nearly equal masses, but they differ in charge. A neutron has no charge, whereas a proton has a positive charge that exactly balances the negative charge on an electron. Table 1-1 lists the charges of these three fundamental particles, and gives their masses expressed in **atomic mass units**. The atomic mass unit (amu) is defined as exactly one-twelfth the mass of the nucleus of a carbon atom consisting of six protons and six neutrons. With this scale, protons and neutrons have masses that are close to, but not precisely, 1 amu each. [As a matter of information at this point, there are approximately 6.022 X 10^{23} amu in 1 gram (g). This number is known as **Avogadro's number**, **N**.]

The number of protons in the nucleus of an atom is known as the **atomic number**, **Z**. It is the same as the number of electrons around the nucleus, because an atom is electrically neutral. When two atoms are close enough to combine chemically - to form *chemical bonds with one another* - each atom "sees" mainly the outermost electrons of the other atom. Hence these outer electrons are the most important factors in the chemical behavior of atoms. Neutrons in the nucleus have little effect on chemical behavior, and the protons are significant only because they determine how many electrons surround the nucleus in a neutral atom. All atoms with the same atomic number behave in much the same way chemically and are classified as the same chemical element. Each element has its own name and a one- or two-letter symbol (usually derived from the element's English or Latin name). For example, the symbol for carbon is C, and the symbol for calcium is Ca. The symbol for sodium is Na - the first two letters of its Latin (and German) name, *natrium* - to distinguish it from nitrogen, N, and sulfur, S.

Note

***O**ne nanometre equals* 10^{-9} *meters (m), or* 10^{-7} *centimeters (cm). Be familiar with metric prefixes from mega (M) on the high end to nano (n) on the low end. Tables of metrix prefix abbreviations are readily available online, for quick reference.*

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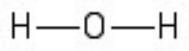
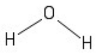
1.2: Molecules

When atoms are close enough to one another that the outer electrons of one atom can interact with the other atoms, then attractions can be set up between atoms, strong enough to hold them together in what is termed a **chemical bond**. In the simplest cases the bond arises from the sharing of two electrons between a pair of atoms, with one or more electrons provided by each of the bonded atoms. Bonds based on electron sharing are known as **covalent bonds**, and two or more atoms held together as a unit by covalent bonds are known as a **molecule**.

In **molecular diagrams**, a covalent, electron-sharing bond is represented by a straight line connecting the bonded atoms. In the water molecule, one atom of oxygen (O) is bonded to two hydrogen (H) atoms. One way of representing this molecule visually is as follows:



The second version acknowledges the fact that a water molecule is not linear; the two H - O bonds make an angle of 105° with one another:



These diagrams show only the connections between atoms in the molecules. They do not show the three-dimensional geometries (or shapes) of the molecules, but you have likely seen such structures in prior chemistry courses. We will not explore those 3-D structures in detail in this course, but will instead typically use one of the two formats above, or the molecular formula approach presented next.

Molecular formulas tell how many atoms of each element are in the molecule, but provides little or no information as to how the atoms are connected. The molecular formula for hydrogen is H_2; water, H_2O; hydrogen sulfide, H_2S; ammonia, NH_3; methane, CH_4 ; methyl alcohol, CH_3OH or CH_4O; and octane, C_8H_{18}.

The sum of the atomic weights of all the atoms in a molecule is its **molecular weight**. Using the atomic weights of individual atoms, we can calculate molecular weights.

The molecular weight of hydrogen, H_2, is

2 X 1.0080 amu = 2.0160 amu

A water molecule, H_2O , has two atoms of hydrogen and one atom of oxygen, so:

(2 X 1.0080 amu) + (15.9994 amu) = 18.0154 amu

In these examples, the atomic weights and, hence, molecular weights, are calculated to four decimal places. For our purposes, you can feel free to be slightly less precise:

If an atomic weight is very near to an integer and would round to 0 in the first decimal place, you can use that integer. Examples include carbon (12.01 --> 12.0), oxygen (15.999 --> 16.0), hydrogen (1.008 --> 1.0), nitrogen (14.007 --> 14.0), and others.

When an atomic weight would not round to an even integer but would have a non-zero value in its first decimal place, include that first decimal place after rounding. Examples include chlorine (35.45 --> 35.5), magnesium (24.31. --> 24.3), iron (55.845 --> 55.8), etc.

Example

Calculate the molecular weight of methanol (methyl alcohol), CH_3OH.

Solution

The molecular formula is CH_3OH or CH_4O. Then:

1 carbon:	1 x 12.0 amu =	12.0 amu
4 hydrogens:	4 x 1.0 amu =	4.0 amu
1 oxygen:	1 x 16.0 amu =	16.0 amu
	Total molecular weight =	32.0 amu

Example

What is the molecular weight of trichloroethylene (TCE), or C_2HCl_3?

Solution

Since the molecular formula is C_2HCl_3 the molecular weight is:

2 carbons:	2 x 12.0 amu =	24.0 amu
1 hydrogen:	1 x 1.0 amu =	4.0 amu
3 chlorines:	3 x 35.5 amu =	106.5 amu
	Total molecular weight =	131.5 amu

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1.3: Forces between Molecules

Forces Between Molecules

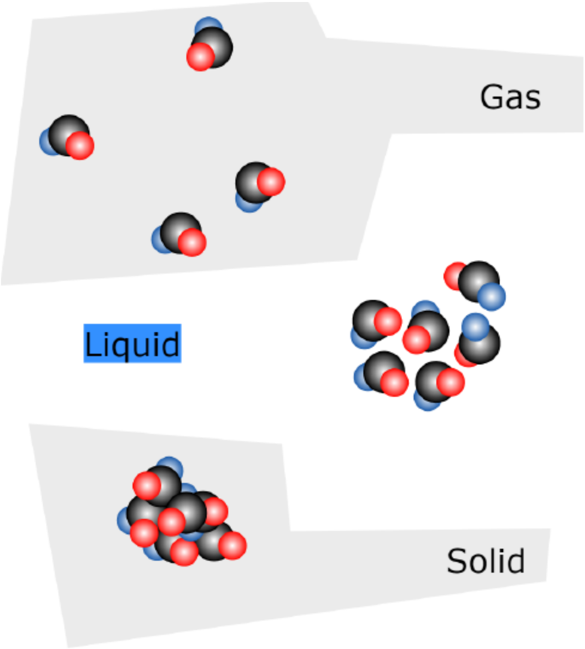

Figure 1.3.1: The three states of matter: (a) In a gas the individual molecules move freely through space, colliding and rebounding. A gas adapts to the shape of its container and can easily be expanded or compressed. (b) Molecules in a liquid are in contact, but free to slide past one another. A liquid also adapts to the shape of its container, but it has a relatively fixed volume. (c) In a crystalline solid. molecules are packed in to a regular array, giving the solid both a fixed volume and a definite shape. Work must be done to break or deform a crystal. Adapted from R. E. Dickerson and 1. Geis. *Chemistry, Matter, and the Universe*, W. A. Benjamin. Menlo Park, Calif.. 1976.

Although the strongest attractions of an atom are for other atoms to which it is bonded in a molecule, two molecules themselves exert small but appreciable attractions on one another. Molecules are slightly "sticky." These forces, caused by momentary fluctuations in electron distributions around the atoms, are known as **van der Waals attractions** (after Dutch physicist Johannes van der Waals). They are responsible for the existence of three states (or phases) of matter at different temperatures: solids, liquids, and gases. **Temperature** is just a measure of the heat energy or energy of motion that a collection of molecules possesses. At low temperatures, the molecules have little energy of motion. The van der Waals attractions hold them together in an orderly, close-packed crystalline array or lattice (Figure 1-3c). This is the **solid** state. If more energy is fed into the crystal so the temperature rises, the molecules will vibrate about their average or equilibrium positions in the crystal. Enough energy will cause the ordered structure of the molecular crystal to break up, and the molecules will be free to slide past one another, although they are still touching (Figure 1-3b). This is the **liquid** state, and the transition temperature between solid and liquid is called the **melting point**, **T_m**. The liquid is still held together by van der Waals attractions, although the molecules have too much energy of motion to be locked into a rigid array. If still more energy is given to the liquid, the molecules will begin to move fast enough to overcome the van der Waals attractions, separate entirely from one another, and travel in independent molecular trajectories through space (Figure 1-3a). This is the **gas** phase, and the transition temperature between liquid and gas is called the **boiling point**, **T_b**. Changes in phase are treated in more detail in Chapter 18.

The melting and boiling points of some simple molecules are compared in Table 1-3. In general, larger molecules have higher melting and boiling points, since they have larger surface areas for van der Waals attractions. Thus at 1 atm. pressure H_2 boils at -252.5°C, CH_4. boils at - 164.0 °C, but C_8H_{18} must be heated to + 125.7°C before the molecules will separate from one another and go into the gas phase.

Table 1-3. Melting and Boiling Points of Some Simple Molecular Substances

Substance	Molecular Formula	T_m(°C)	T_b(°C)
Gases			
Hydrogen	H_2	-259.1	-252.5
Oxygen	O_2	-218.4	-183.0
Methane	CH_4	-182.5	-164.0
Hydrogen Sulfide	H_2S	-85.5	-60.7
Chlorine	Cl_2	-101.0	-34.6
Ammonia	NH_3	-77.7	-33.4
Liquids			
Bromine	Br_2	-7.2	+58.8
Methanol	CH_3OH	-93.9	+65.0
Water	H_2O	0	+100
n-Octane	C_8H_{18}	+185	+125.7
Solids			
Iodine	I_2	+113.5	+184.4
Sucrose (cane sugar)	$C_{12}H_{22}O_{11}$	+185	decomposes

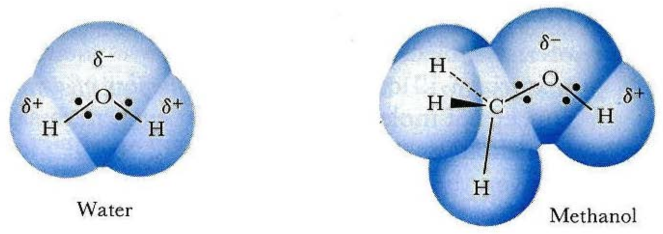

Figure 1-4 The O–H bonds in water and methanol (methyl alcohol) are polar because the oxygen atom has the stronger attraction for the electron pair and pulls negative charge toward itself, leaving the hydrogen with a fractional positive charge. This polarity is of great importance in interactions between molecules. Source: *Chemical Principles*, by Dickerson, Gray, and Haight, 3rd ed., 1979. Retrieved from CaltechAUTHORS, Aug 10, 2020.

A second kind of force between molecules also influences melting and boiling points: the **polarity** of the molecules. If two atoms that are connected by an electron-pair covalent bond do not have the same attraction for electrons, then the electron pair will shift toward the atom with the greater electron pulling power. This will give that atom a slight excess of negative charge (represented by δ- rather than by just a minus sign, which would imply a full electron charge), and will confer a slight positive charge (δ+) on the atom that lost out in the tug-of-war for the electron pair. Because the electron-attracting power (**electronegativity**) of oxygen is greater than that of hydrogen, the oxygen atom in a molecule of water or methyl alcohol is slightly negative, and the hydrogen atoms are slightly positive (Figure 1-4). Such a molecule is termed polar because it behaves like a tiny electric dipole; that is, the negative charge on the oxygen attracts other nearby positive charges, and the positive charge on each hydrogen attracts other negative charges. This is another attractive force between molecules, in addition to van der Waals attractions. Because of the forces binding its molecules, methanol melts and boils at much higher temperatures than methane, which is similar to it in molecular size. Methanol is a liquid at room temperature, whereas methane is a gas. In water, the attractions between hydrogen and oxygen from different molecules are so strong that they are given the name of **hydrogen bonds**. Hydrogen bonds are especially' important in proteins and other giant molecules in living organisms. If it were not for polarity and hydrogen bonding, water would melt and boil at lower temperatures even than H_2S (Table 1-3). It would be a gas at room temperature, rather than the Earth's most common liquid.

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1.4: Ions

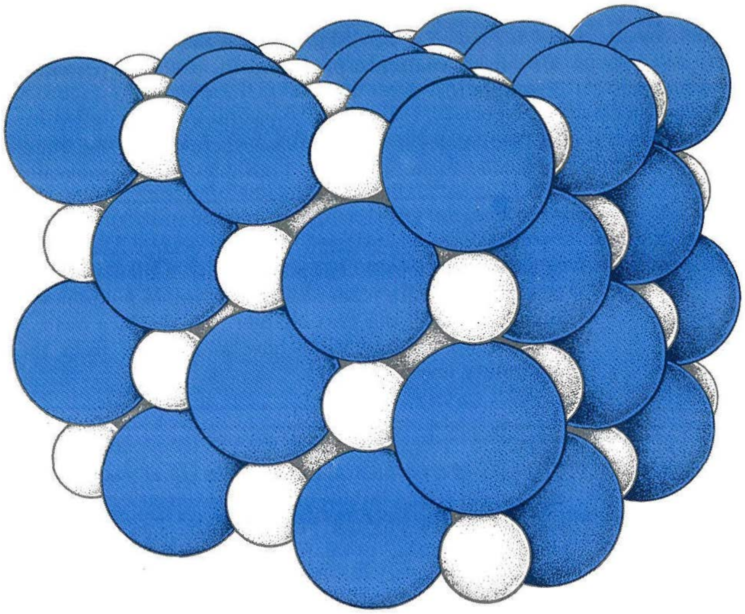


Figure 1-5 Common table salt (sodium chloride. NaCl) is built from closely packed sodium ions, Na^+ (small spheres). and chloride ions. Cl^- (large. colored spheres). Each ion of one charge is surrounded by six ions of the opposite charge at the four compass points and above and below. This is a particularly stable arrangement of charges. and it occurs in many salts. From Dickerson, Gray, and Haight, *Chemical Principles*, 3rd ed., 1979. Retrieved from CaltechAUTHORS, Aug 10, 2020.

The idea of a covalent bond suggests equal sharing of the electron pair by the bonded atoms, but the brief discussion of polarity in Section 1-4 indicated that the sharing is not always equal. The relative electronegativity or electron-attracting power of atoms is of great importance in explaining chemical behavior, and is treated in detail in Chapters 9 and 10. Sodium atoms (and all metals in general) have a weak hold on electrons, whereas chlorine atoms are very electronegative. Hence in common table salt (sodium chloride, NaCl), each sodium atom, Na, loses one electron (e^-) to form a sodium ion, Na^+. Each chlorine atom picks up one electron to become a chloride ion, Cl^-:

$$\mathrm{Na} \rightarrow \mathrm{Na}^+ + e^- \qquad \text{and} \qquad \tfrac{1}{2}\,\mathrm{Cl}_2 + e^- \rightarrow \mathrm{Cl}^-$$

We write $\frac{1}{2}$ Cl_2 because free chlorine gas exists as **diatomic** (two-atom) molecules, not as free chlorine atoms. Solid sodium chloride (Figure 1-5) has sodium and chloride ions packed into a three-dimensional lattice in such a way that each positive Na^+ ion is surrounded on four sides and top and bottom by negative Cl^- ions, and each Cl^- is similarly surrounded by six nearest neighbor Na^+ ions. This is a particularly stable arrangement of positive and negative charges.

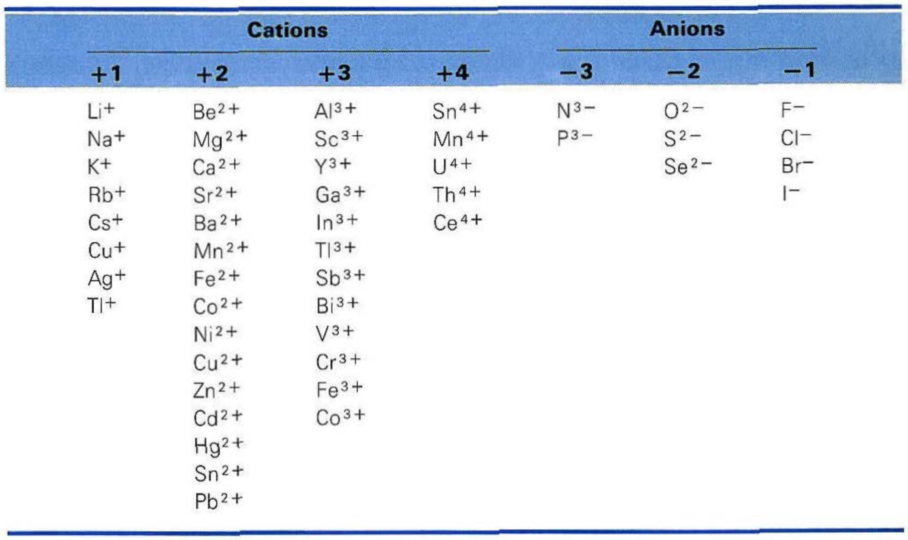
Metals in general lose one to three electrons easily to become positively charged ions, or **cations**:

Li	→	Li^+	+	e^-		lithium ion
Na	→	Na^+	+	e^-		sodium ion
K	→	K^+	+	e^-		potassium ion
Mg	→	Mg^{+2}	+	$2e^-$		magnesium ion
Ca	→	Ca^{+2}	+	$2e^-$		calcium ion
Al	→	Al^{+3}	+	$3e^-$		aluminum ion

Some nonmetals, in contrast, pick up electrons to become negatively charged ions, or **anions**:

$\frac{1}{2}$ F_2	+	e^-	→	F^-		fluoride ion
$\frac{1}{2}$ Cl_2	+	e^-	→	Cl^-		chloride ion
$\frac{1}{2}$ O_2	+	$2e^-$	→	O^{-2}		oxide ion
$\frac{1}{2}$ S_2	+	$2e^-$	→	S^{-2}		sulfide ion

Table 1-4 Some Simple Ions of Elements. From Dickerson, Gray, and Haight, *Chemical Principles*, 3rd ed., 1979. Retrieved from CaltechAUTHORS, Aug 10, 2020.



Cations				Anions		
+1	+2	+3	+4	−3	−2	−1
Li^+	Be^{2+}	Al^{3+}	Sn^{4+}	N^{3-}	O^{2-}	F^-
Na^+	Mg^{2+}	Sc^{3+}	Mn^{4+}	P^{3-}	S^{2-}	Cl^-
K^+	Ca^{2+}	Y^{3+}	U^{4+}		Se^{2-}	Br^-
Rb^+	Sr^{2+}	Ga^{3+}	Th^{4+}			I^-
Cs^+	Ba^{2+}	In^{3+}	Ce^{4+}			
Cu^+	Mn^{2+}	Tl^{3+}				
Ag^+	Fe^{2+}	Sb^{3+}				
Tl^+	Co^{2+}	Bi^{3+}				
	Ni^{2+}	V^{3+}				
	Cu^{2+}	Cr^{3+}				
	Zn^{2+}	Fe^{3+}				
	Cd^{2+}	Co^{3+}				
	Hg^{2+}					
	Sn^{2+}					
	Pb^{2+}					

Other simple ions made from single atoms are shown in Table 1-4.

Fe^{2+}		iron(II) or ferrous		Fe^{3+}		iron(III) or ferric

Cu^+	tt	copper(I) or cuprous	break	Cu^{2+}	tt	copper(II) or cupric
Sn^{2+}		tin(II) or stannous		Sn^{4+}		tin(IV) or stannic

A **salt** is a compound made up of positive and negative ions. Because a salt must be electrically neutral, the total charge on its positive and negative ions must be zero. Since each ion of Sn^{2+} has a charge of +2, twice as many chloride ions with -1 charge each are required to produce a zero net charge. Hence the salt of Sn^{2+} and Cl^- ions has the overall composition $SnCl_2$, rather than SnCl or $SnCl_3$. It is called stannous chloride or tin (II) chloride. The formula for stannic chloride or tin(IV) chloride is $SnCl_4$.

Melting Points and Boiling Points of Salts

A salt crystal represents a particularly stable balance of positive and negative charges, with each type of ion being kept out of the way of others of like charge. Melting a salt crystal means upsetting this delicate balance of charges, and allowing mutually repelling ions to come closer together from time to time as the ions flow past one another. This disruption of structure requires large amounts of energy to accomplish, so the melting points of salts are higher than those of molecular solids. The melting points of two salts, sodium chloride (NaCI) and potassium sulfate (K_2SO_4), are compared in Table 1-7 with those of the elements from which the salts are made.

***Table 1-7**. Melting and Boiling Points of Two Salts and Their Component Elements*

Substance	Chemical Formula	T_m(°C)	T_b(°C)
Sodium metal	Na	97.8	882.9
Chlorine Gas	Cl_2	-101.0	-34.6
Sodium Chloride (salt)	NaCl	801	1413
Potassium metal	K	64	774
Sulfur	S	119	445
Oxygen gas	O_2	-218	-183
Potassium sulfate (salt)	K_2SO_4	1069	1689

Metallic sodium melts at 97.8°C, and solid chlorine melts at -101°C, but their combination, sodium chloride (common table salt), requires a temperature of 801°C before it will melt. Boiling or vaporizing a salt is even more difficult. The ions remain ions in the liquid state, tumbling past one another as in any other liquid; but before the gas phase can be attained, Na^+ and CI^- ions must pair off into neutral NaCl molecules. To accomplish this pairing, electrons have to be pulled away from CI^- ions, which have a strong attraction for them, and pushed toward Na^+ ions, which do not want them. The NaCl bond in sodium chloride vapor is extremely polar, with the electron pair skewed strongly toward the chlorine atom, but the separation still is not as complete as in Na^+ and CI^- ions. Much energy is required to push electrons where they are not wanted and to make NaCl molecules from Na^+ and CI^- ions, so high temperatures are required before this can happen. Hence the very high boiling points of salts in comparison with molecular compounds, as illustrated in Table 1-7.

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1.5: Units of Concentration - Molarity

Learning Objectives

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

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (Figure $1.5.1$). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

Figure $1.5.1$: Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

Solutions

Solutions are homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. Here we will introduce some of the basic properties of solutions.

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

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

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

$$M=\frac{\text{mol solute}}{\text{L solution}} \tag{1.5.1}$$

Example 1.5.1: Calculating Molar Concentrations

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

Solution

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

$$\begin{aligned} M &= \frac{mol\ solute}{L\ solution} \\ &= \frac{0.133\ mol}{355\ mL \times \frac{1\ L}{1000\ mL}} \\ &= 0.375\ M \end{aligned}$$

Exercise 1.5.1

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

Answer

0.05 M

Example 1.5.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 1.5.1?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in Example 3.4.2, 0.375 *M*:

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

$$\begin{aligned} \text{mol solute} &= \text{M} \times \text{L solution} \\ \text{mol solute} &= 0.375\ \frac{\text{mol sugar}}{\text{L}} \times \left(10\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}\right) \qquad = 0.004\ \text{mol sugar} \end{aligned}$$

Exercise 1.5.2

What volume (mL) of the sweetened tea described in Exercise 1.5.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

Example 1.5.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 1.5.2) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?

Figure 1.5.3: Distilled white vinegar is a solution of acetic acid in water.

Solution

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

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\text{ g CH}_3\text{CO}_2\text{H} \times \frac{1\text{ mol CH}_3\text{CO}_2\text{H}}{60.052\text{ g CH}_3\text{CO}_2\text{H}}}{0.500\text{ L solution}} = 0.839\ M$$

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

Exercise 1.5.3

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

Answer

0.674 M

Example 1.5.4: Determining the Mass of Solute in a Given Volume of Solution

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

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 1.5.3:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{1.5.2}$$

$$\text{mol solute} = M \times \text{L solution} \tag{1.5.3}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\text{ L} = 1.325\text{ mol NaCl} \tag{1.5.4}$$

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

$$1.325\text{ mol NaCl} \times \frac{58.44\text{ g NaCl}}{\text{mol NaCl}} = 77.4\text{ g NaCl} \tag{1.5.5}$$

Exercise 1.5.4

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

Answer

5.55 g $CaCl_2$

We can also perform computations in a single step (Example 1.5.5). This eliminates intermediate steps so that only the final result is rounded.

Example 1.5.5: Determining the Volume of Solution

In Example 1.5.3, we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

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

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \tag{1.5.6}$$

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

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{1.5.7}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{1.5.8}$$

$$75.6 \text{ g } \mathrm{CH_3CO_2H} \left(\frac{\text{mol } \mathrm{CH_3CO_2H}}{60.05 \text{ g}}\right)\left(\frac{\text{L solution}}{0.839 \text{ mol } \mathrm{CH_3CO_2H}}\right) = 1.50 \text{ L solution} \tag{1.5.9}$$

Exercise 1.5.5:

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

Answer

0.370 L

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 1.5.2).

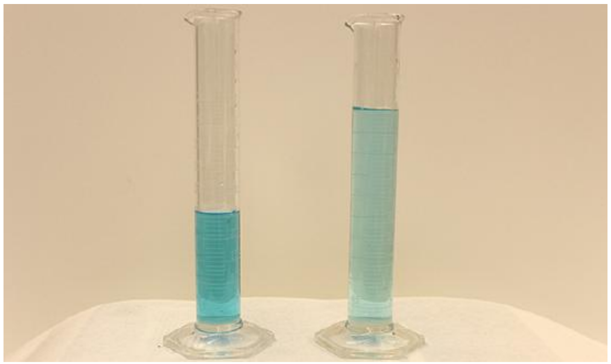

Figure 1.5.2: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated **stock solution**, we can achieve a particular concentration. This is a very common practice for the preparation of a number of common laboratory reagents (Figure 1.5.3) or in full-scale engineering applications where a chemical needs to be dosed into a flow stream for a desired reaction (e.g., coagulation, disinfection).

Figure 1.5.3: A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of KMnO4 in a flask. (credit: modification of work by Mark Ott)

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

$$n = ML \tag{1.5.10}$$

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

$$n_1 = M_1L_1 \tag{1.5.11}$$

$$n_2 = M_2L_2 \tag{1.5.12}$$

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

$$M_1L_1 = M_2L_2 \tag{1.5.13}$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1V_1 = C_2V_2 \tag{1.5.14}$$

where C and V are concentration and volume, respectively.

Example 1.5.6: Determining the Concentration of a Diluted Solution

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

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

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

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

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

Exercise 1.5.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH3OH to 500.0 mL?

Answer

0.102 M CH_3OH

Example 1.5.7: Volume of a Diluted Solution

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

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

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

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

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

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

Exercise 1.5.7

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

Answer

3.76 L

Example 1.5.8: Volume of a Concentrated Solution Needed for Dilution

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

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

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

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

$$V_1 = 0.314\text{ L}$$

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

Exercise 1.5.8

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

Answer

0.261 L

Contributors and Attributions

Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution

solution for which water is the solvent

concentrated

qualitative term for a solution containing solute at a relatively high concentration

concentration

quantitative measure of the relative amounts of solute and solvent present in a solution

dilute

qualitative term for a solution containing solute at a relatively low concentration

dilution

process of adding solvent to a solution in order to lower the concentration of solutes

dissolved

describes the process by which solute components are dispersed in a solvent

molarity (*M*)

unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute

solution component present in a concentration less than that of the solvent

solvent

solution component present in a concentration that is higher relative to other components

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1.6: Other Units for Solution Concentrations

Learning Objectives

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

In the previous section, we introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. In this section, we will introduce some other units of concentration that are commonly used in various applications, either for convenience or by convention.

Mass Percentage

The **mass percentage** of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\% \tag{1.6.1}$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

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

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 1.6.1) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being between 6% and 8% by mass. A 100.0-g sample of bleach solution, including both the bleach itself as well as the water, would therefore contain 7.4 g of NaOCl.

Figure 1.6.1: Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

Example 1.6.1: Calculation of Percent by Mass

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

Solution

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

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

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

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

Exercise 1.6.1

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

Answer

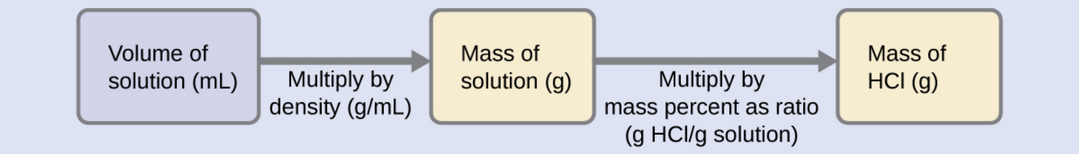
14.8%

Example 1.6.2: Calculations using Mass Percentage

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

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn’t greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or $5 \times 40 = 200\text{ g}$. To derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can convert the solution’s volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



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

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

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

Exercise 1.6.2

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

Answer

282 mL

Volume Percentage

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

$$\text{volume percentage}=\frac{\text{volume solute}}{\text{volume solution}}\times 100\% \tag{1.6.2}$$

Example 1.6.3: Calculations using Volume Percentage

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

Solution

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

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

Exercise 1.6.3

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

Answer

1.5 mol ethanol

Parts per Million and Parts per Billion

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

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

$$\text{ppm}=\frac{\text{mass solute}}{\text{mass solution}}\times 10^6\text{ ppm} \tag{1.6.3}$$

$$\text{ppb}=\frac{\text{mass solute}}{\text{mass solution}}\times 10^9\text{ ppb} \tag{1.6.4}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, EPA's Lead and Copper Rule has maintained the Action Level for lead in drinking water to be 15 ppb. Inline water filters are often used with the intent of reducing the concentration of trace-level contaminants in tap water (Figure 1.6.3).

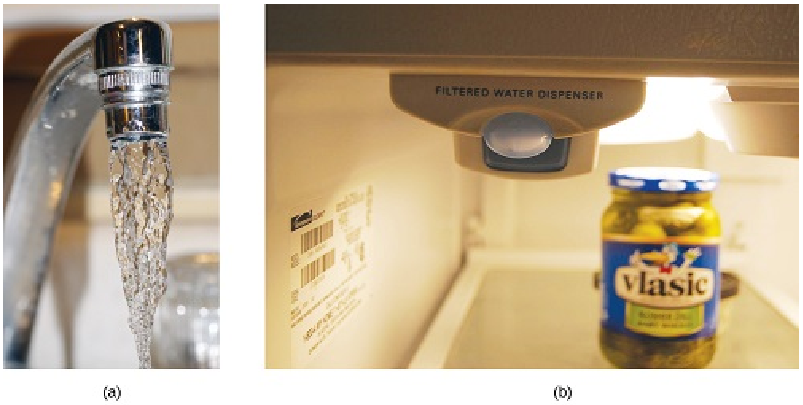


Figure 1.6.3: (a) In some areas, trace-level concentrations of contaminants can render tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons).

Example 1.6.4: Parts per Million and Parts per Billion Concentrations

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

Solution

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

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

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

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

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

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

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

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

Exercise 1.6.4

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

Answer

9.6 ppm, 9600 ppb

Summary

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components’ masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Glossary

mass percentage

ratio of solute-to-solution mass expressed as a percentage

mass-volume percent

ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)

ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)

ratio of solute-to-solution mass multiplied by 10^6

volume percentage

ratio of solute-to-solution volume expressed as a percentage

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1.7: Writing and Balancing Chemical Equations

Learning Objectives

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a chemical equation.

Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 1.7.1, with space-filling molecular models shown in the lower half of the figure.

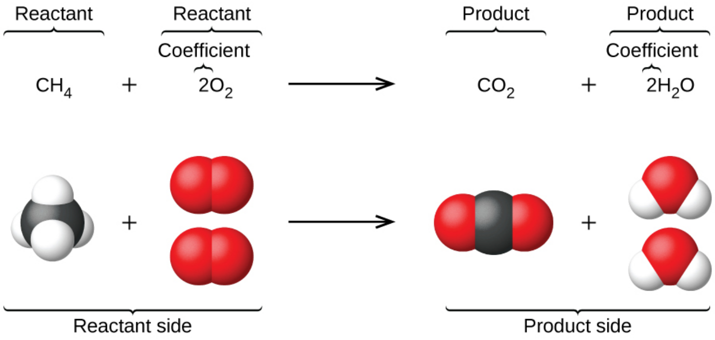

Figure 1.7.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called **products**, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow ($\longrightarrow$) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 1.7.2). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.
- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

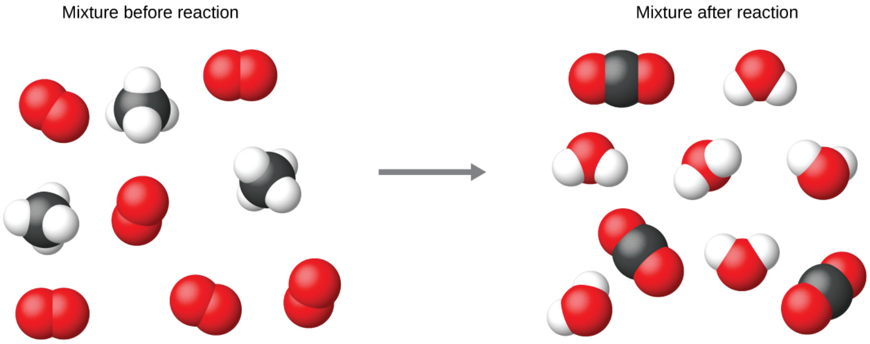

Figure 1.7.2: Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.

Balancing Equations

When a chemical equation is balanced it means that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1 \;\; CO_2 \; \cancel{\text{molecule}} \times \frac{2 \text{ O atoms}}{CO_2 \; \cancel{\text{molecule}}}\right) + \left(2 \, H_2O \; \cancel{\text{molecule}} \times \frac{1 \text{ O atom}}{H_2O \; \cancel{\text{molecule}}}\right) = 4 \text{ O atoms} \tag{1.7.1}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \tag{1.7.2}$$

Element	Reactants (Left Hand Side, or LHS)	Products (Right Hand Side, or RHS)	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$H_2O \rightarrow H_2 + O_2 \tag{unbalanced}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2\,H_2O \rightarrow H_2 + O_2 \tag{unbalanced}$$

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \tag{balanced}$$

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 2	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \tag{1.7.3}$$

Example 1.7.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \rightarrow N_2O_5 \tag{unbalanced}$$

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \tag{unbalanced}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2\,N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \tag{1.7.4}$$

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Exercise 1.7.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$$2\,NH_4NO_3 \rightarrow 2\,N_2 + O_2 + 4\,H_2O$$

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \rightarrow H_2O + CO_2 \qquad \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \rightarrow 3\,H_2O + 2\,CO_2 \qquad \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \tfrac{7}{2}O_2 \rightarrow 3\,H_2O + 2\,CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 6\,H_2O + 4\,CO_2 \tag{1.7.5}$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3\,N_2 + 9\,H_2 \rightarrow 6\,NH_3 \tag{1.7.6}$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \tag{1.7.7}$$

Phet Simulation

Use this interactive tutorial for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include **s for solids, l for liquids, g for gases, and aq for substances dissolved in water** (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\,Na(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + H_2(g) \tag{1.7.8}$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$\mathrm{CaCO_3}(s) \xrightarrow{\Delta} \mathrm{CaO}(s) + \mathrm{CO_2}(g) \tag{1.7.9}$$

Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $\mathrm{CaCl_2}$ and $\mathrm{AgNO_3}$ are mixed, a reaction takes place producing aqueous $\mathrm{Ca(NO_3)_2}$ and solid AgCl:

$$\mathrm{CaCl_2}(aq) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Ca(NO_3)_2}(aq) + 2\,\mathrm{AgCl}(s) \tag{1.7.10}$$

This balanced equation, derived in the usual fashion, is called a molecular equation because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may **dissociate** into their constituent ions, which are subsequently dispersed homogeneously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$\mathrm{CaCl_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \tag{1.7.11}$$

$$2\,\mathrm{AgNO_3}(aq) \rightarrow 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{NO_3^-}(aq) \tag{1.7.12}$$

$$\mathrm{Ca(NO_3)_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq) \tag{1.7.13}$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *(s)*.

Explicitly representing all dissolved ions results in a complete ionic equation. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$\mathrm{Ca^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{NO_3^-}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq) + 2\,\mathrm{Ag\,Cl}(s) \tag{1.7.14}$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $\mathrm{Ca^{2+}(aq)}$ and $\mathrm{NO_3^-}(aq)$. These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a net ionic equation:

$$\cancel{\mathrm{Ca^{2+}}(aq)} + 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Ag^+}(aq) + \cancel{2\,\mathrm{NO_3^-}(aq)} \rightarrow \cancel{\mathrm{Ca^{2+}}(aq)} + \cancel{2\,\mathrm{NO_3^-}(aq)} + 2\,\mathrm{AgCl}(s) \tag{1.7.15}$$

$$2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Ag^+}(aq) \rightarrow 2\,\mathrm{AgCl}(s) \tag{1.7.16}$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$\mathrm{Cl^-}(aq) + \mathrm{Ag^+}(aq) \rightarrow \mathrm{AgCl}(s) \tag{1.7.17}$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of $\mathrm{Cl^-}$ and $\mathrm{Ag^+}$.

Example 1.7.2: Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$\mathrm{CO_2(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)} \qquad \text{(unbalanced)}$$

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$\mathrm{CO_2(aq)^{+}_{2}NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O}(l)$$

The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:

$$\mathrm{CO_2(aq) + 2\,Na^{+}(aq) + 2\,OH^{-}(aq) \rightarrow 2\,Na^{+}(aq) + CO_3^{2-}(aq) + H_2O(l)}$$

Finally, identify the spectator ion(s), in this case $Na^{+}(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$\begin{aligned} \mathrm{CO_2}(aq) + \cancel{2\,\mathrm{Na^{+}}(aq)} + 2\,\mathrm{OH^{-}}(aq) &\rightarrow \cancel{2\,\mathrm{Na^{+}}(aq)} + \mathrm{CO_3^{2-}}(aq) + \mathrm{H_2O}(l) \\ \mathrm{CO_2}(aq) + 2\,\mathrm{OH^{-}}(aq) &\rightarrow \mathrm{CO_3^{2-}}(aq) + \mathrm{H_2O}(l) \end{aligned}$$

Exercise 1.7.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$\mathrm{NaCl(aq) + H_2O(l) \xrightarrow{\mathit{electricity}} NaOH(aq) + H_2(g) + Cl_2(g)}$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

Balanced molecular equation:

\ce{2NaCl}(aq)+\ce{2H2O}(l)\rightarrow \ce{2NaOH}(aq)+\ce{H2}(g)+\ce{Cl2}(g)} \nonumber

Balanced ionic equation:

\ce{2Na+}(aq)+\ce{2Cl-}(aq)+\ce{2H2O}(l)\rightarrow \ce{2Na+}(aq)+\ce{2OH-}(aq)+\ce{H2}(g)+\ce{Cl2}(g)} \nonumber

Balanced net ionic equation:

\ce{2Cl-}(aq)+\ce{2H2O}(l)\rightarrow \ce{2OH-}(aq)+\ce{H2}(g)+\ce{Cl2}(g) } \nonumber

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Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Glossary

balanced equation

chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation

symbolic representation of a chemical reaction

coefficient

number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation

chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation

chemical equation in which all reactants and products are represented as neutral substances

net ionic equation

chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product

substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant

substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion

ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

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CHAPTER OVERVIEW

2: Equilibrium

2.1: Equilibrium Introduction

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

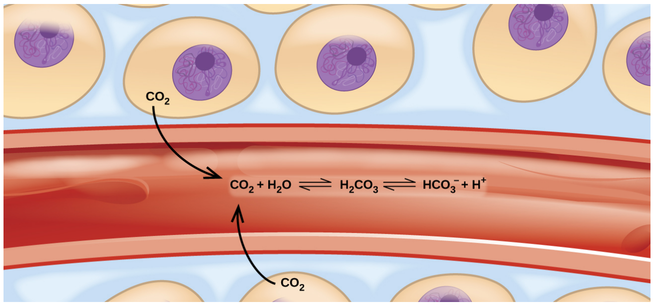

Figure $2.1.1$: Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions. An image depicts three tan squares, lying side-by-side along the upper left corner. Two of the same squares also lie side-by-side in the lower right corner. Each square has a black dot in the center. One of the squares is labeled, “C O subscript 2,” and has a double-headed arrow pointing from it to a red tube-like structure that runs between the squares across the image from the upper right to the lower left. This arrow is labeled, “C O subscript 2 dissolved in plasma.” The red tube has two round red shapes in it, and the upper one is labeled, “C O subscript 2 carried in red blood cells.” The gaps between the squares and the red tube are colored light blue. One of the squares along the top of the image is labeled, “C O subscript 2,” and is connected by a double-headed arrow to an equation in the red tube that is labeled, “C O subscript 2, a plus sign, H subscript 2 O, right-facing arrow, H subscript 2 C O subscript 3, right-facing arrow, H C O subscript 3 superscript negative sign, plus sign, H superscript positive sign.” The compound “H C O subscript 3 superscript negative sign” is then connected by a double-headed arrow to the space in the red tube and is labeled, “H C O subscript 3 superscript negative sign dissolved in plasma as carbonic acid.”

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (HCO_3^-) (Figure $2.1.1$). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

2.2: Chemical Equilibria

Learning Objectives

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

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

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

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{2.2.1}$$

The color becomes darker as $\mathrm{N_2O_4}$ is converted to $\mathrm{NO_2}$. When the system reaches equilibrium, both $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ are present (Figure 2.2.1).

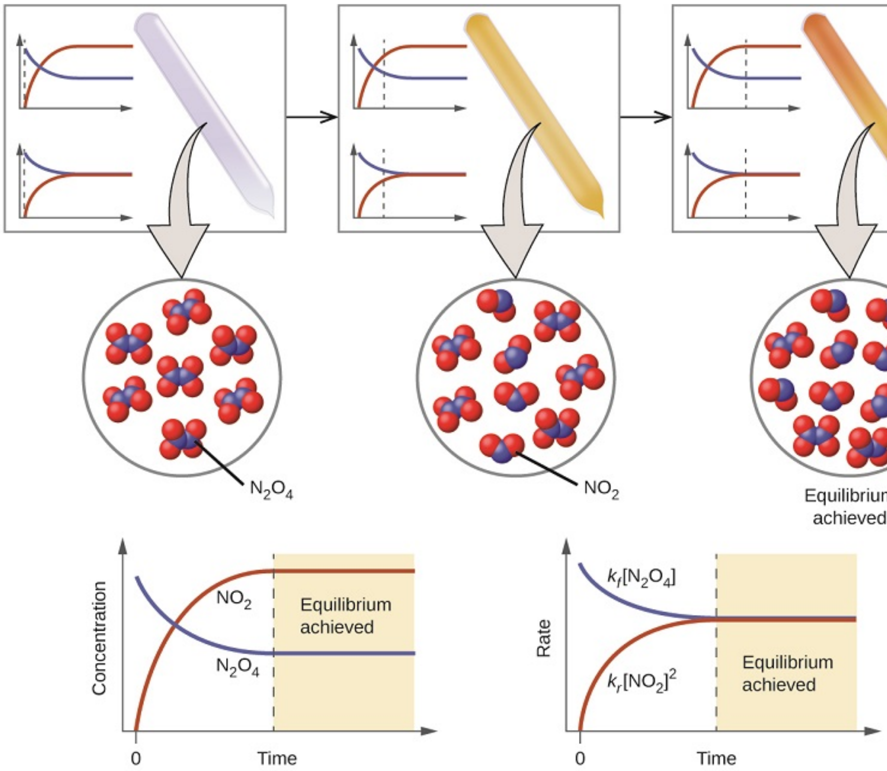

Figure 2.2.1: A mixture of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ moves toward equilibrium. Colorless $\mathrm{N_2O_4}$ reacts to form brown $\mathrm{NO_2}$. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of $\mathrm{NO_2}$.

The formation of $\mathrm{NO_2}$ from $\mathrm{N_2O_4}$ is a reversible reaction, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of $\mathrm{NO_2}$ from $\mathrm{N_2O_4}$, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can $\mathrm{N_2O_4}$ decompose to form $\mathrm{NO_2}$, but the $\mathrm{NO_2}$ produced can react to form $\mathrm{N_2O_4}$. As soon as the forward reaction produces any $\mathrm{NO_2}$, the reverse reaction begins and $\mathrm{NO_2}$ starts to react to form $\mathrm{N_2O_4}$. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure $2.2.2$).

Figure $2.2.2$: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which they receive clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure $2.2.1$.

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

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure $2.2.1$ shows the reaction:

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{2.2.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure $2.2.1$, the rate of the forward reaction

$$\mathrm{2\,NO_2(g) \rightarrow N_2O_4(g)} \tag{2.2.3}$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4(g) \rightarrow 2\,NO_2(g)} \tag{2.2.4}$$

Equilibrium and Soft Drinks

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

$$\mathrm{H_2SO_4(l) + CaCO_3(s) \rightarrow CO_2(g) + H_2O(l) + CaSO_4(aq)}$$

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

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

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure 2.2.3). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."

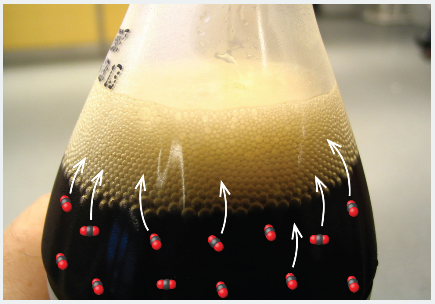

Figure 2.2.3: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

Sublimation of Bromine

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

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

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 2.2.4 shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.

Figure 2.2.4: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: http://images-of-elements.com/bromine.php).

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Summary

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

Glossary

equilibrium

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

reversible reaction

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

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2.3: Equilibrium Constants and Reaction Quotients

Learning Objectives

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol ($\rightleftharpoons$) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$m\mathrm{A} + n\mathrm{B} + \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{2.3.1}$$

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c or just Q. For now, we use brackets to indicate molar concentrations of reactants and products. (The proper approach is to use a term called the chemical's 'activity,' or reactivity. But, in relatively dilute systems the activity of each reaction species is very similar to its molar concentration or, as we will see below, its partial pressure.)

$$Q = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \tag{2.3.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)} \tag{2.3.3}$$

is given by this expression:

$$Q = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{2.3.4}$$

Example 2.3.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,\mathrm{O}_{2(g)} \rightleftharpoons 2\,\mathrm{O}_{3(g)}$
b. $\mathrm{N}_{2(g)} + 3\,\mathrm{H}_{2(g)} \rightleftharpoons 2\,\mathrm{NH}_{3(g)}$
c. $4\,\mathrm{NH}_{3(g)} + 7\,\mathrm{O}_{2(g)} \rightleftharpoons 4\,\mathrm{NO}_{2(g)} + 6\,\mathrm{H_2O}_{(g)}$

Solution

a. $Q = \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3}$
b. $Q = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$
c. $Q = \frac{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}$

Exercise 2.3.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
b. $\mathrm{C_4H_8}(g) \rightleftharpoons 2\,\mathrm{C_2H_4}(g)$
c. $2\,\mathrm{C_4H_{10}}(g) + 13\,\mathrm{O_2}(g) \rightleftharpoons 8\,\mathrm{CO_2}(g) + 10\,\mathrm{H_2O}(g)$

Answer a

$$Q_c = \frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$$

Answer b

$$Q_c = \frac{[\mathrm{C_2H_4}]^2}{[\mathrm{C_4H_8}]}$$

Answer c

$$Q_c = \frac{[\mathrm{CO_2}]^8[\mathrm{H_2O}]^{10}}{[\mathrm{C_4H_{10}}]^2[\mathrm{O_2}]^{13}}$$

The numeric value of Q for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q is determined. When pure reactants are mixed, Q is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure $2.3.1$). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

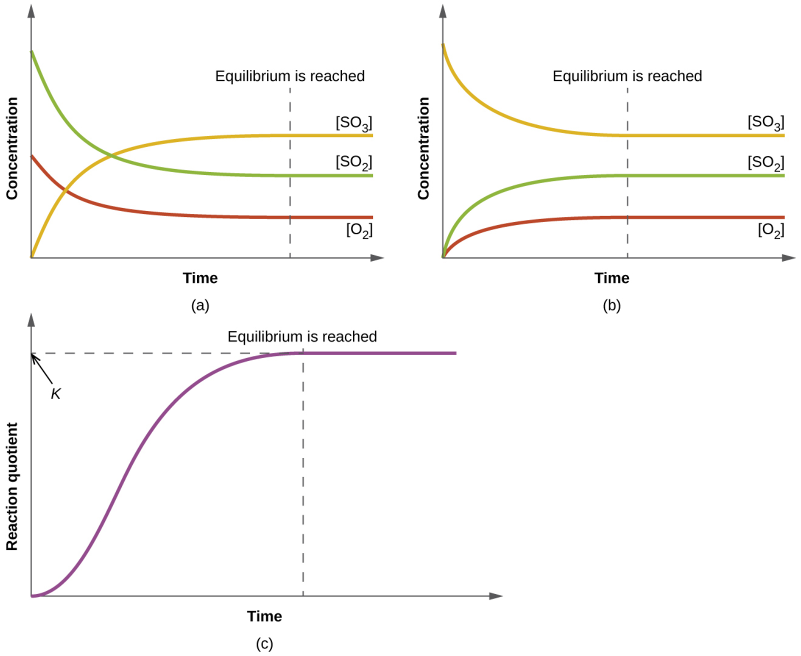

Figure $2.3.1$: (a) The change in the concentrations of reactants and products is depicted as the $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

When a mixture of reactants and products reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the **equilibrium constant** (K) of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it could be noted as K_c. But we will more often call it K_{eq}.

The phenomenon of a reaction quotient always reaching the same value at equilibrium can be expressed as:

$$Q \text{ at equilibrium} = K_{eq} = \frac{[\mathrm{C}]^x[\mathrm{D}]^y\ldots}{[\mathrm{A}]^m[\mathrm{B}]^n\ldots} \tag{2.3.5}$$

This equation is a mathematical statement of the **Law of Mass Action**: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 2.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[NO_2]$ = 0.016 M and $[N_2O_4]$ = 0.042 M.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[NO_2] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\,M$, and $[N_2O_4]$ = 0 M. Thus,

$$Q = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0 \tag{2.3.6}$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_{eq} = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2. \tag{2.3.7}$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_{eq} value should be M^{-1}. However, it is common practice to omit units for K_{eq} values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless 'activities' instead of concentrations, and so K_{eq} values are truly unitless.

Exercise 2.3.2

For the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

the concentrations at equilibrium are $[SO_2]$ = 0.90 M, $[O_2]$ = 0.35 M, and $[SO_3]$ = 1.1 M. What is the value of the equilibrium constant, K_{eq}?

Answer

K_{eq} = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_{eq} indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_{eq}—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_{eq} is known for a reaction, it can be used to predict directional shifts when compared to the value of Q. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 2.3.2 illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q changes until it equals the value of K_{eq}). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_eq = 0.640 \quad \mathrm{T} = 800^\circ\mathrm{C} \tag{2.3.8}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 2.3.2 when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

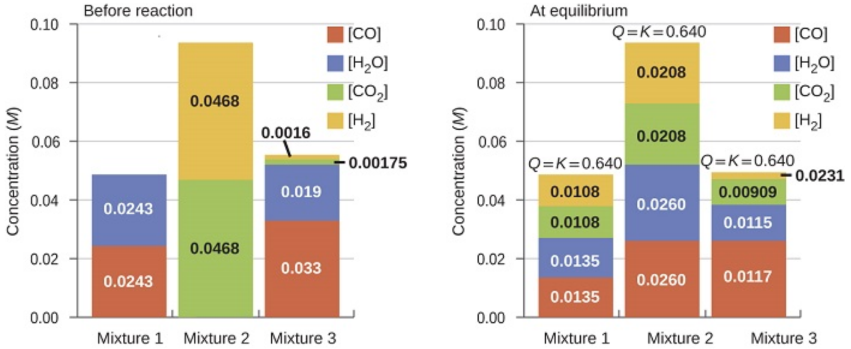

Figure 2.3.2: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 2.3.8).

Example 2.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO}(g)+\mathrm{H_2O}(g)\rightleftharpoons \mathrm{CO_2}(g)+\mathrm{H_2}(g)$$

with $K_{eq}=0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[\mathrm{CO}]_\mathrm{i}$	0.0203 *M*	0.011 *M*	0.0094 *M*
$[\mathrm{H_2O}]_\mathrm{i}$	0.0203 *M*	0.0011 *M*	0.0025 *M*
$[\mathrm{CO_2}]_\mathrm{i}$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[\mathrm{H_2}]_\mathrm{i}$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q=\frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]}=\frac{(0.0040)(0.0040)}{(0.0203)(0.0203)}=0.039.$$

$Q < K_{eq}$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q=\frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]}=\frac{(0.037)(0.046)}{(0.011)(0.0011)}=1.4\times 10^2$$

$Q > K_{eq}$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q=\frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]}=\frac{(0.0015)(0.0076)}{(0.0094)(0.0025)}=0.48$$

$Q < K_{eq}$ (0.48 < 0.64)

The reaction will shift to the right.

Exercise 2.3.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g) \quad K_{eq} = 4.6\times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \quad K_{eq} = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \quad K_{eq} = 0.230$$

Answer a

$Q = 6.45 \times 10^3$, shifts right.

Answer b

$Q = 0.12$, shifts left.

Answer c

$Q = 0$, shifts right

In Example 2.3.2, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_{eq} values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. A few important aspects of using this approach to equilibrium:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.

As a consequence of this last consideration, Q and K_{eq} expressions do not contain terms for solids or liquids (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$\mathrm{C_2H_2}(aq) + 2\,\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \tag{2.3.9}$$

with associated equilibrium constant

$$K_{eq} = \frac{[\mathrm{C_2H_2Br_4}]}{[\mathrm{C_2H_2}][\mathrm{Br_2}]^2} \tag{2.3.10}$$

Example 2

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{2.3.11}$$

with associated equilibrium constant

$$K_{eq} = \frac{[I_3^-]}{[I_2][I^-]} \tag{2.3.12}$$

Example 3

$$Hg_2^{2+}(aq) + NO_3^-(aq) + 3\,H_3O^+(aq) \rightleftharpoons 2\,Hg^{2+}(aq) + HNO_2(aq) + 4\,H_2O(l) \tag{2.3.13}$$

with associated equilibrium constant

$$K_{eq} = \frac{[Hg^{2+}]^2[HNO_2]}{[Hg_2^{2+}][NO_3^-][H_3O^+]^3} \tag{2.3.14}$$

Example 4

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \tag{2.3.15}$$

with associated equilibrium constant

$$K_{eq} = \frac{[H_3O^+][F^-]}{[HF]} \tag{2.3.16}$$

Example 5

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{2.3.17}$$

with associated equilibrium constant

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{2.3.18}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, its concentration **does not** appear as a term in the K_{eq} expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \tag{2.3.19}$$

with associated equilibrium constant

$$K_{eq} = \frac{[C_2H_4][H_2]}{[C_2H_6]} \tag{2.3.20}$$

Example 2

$$3\,O_2(g) \rightleftharpoons 2\,O_3(g) \tag{2.3.21}$$

with associated equilibrium constant

$$K_{eq} = \frac{[O_3]^2}{[O_2]^3} \tag{2.3.22}$$

Example 3

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{2.3.23}$$

with associated equilibrium constant

$$K_{eq} = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} \tag{2.3.24}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{2.3.25}$$

with associated equilibrium constant

$$K_{eq} = \frac{[\mathrm{CO_2}]^3[\mathrm{H_2O}]^4}{[\mathrm{C_3H_8}][\mathrm{O_2}]^5} \tag{2.3.26}$$

Note that the concentration of $\mathrm{H_2O}_{(g)}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where *M* is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{2.3.27}$$

$$P = \left(\frac{n}{V}\right) RT \tag{2.3.28}$$

$$= MRT \tag{2.3.29}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{2.3.30}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{2.3.31}$$

In this equation we could use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of C_2H_6; $P_{\mathrm{H_2}}$, the partial pressure of H_2; and $P_{\mathrm{C_2H_6}}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{2.3.32}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

However, the utility of Q and K is often found in comparing the two to one another in order to examine reaction spontaneity in either direction. So, if gases are used to calculate one, gases can be used to calculate the other. Likewise, if concentrations are used to calculate one parameter, concentrations can be used to calculate the other. Therefore, for this course we will use partial pressures for gases and molar concentrations for aqueous solutes, all in the same expressions as shown below. Examples using this approach will be provided in class, as in-class activities, and in homework.

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$\mathrm{PbCl_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \tag{2.3.33}$$

with associated equilibrium constant

$$K_{eq} = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \tag{2.3.34}$$

Example 1

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{2.3.35}$$

with associated equilibrium constant

$$K_{eq} = \frac{1}{P_{\mathrm{CO_2}}} \tag{2.3.36}$$

Example 1

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{2.3.37}$$

with associated equilibrium constant

$$K_{eq} = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{2.3.38}$$

Summary

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

Key Equations

- $Q = \dfrac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \quad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q = \dfrac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n} \quad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$

Glossary

equilibrium constant (K_{eq})

value of the reaction quotient for a system when at equilibrium, when the rate of forward reaction equals the rate of reverse reaction

heterogeneous equilibria

equilibria between reactants and products in different phases

homogeneous equilibria

equilibria within a single phase

Law of Mass Action

when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (Q)

ratio of the product of activities (in dilute solutions, molar concentrations or pressures) of the products to that of the reactants, each activity (or M concentration or pressure) value being raised to the power equal to the coefficient in the equation

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2.4: Le Chatelier’s Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier’s principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by **Le Chatelier's principle:** When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)} \tag{2.4.1}$$

$$K_{eq} = 50.0 \text{ at } 400^\circ C \tag{2.4.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q = K_{eq} = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_{eq} \tag{2.4.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that, while equilibrium constants are defined with chemical activity, we typically approximate chemical activity with either concentration or partial pressure. Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \tag{2.4.4}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{2.4.5}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved. Delta H, or the change in enthalpy, is a topic we will learn about in a few pages from now.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4 \text{ kJ (exothermic)} \tag{2.4.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \text{heat} \tag{2.4.7}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20 \text{ kJ} \tag{2.4.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{2.4.9}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Catalysts Do Not Affect Equilibrium

A catalyst can speed up the rate (kinetics) of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

Case Study: Synthesis of Industrial Ammonia

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.4.10}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. It is used in the production of fertilizers and is a fertilizer itself. Large quantities of ammonia are also converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.4.11}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat shifts the reaction to the right.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is still slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)} \quad \Delta H = -92.2\ \mathrm{kJ} \tag{2.4.12}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure $2.4.2$).

However, the benefit of this 'fixed' nitrogen comes at a significant cost. First, the energy consumed to generate the high temperatures and pressures in this process has historically been created from the combustion of fossil fuels such as natural gas. The concentration of the combustion product, carbon dioxide, has risen steadily in Earth's atmosphere since the industrial revolution, driving anthropogenic climate change. Second, the readily available fixed nitrogen makes it more likely that agricultural fields are overfertilized. Rain falling on and running off of cropland carries excess nitrogen (and phosphorus) towards surface waterways such as streams, rivers, and estuaries where those nutrients, combined with abundant sunlight and atmospheric CO2, stimulate algal blooms. These algal blooms have led to rampant eutrophication and deterioration of marine fisheries and water quality, both of which carry negative implications for economies, human health, and quality of life. As a result, more sustainable approaches to nutrient management are being considered by modern society to reduce the abundance of industrial fixed nitrogen production. These include more sustainable farming practices, nutrient recovery from waste streams, and others. Indeed, "Manage the Nitrogen Cycle" is one of the Grand Challenges for engineers set forth by the National Academy of Engineering.

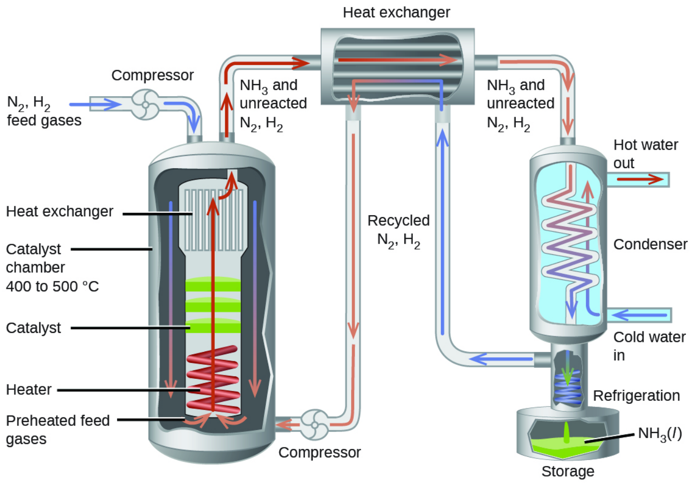

Figure 2.4.2: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Table 2.4.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

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CHAPTER OVERVIEW

3: Thermodynamics

3.1: Prelude to Thermochemistry

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2019, about 80% of US energy consumption came from the combustion of fossil carbon energy sources, 8% from nuclear reactions, and 11% from renewable sources. We use this energy for residential energy (16%); to transport food, raw materials, manufactured goods, and people (37%); for industrial production (35%); and for commercial facilities (12%).[1] While these energy systems help us meet our essential needs, combustion of the fossil fuel sources are the primary contributor to global anthropogenic climate change.

Figure 3.1.1: Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes).

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

Footnotes

1. US Energy Information Administration, *Total Energy, Annual Energy Review*, https://www.eia.gov/totalenergy/data/annual/ Data derived from US Energy Information Administration (August 2020).

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3.2: Energy Basics

Learning Objectives

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 3.2.1). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We continue to burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.


(a) (b) (c)

Figure 3.2.1: The energy involved in chemical changes is important to our daily lives: (a) A veggie burger provides hundreds of calories for metabolic processes ; (b) the combustion of liquid fuel transforms stored chemical energy into mechanical energy to drive vehicles; and (c) coke, a processed form of coal, provides the energy to convert iron ore into iron, which is used for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner; additional modifications by K. Gilmore).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the **energetics** of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. Energy providers and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 3.2.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.

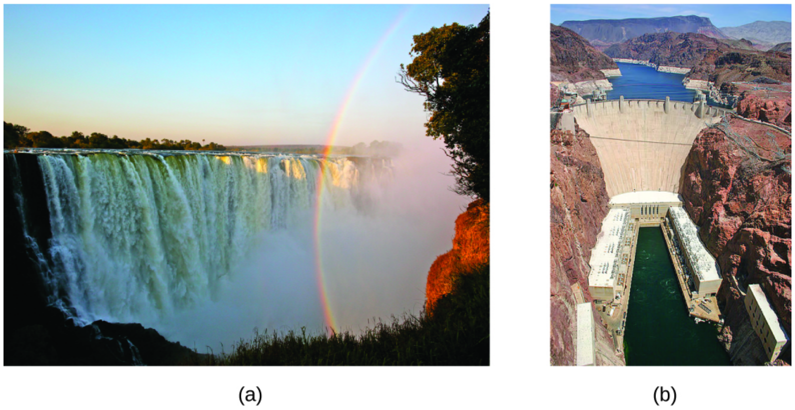


Figure 3.2.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the **Law of Conservation of Energy**: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the First Law of Thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the Law of Conservation of Matter, there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 3.2.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

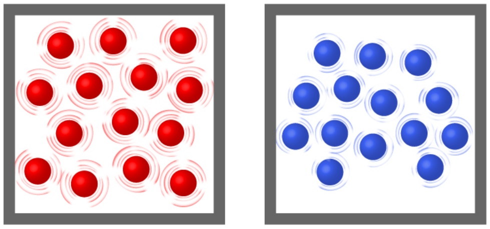
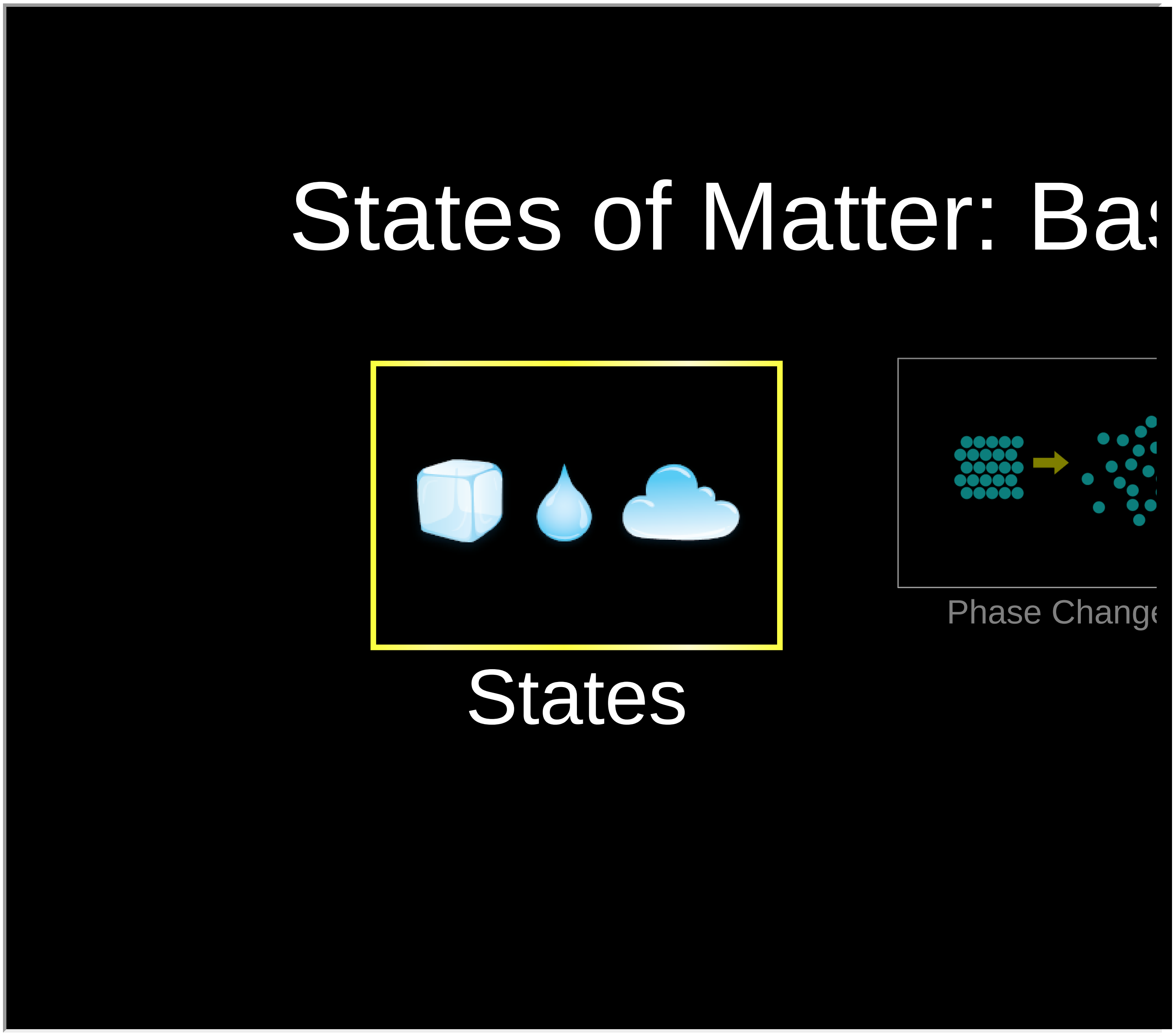


Figure 3.2.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.



States of Matter: Bas

States

Phase Chang

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 3.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

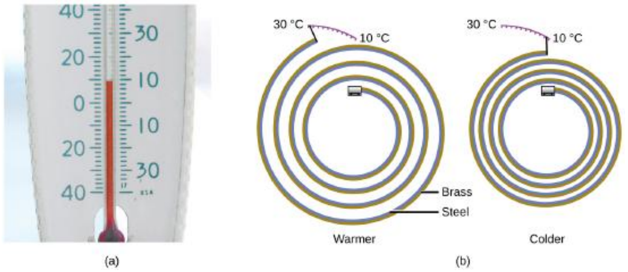


Figure 3.2.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr).

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 3.2.5).

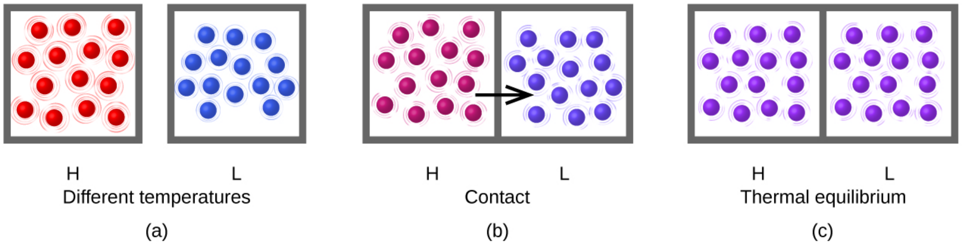


Figure 3.2.5: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic** process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch’s flame (Figure 3.2.6a). A reaction or change that absorbs heat is an **endothermic** process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

Figure 3.2.6: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by “Skatebiker”/Wikimedia commons).

Measuring Energy and Heat Capacity

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy change in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity** (C) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{3.2.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an **extensive property**—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ °C}} = 363 \text{ J/°C} \tag{3.2.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ °C}} = 1814 \text{ J/°C} \tag{3.2.3}$$

The **specific heat capacity** (c) of a substance, commonly called its "**specific heat**," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{\text{m}\Delta \text{T}} \tag{3.2.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an **intensive property**—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{3.2.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{3.2.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure $3.2.7$).

Figure 3.2.7: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 3.2.1.

Table 3.2.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	$Al(s)$	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	$Ar(g)$	0.522
iron	$Fe(s)$	0.449
copper	$Cu(s)$	0.385
lead	$Pb(s)$	0.130
gold	$Au(s)$	0.129
silicon	$Si(s)$	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, q, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q &= (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change}) \\ q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned}$$

In this equation, c is the specific heat of the substance, m is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of q is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of q is negative.

Example 3.2.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

$$= (4.184\ \text{J}/\cancel{\text{g}}\,^\circ\text{C}) \times (800\ \cancel{\text{g}}) \times (85 - 21)^\circ\text{C}$$

$$= (4.184\ \text{J}/\cancel{\text{g}}\,^\circ\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^\circ\cancel{\text{C}}$$

$$= 210,000\ \text{J}(= 210\ \text{kJ})$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 3.2.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 3.2.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \tag{3.2.7}$$

Substituting the known values:

$$6,640\ \text{J} = c \times (348\ \text{g}) \times (43.6 - 22.4)\ ^\circ\text{C} \tag{3.2.8}$$

Solving:

$$c = \frac{6,640\ \text{J}}{(348\ \text{g}) \times (21.2^\circ\text{C})} = 0.900\ \text{J/g}\ ^\circ\text{C} \tag{3.2.9}$$

Comparing this value with the values in Table 3.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 3.2.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45\ \mathrm{J/g}\ ^\circ\mathrm{C}$; the metal is likely to be iron from checking Table 3.2.1

Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 3.2.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

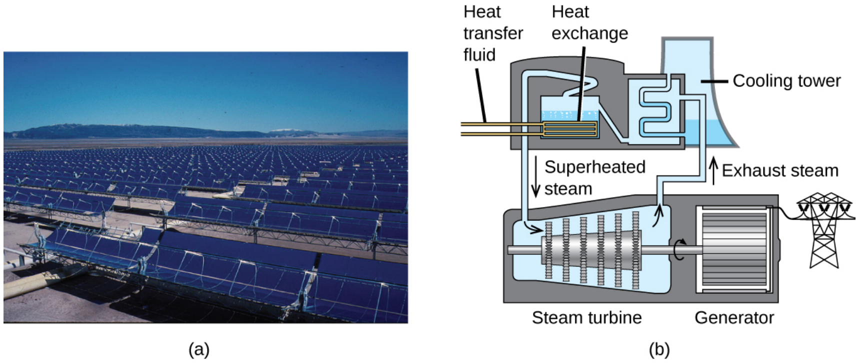


Figure 3.2.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 3.2.9). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.

(a)

(b)

Figure 3.2.9: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

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Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (*q*)

transfer of thermal energy between two bodies

heat capacity (*C*)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (*c*)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (*w*)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

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3.3: Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure $3.3.1$). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

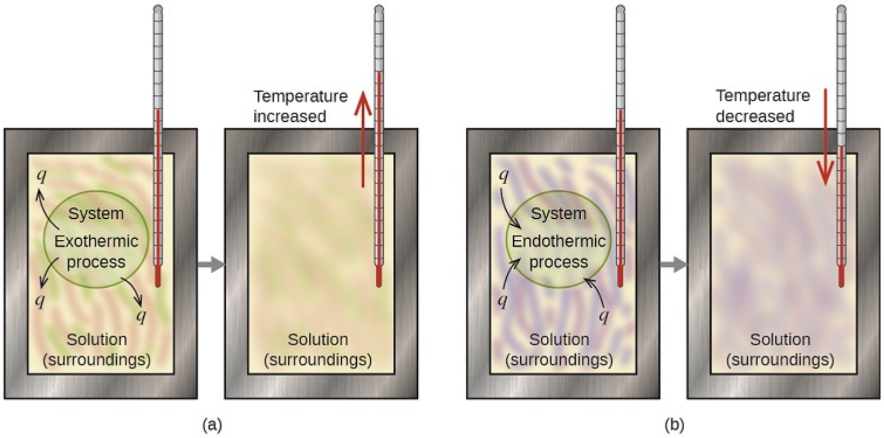


Figure $3.3.1$: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system. Two diagrams labeled a and b are shown. Each is made up of two rectangular containers with a thermometer inserted into the top right and extending inside. There is a right facing arrow connecting each box in each diagram. The left container in diagram a depicts a pink and green swirling solution with the terms “Exothermic process” and “System” written in the center with arrows facing away from the terms pointing to “q.” The labels “Solution” and “Surroundings” are written at the bottom of the container. The right container in diagram a has the term “Solution” written at the bottom of the container and a red arrow facing up near the thermometer with the phrase “Temperature increased” next to it. The pink and green swirls are more blended in this container. The left container in diagram b depicts a purple and blue swirling solution with the terms “Endothermic process” and “System” written in the center with arrows facing away from the terms and “Solution” and “Surroundings” written at the bottom. The arrows point away from the letter “q.” The right container in diagram b has the term “Solution” written at the bottom and a red arrow facing down near the thermometer with the phrase “Temperature decreased” next to it. The blue and purple swirls are more blended in this container.

> By convention, q is given a negative (-) sign when the system releases heat to the surroundings (exothermic); q is given a positive (+) sign when the system absorbs heat from the surroundings (endothermic).

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure $3.3.2$). These easy-to-use “coffee cup” calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

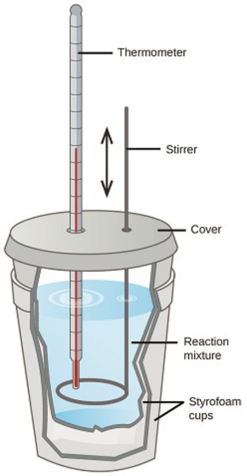


Figure $3.3.2$ A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture. Two Styrofoam cups are shown nested in one another with a cover over the top. A thermometer and stirring rod are inserted through the cover and into the solution inside the cup, which is shown as a cut-away. The stirring rod has a double headed arrow next to it facing up and down. The liquid mixture inside the cup is labeled “Reaction mixture.”

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure $3.3.3$).

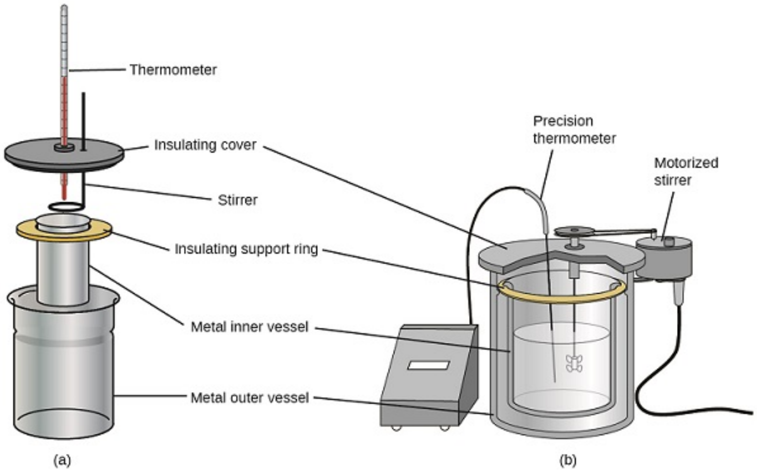


Figure $3.3.3$ Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research. Two diagrams are shown and labeled a and b. Diagram a depicts a thermometer which passes through a disk-like insulating cover and into a metal cylinder which is labeled “metal inner vessel,” which is in turn nested in a metal cylinder labeled “metal outer vessel.” The inner cylinder rests on an insulating support ring. A stirrer passes through the insulating cover and into the inner cylinder as well. Diagram b shows an inner metal vessel half full of liquid resting on an insulating support ring and nested in a metal outer vessel. A precision temperature probe and motorized stirring rod are placed into the solution in the inner vessel and connected by wires to equipment exterior to the set-up.

Before we practice calorimetry problems involving chemical reactions, consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure $3.3.4$). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter’s surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{3.3.1}$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{3.3.2}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{substance\ M}$ and $q_{substance\ W}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{substance\ M}$ is a negative value and $q_{substance\ W}$ is positive, since heat is transferred from M to W.

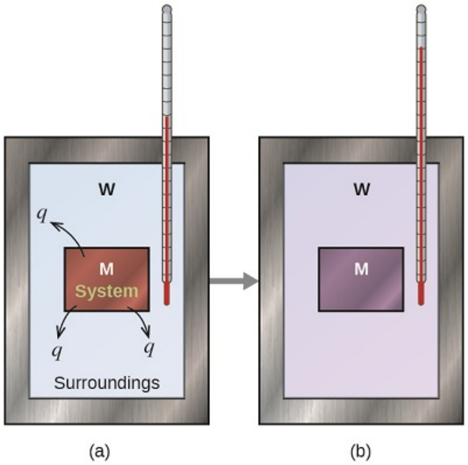


Figure $3.3.4$ In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature. Two diagrams are shown and labeled a and b. Each diagram is composed of a rectangular container with a thermometer inserted inside from the top right corner. Both containers are connected by a right-facing arrow. Both containers are full of water, which is depicted by the letter “W,” and each container has a square in the middle which represents a metal which is labeled with a letter “M.” In diagram a, the metal is drawn in brown and has three arrows facing away from it. Each arrow has the letter “q” at its end. The metal is labeled “system” and the water is labeled “surroundings.” The thermometer in this diagram has a relatively low reading. In diagram b, the metal is depicted in purple and the thermometer has a relatively high reading.

✓ Example 3.3.1: Heat Transfer between Substances at Different Temperatures

A hot 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water is measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the surroundings, then heat given off by rebar = − heat taken in by water, or:

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

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g}\ ^{\circ}\text{C})(360\text{g})(42.7^{\circ}\text{C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g}\ ^{\circ}\text{C})(425\ \text{g})(42.7^{\circ}\text{C} - 24.0^{\circ}\text{C})$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g}\ ^{\circ}\text{C})(425\ \text{g})(42.7^{\circ}\text{C} - 24.0^{\circ}\text{C})}{(0.449\ \text{J/g}\ ^{\circ}\text{C})(360\ \text{g})} + 42.7^{\circ}\text{C}$$

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

? Exercise $3.3.1A$

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6 °C.

? Exercise $3.3.1B$

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.7 °C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

✓ Example 3.3.2: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = −heat taken in by water, or:

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

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\text{ g})(28.5^\circ\text{C} - 100.0^\circ\text{C}) = -(4.18\text{ J/g }^\circ\text{C})(60.0\text{ g})(28.5^\circ\text{C} - 22.0^\circ\text{C})$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\text{ J/g }^\circ\text{C})(60.0\text{ g})(6.5^\circ\text{C})}{(59.7\text{ g})(-71.5^\circ\text{C})} = 0.38\text{ J/g }^\circ\text{C}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

? Exercise 3.3.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$c_{metal} = 0.13\ J/g\ ^\circ C$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the “system”), q_{reaction}, plus the heat absorbed or lost by the solution (the “surroundings”), $q_{solution}$, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{3.3.3}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{3.3.4}$$

This concept lies at the heart of all calorimetry problems and calculations.

✓ Example 3.3.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184 \text{ J/g }^\circ\text{C})(1.0 \times 10^2 \text{ g})(28.9\,^\circ\text{C} - 22.0\,^\circ\text{C}) = 2.89 \times 10^3 \text{ J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.89 \times 10^3\ J$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

? Exercise 3.3.3

When 100 mL of 0.200 M NaCl(*aq*) and 100 mL of 0.200 M AgNO_3(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer

$1.34 \times 10^3\ J$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 3.3.5). A common reusable hand warmer contains a supersaturated solution of $\text{NaC}_2\text{H}_3\text{O}_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $\text{NaC}_2\text{H}_3\text{O}_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\text{NaC}_2\text{H}_3\text{O}_2(aq) \longrightarrow \text{NaC}_2\text{H}_3\text{O}_2(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $\text{NaC}_2\text{H}_3\text{O}_2$ redissolves and can be reused.

Figure 3.3.5 Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube) A series of three photos is shown. There are two right-facing arrows connecting one photo to the next. The first photo shows a chemical hand warmer. It is a bag that contains a clear, colorless liquid. There is a white disk located to the right inside the bag. The second photo shows the same thing, except the white disc has become a white, cloudy substance. The third photo shows the entire bag filled with this white substance.

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$2\,\mathrm{Fe(s)} + \tfrac{3}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{Fe_2O_3(s)}.\ n$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

✓ Example 3.3.4: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack” (Figure 3.3.5). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of *q* for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.

Figure 3.3.5 An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{\mathrm{rxn}} = -q_{\mathrm{soln}}$$

with “rxn” and “soln” used as shorthand for “reaction” and “solution,” respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{\mathrm{rxn}} &= -q_{\mathrm{soln}} = -(c \times m \times \Delta T)_{\mathrm{soln}} \\ &= -[(4.184\mathrm{J/g}\ ^\circ\mathrm{C}) \times (53.2\ \mathrm{g}) \times (20.3\,^\circ\mathrm{C} - 24.9\,^\circ\mathrm{C})] \\ &= -[(4.184\mathrm{J/g}\ ^\circ\mathrm{C}) \times (53.2\ \mathrm{g}) \times (-4.6\,^\circ\mathrm{C})] \\ &+1.0 \times 10^3\ \mathrm{J} = +1.0\ \mathrm{kJ} \end{aligned}$$

The positive sign for *q* indicates that the dissolution is an endothermic process.

Exercise 3.3.4

When a 3.00-g sample of KCl was added to 3.00 × 10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

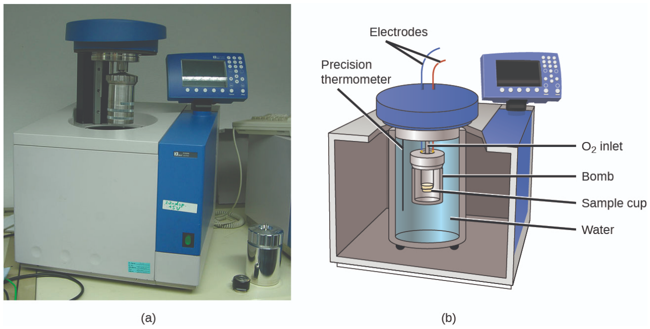
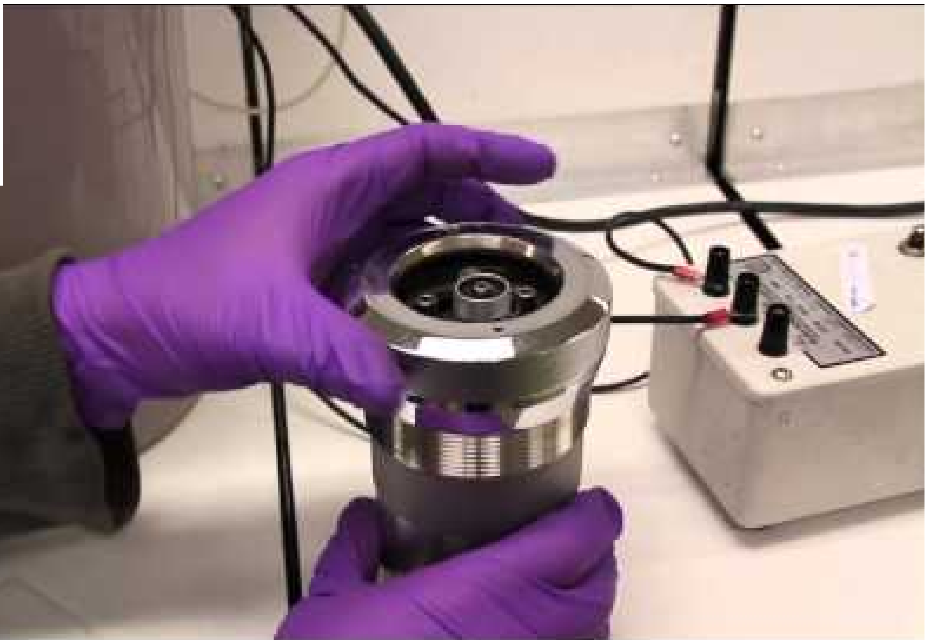


Figure 3.3.6 (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons) A picture and a diagram are shown, labeled a and b, respectively. Picture a depicts a bomb calorimeter. It is a cube-shaped machine with a cavity in the top, a metal cylinder that is above the cavity, and a read-out panel attached to the top-right side. Diagram b depicts a cut away figure of a cube with a cylindrical container full of water in the middle of it. Another container, labeled "bomb," sits inside of a smaller cylinder which holds a sample cup and is nested in the cylindrical container surrounded by the water. A black line extends into the water and is labeled "Precision thermometer." Two wires labeled "Electrodes" extend away from a cover that sits on top of the interior container. A read-out panel is located at the top right of the cube.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure 3.3.6). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.



Video $3.3.1$: Video of view how a bomb calorimeter is prepared for action.

✓ Example $3.3.5$: Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ &= -[(4.184\ \text{J/g}\ ^\circ\text{C}) \times (775\ \text{g}) \times (35.6^\circ\text{C} - 23.8^\circ\text{C}) + 893\ \text{J}/^\circ\text{C} \times (35.6^\circ\text{C} - 23.8^\circ\text{C})] \\ &= -(38,300\ \text{J} + 10,500\ \text{J}) \\ &= -48,800\ \text{J} = -48.8\ \text{kJ} \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

? Exercise $3.3.5$

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Answer

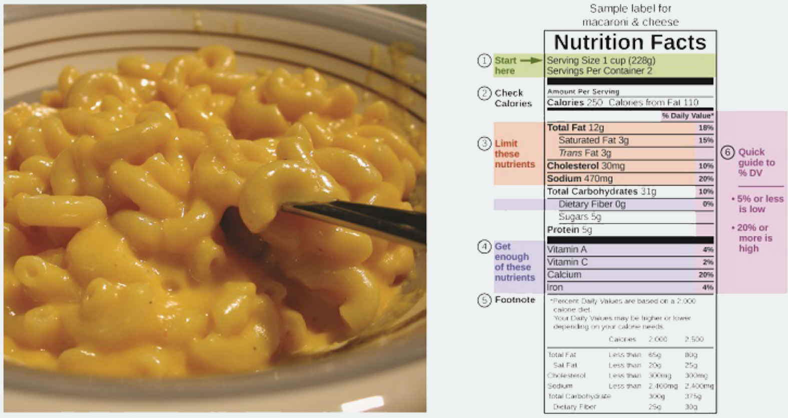
39.0 kJ

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[1] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure $3.3.7$).



(a) (b)

Figure $3.3.7$: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5\text{ g protein}\times 4\text{ Calories/g})+(31\text{ g carb}\times 4\text{ Calories/g})+(12\text{ g fat}\times 9\text{ Calories/g})=252\text{ Calories} \tag{3.3.5}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations. Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Footnotes

1. 1 Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, The Snellen human calorimeter revisited, re-engineered and upgraded: design and performance characteristics [link.springer.com].

Glossary

bomb calorimeter

device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter	device used to measure the amount of heat absorbed or released in a chemical or physical process
calorimetry	process of measuring the amount of heat involved in a chemical or physical process
nutritional calorie (Calorie)	unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal
surroundings	all matter other than the system being studied
system	portion of matter undergoing a chemical or physical change being studied

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3.4: Enthalpy

Learning Objectives

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the internal energy (U), sometimes symbolized as E.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (q) from the surroundings or when the surroundings do work (w) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w \tag{3.4.1}$$

as shown in Figure $3.4.1$. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

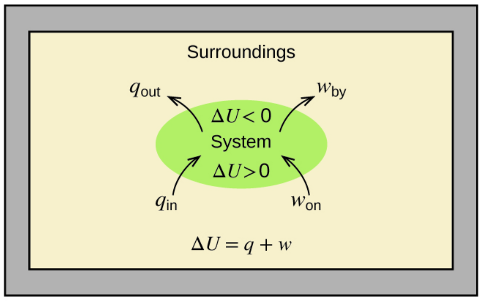

Figure $3.4.1$: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

As discussed, the relationship between internal energy, heat, and work can be represented as ΔU = q + w. Internal energy is a type of quantity known as a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 3.4.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

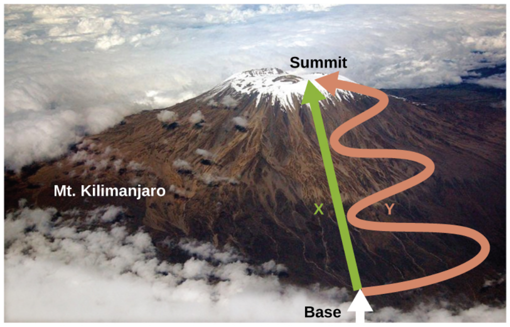

Figure 3.4.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as enthalpy (H) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (U) and the mathematical product of its pressure (P) and volume (V):

$$H = U + PV \tag{3.4.2}$$

Since it is derived from three state functions (U, P, and V), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy changes for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V \tag{3.4.3}$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will always be opposite:

$$P\Delta V = -w \tag{3.4.4}$$

Substituting Equation 3.4.4 and the definition of internal energy (Equation 3.4.1) into Equation 3.4.3 yields:

$$\Delta H = \Delta U + P\Delta V \tag{3.4.5}$$

$$= q_\mathrm{p} + \cancel{w} - \cancel{w} \tag{3.4.6}$$

$$= q_\mathrm{p} \tag{3.4.7}$$

where q_p is the heat of reaction under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products as shown in the chemical equation. For example, consider this equation:

   $$\mathrm{H_2(g)+\tfrac{1}{2}O_2(g)\longrightarrow H_2O(l)}\quad \Delta H=-286\ \mathrm{kJ} \tag{3.4.8}$$

   This equation indicates that when 1 mole of hydrogen gas and 12 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property).

   $$\begin{array}{l}\text{(two-fold increase in amounts)}\\ 2\,\mathrm{H_2}(g)+\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{H_2O}(l)\quad \Delta H=2\times(-286\ \mathrm{kJ})=-572\ \mathrm{kJ}\\ \text{(two-fold decrease in amounts)}\\ \frac{1}{2}\mathrm{H_2}(g)+\frac{1}{4}\mathrm{O_2}(g)\longrightarrow \frac{1}{2}\mathrm{H_2O}(l)\quad \Delta H=\frac{1}{2}\times(-286\ \mathrm{kJ})=-143\ \mathrm{kJ}\end{array}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 12 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

   $$\mathrm{H_2(g)+\tfrac{1}{2}O_2(g)\longrightarrow H_2O(g)}\quad \Delta H=-242\ \mathrm{kJ} \tag{3.4.9}$$

3. A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Example 3.4.1: Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is ΔH, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described ?

$$\mathrm{HCl(aq)+NaOH(aq)\rightarrow NaCl(aq)+H_2O(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H=1\ \ \mathrm{mol}\ \cancel{\mathrm{HCl}}\times\frac{-2.9\ \mathrm{kJ}}{0.0500\ \ \mathrm{mol}\ \cancel{\mathrm{HCl}}}=-58\ \mathrm{kJ}$$

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$\mathrm{HCl}_{(aq)}+\mathrm{NaOH}_{(aq)}\longrightarrow \mathrm{NaCl}_{(aq)}+\mathrm{H_2O}_{(l)}\quad \Delta H=-58\ \mathrm{kJ}$$

Exercise 3.4.1

When 1.34 g Zn(s) reacts with 60.0 mL of 0.750 M HCl(aq), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$Zn_{(s)} + 2\,HCl_{(aq)} \longrightarrow ZnCl_{(aq)} + H_{2(g)}$$

Answer

ΔH = −153 kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the Δ*H* for a chemical reaction.

Example 3.4.2: Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$C_{12}H_{22}O_{11}(aq) + 8\,KClO_3(aq) \longrightarrow 12\,CO_2(g) + 11\,H_2O(l) + 8\,KCl(aq)$$

Solution

We have $2.67\ \cancel{g} \times \frac{1\text{ mol}}{342.3\ \cancel{g}} = 0.00780\text{ mol }C_{12}H_{22}O_{11}$ available, and

$7.19\ \cancel{g} \times \frac{1\text{ mol}}{122.5\ \cancel{g}} = 0.0587\text{ mol }KClO_3$ available.

Since

$0.0587\text{ mol }KClO_3 \times \frac{1\text{ mol }C_{12}H_{22}O_{11}}{8\text{ mol }KClO_3} = 0.00734\text{ mol }C_{12}H_{22}O_{11}$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\frac{-43.7\text{ kJ}}{0.0587\text{ mol }KClO_3}$, so we have $\Delta H = 8\text{ mol} \times \frac{-43.7\text{ kJ}}{0.0587\text{ mol }KClO_3} = -5960\text{ kJ}$. The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\ \text{kJ}$$

Exercise 3.4.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_{2(s)}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2(s)$ is produced?

Answer

ΔH = −338 kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and **does not specify a temperature** (it used too). Many thermochemical tables list values with a standard state of 1 atm. Because the Δ*H* of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), Δ*H* values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol Δ*H* is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH_C°) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2} + 3\,\mathrm{H_2O}(l) \quad \Delta H^\circ_{298} = -1366.8\ \mathrm{kJ} \tag{3.4.10}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 3.4.1. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table 3.4.1: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H_c^\circ \left(\frac{\mathrm{kJ}}{\mathrm{mol}}\ \text{at}\ 25^\circ\mathrm{C}\right)$
carbon	$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	−393.5
hydrogen	$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l)$	−285.8
magnesium	$\mathrm{Mg}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{MgO}(s)$	−601.6
sulfur	$\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$	−296.8
carbon monoxide	$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$	−283.0
methane	$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$	−890.8
acetylene	$\mathrm{C_2H_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + \mathrm{H_2O}(l)$	−1301.1
ethanol	$\mathrm{C_2H_5OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$	−1366.8
methanol	$\mathrm{CH_3OH}(l) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$	−726.1
isooctane	$\mathrm{C_8H_{18}}(l) + \frac{25}{2}\mathrm{O_2}(g) \longrightarrow 8\,\mathrm{CO_2}(g) + 9\,\mathrm{H_2O}(l)$	−5461

Example 3.4.3: Using Enthalpy of Combustion

As Figure 3.4.3 suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.

Figure 3.4.3: The combustion of gasoline is very exothermic. (credit: modification of work by “AlexEagle”/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 3.4.1 gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \text{L}\ \cancel{C_8H_{18}} \times \frac{1000\ \text{mL}\ \cancel{C_8H_{18}}}{1\ \text{L}\ \cancel{C_8H_{18}}} \times \frac{0.692\ \text{g}\ \cancel{C_8H_{18}}}{1\ \text{mL}\ \cancel{C_8H_{18}}} \times \frac{1\ \text{mol}\ \cancel{C_8H_{18}}}{114\ \text{g}\ \cancel{C_8H_{18}}} \times \frac{-5460\ \text{kJ}}{1\ \text{mol}\ \cancel{C_8H_{18}}} = -3.31 \times 10^4\ \text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$\begin{aligned}
&1.00\ \text{L}\ C_8H_{18} \longrightarrow 1.00 \times 10^3\ \text{mL}\ C_8H_{18}\\
&1.00 \times 10^3\ \text{mL}\ C_8H_{18} \longrightarrow 692\ \text{g}\ C_8H_{18}\\
&692\ \text{g}\ C_8H_{18} \longrightarrow 6.07\ \text{mol}\ C_8H_{18}\\
&692\ \text{g}\ C_8H_{18} \longrightarrow -3.31 \times 10^4\ \text{kJ}
\end{aligned}$$

Exercise 3.4.3

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25×10^3 kJ

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 3.4.4). The species of algae used are nontoxic, biodegradable, and among the world’s fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.

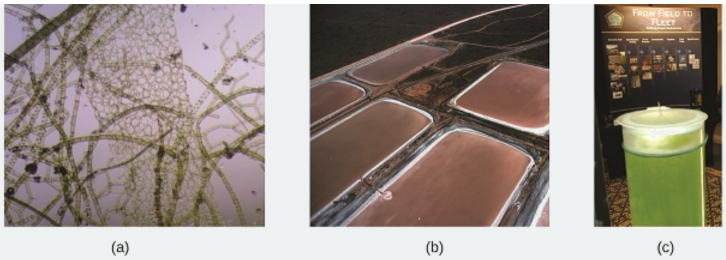
(a) (b) (c)

Figure 3.4.4: (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure 3.4.5).

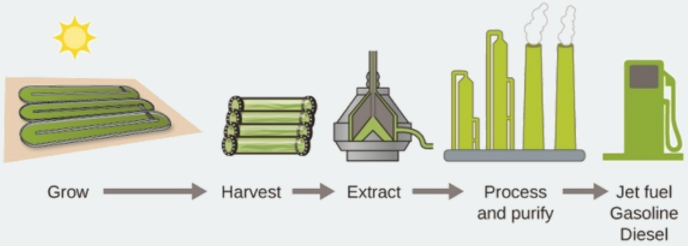

Figure 3.4.5: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

A standard enthalpy of formation $\Delta H_\mathrm{f}^\circ$ is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\mathrm{C}(s)+\mathrm{O}_2(g)\longrightarrow \mathrm{CO}_2(g)\quad \Delta H_\mathrm{f}^\circ=\Delta H_{298}^\circ=-393.5\ \mathrm{kJ} \tag{3.4.11}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $\mathrm{NO}_{2(g)}$, $\Delta H_\mathrm{f}^\circ$ is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}\mathrm{N}_2(g)+\mathrm{O}_2(g)\longrightarrow \mathrm{NO}_2(g)\quad \Delta H_\mathrm{f}^\circ=\Delta H_{298}^\circ=+33.2\ \mathrm{kJ} \tag{3.4.12}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Tables T1 and T2. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 3.4.4: Evaluating an Enthalpy of Formation

Ozone, $O_3(g)$, forms from oxygen, $O_2(g)$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

$$3\,\text{O}_2(g) \longrightarrow 2\,\text{O}_3(g) \qquad \Delta H_{298}^\circ = +286\text{ kJ}$$

Solution ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $O_3(g)$ is the enthalpy change for the reaction:

$$\frac{3}{2}\text{O}_2(g) \longrightarrow \text{O}_3(g)$$

For the formation of 2 mol of $O_3(g)$, $\Delta H_{298}^\circ = +286\text{ kJ}$. This ratio, $\left(\frac{286\text{ kJ}}{2\text{ mol O}_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

$$\Delta H^\circ \text{ for 1 mole of } \text{O}_3(g) = 1\ \cancel{\text{mol O}_3} \times \frac{286\text{ kJ}}{2\ \cancel{\text{mol O}_3}} = 143\text{ kJ}$$

Therefore, $\Delta H_\text{f}^\circ[\text{O}_3(g)] = +143\ \text{kJ/mol}$.

Exercise 3.4.4

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, $HCl(g)$. What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $HCl(g)$ is −92.3 kJ/mol.

Answer

For the reaction

$$\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{HCl}(g) \qquad \Delta H_{298}^\circ = -184.6\text{ kJ}$$

Example 3.4.5: Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

a. $\text{C}_2\text{H}_5\text{OH}_{(l)}$
b. $\text{Ca}_3(\text{PO}_4)_{2(s)}$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,\text{C}(s,\ \text{graphite}) + 3\,\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{C}_2\text{H}_5\text{OH}(l)$
b. $3\,\text{Ca}(s) + \frac{1}{2}\text{P}_4(s) + 4\,\text{O}_2(g) \longrightarrow \text{Ca}_3(\text{PO}_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 3.4.5

Write the heat of formation reaction equations for:

a. $\text{C}_2\text{H}_5\text{OC}_2\text{H}_{5(l)}$
b. $\text{Na}_2\text{CO}_{3(s)}$

Answer a

> $4\,\mathrm{C}(s,\ \text{graphite}) + 5\,\mathrm{H_2}(g) + \tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{C_2H_5OC_2H_5}(l)$;
>
> **Answer b**
>
> $$2\,\mathrm{Na}(s) + \mathrm{C}(s,\ \text{graphite}) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Na_2CO_3}(s)$$

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{2(g)} \quad \Delta H^\circ_{298} = -394\ \mathrm{kJ} \tag{3.4.13}$$

In the two-step process, first carbon monoxide is formed:

$$\mathrm{C}_{(s)} + \frac{1}{2}\mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{(g)} \quad \Delta H^\circ_{298} = -111\ \mathrm{kJ} \tag{3.4.14}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H^\circ_{298} = -283\ \mathrm{kJ} \tag{3.4.15}$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{array}{l}
\text{Step 1: } \mathrm{C}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) \\
\text{Step 2: } \mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \\
\hline
\text{Sum: } \mathrm{C}(s) + \frac{1}{2}\mathrm{O_2}(g) + \mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) + \mathrm{CO_2}(g)
\end{array}$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$\mathrm{C}_{(s)} + \mathrm{O}_{2(g)} \longrightarrow \mathrm{CO}_{2(g)} \tag{3.4.16}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 3.4.1 to find the enthalpy change of the entire reaction from its two steps:

$$\begin{array}{ll}
\mathrm{C}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) & \Delta H^\circ_{298} = -111\ \mathrm{kJ} \\
\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{298} = -283\ \mathrm{kJ} \\
\hline
\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) & \Delta H^\circ_{298} = -394\ \mathrm{kJ}
\end{array}$$

The result is shown in Figure 3.4.6. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

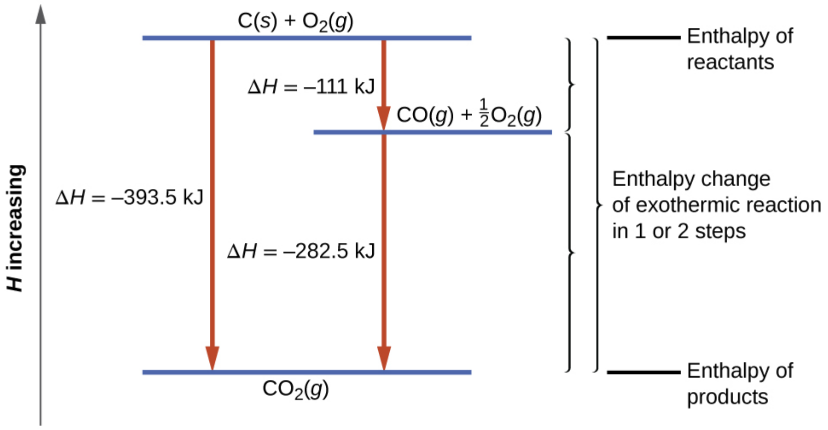

Figure 3.4.6: The formation of CO_2(g) from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

$$\frac{1}{2}\mathrm{N_2}(g)+\mathrm{O_2}(g)\longrightarrow \mathrm{NO_2}(g)\quad \Delta H=+33.2\ \mathrm{kJ} \tag{3.4.17}$$

   When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

$$\mathrm{N_2}(g)+2\,\mathrm{O_2}(g)\longrightarrow 2\,\mathrm{NO_2}(g)\quad \Delta H=+66.4\ \mathrm{kJ} \tag{3.4.18}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

$$\mathrm{H_2}(g)+\mathrm{Cl_2}(g)\longrightarrow 2\,\mathrm{HCl}(g)\quad \Delta H=-184.6\ \mathrm{kJ} \tag{3.4.19}$$

   Then, for the "reverse" reaction, the enthalpy change is also "reversed":

$$2\,\mathrm{HCl}(g)\longrightarrow \mathrm{H_2}(g)+\mathrm{Cl_2}(g)\quad \Delta H=+184.6\ \mathrm{kJ} \tag{3.4.20}$$

Example 3.4.6: Stepwise Calculation of $\Delta H^\circ_\mathrm{f}$

Using Hess's Law Determine the enthalpy of formation, $\Delta H^\circ_\mathrm{f}$, of $FeCl_3$(s) from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe}(s)+\mathrm{Cl_2}(g)\longrightarrow \mathrm{FeCl_2}(s)\quad \Delta H^\circ=-341.8\ \mathrm{kJ}$$

$$\mathrm{FeCl_2}(s)+\frac{1}{2}\mathrm{Cl_2}(g)\longrightarrow \mathrm{FeCl_3}(s)\quad \Delta H^\circ=-57.7\ kJ$$

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH° for the reaction:

$$\mathrm{Fe}(s)+\frac{3}{2}\mathrm{Cl_2}(g)\longrightarrow \mathrm{FeCl_3}(s)\quad \Delta H^\circ_\mathrm{f}=?$$

Looking at the reactions, we see that the reaction for which we want to find $\Delta H°$ is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:

$$\begin{array}{ll}
\mathrm{Fe}(s)+\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_2}(s) & \Delta H^\circ=-341.8\ \mathrm{kJ}\\
\mathrm{FeCl_2}(s)+\frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) & \Delta H^\circ=-57.7\ \mathrm{kJ}\\
\hline
\mathrm{Fe}(s)+\frac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{FeCl_3}(s) & \Delta H^\circ=-399.5\ \mathrm{kJ}
\end{array}$$

The enthalpy of formation, $\Delta H_\mathrm{f}^\circ$, of $FeCl_3$(s) is −399.5 kJ/mol.

Exercise 3.4.6

Calculate ΔH for the process:

$$\mathrm{N_2}(g)+2\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g)$$

from the following information:

$$\mathrm{N_2}(g)+\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta H=180.5\ \mathrm{kJ}$$

$$\mathrm{NO}(g)+\frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{NO_2}(g) \quad \Delta H=-57.06\ \mathrm{kJ}$$

Answer

66.4 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and n standing for the stoichiometric coefficients:

$$\Delta H^\circ_\mathrm{reaction}=\sum n\times\Delta H^\circ_\mathrm{f}(\mathrm{products})-\sum n\times\Delta H^\circ_\mathrm{f}(\mathrm{reactants}) \tag{3.4.21}$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 3.4.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,\mathrm{NO_2}(g)+\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{HNO_3}(aq)+\mathrm{NO}(g) \quad \Delta H^\circ=?$$

Solution 1: Using the Equation

Alternatively, we could use the special form of Hess's law given previously:

$$\Delta H^\circ_\mathrm{reaction}=\sum n\times\Delta H^\circ_\mathrm{f}(\mathrm{products})-\sum n\times\Delta H^\circ_\mathrm{f}(\mathrm{reactants})$$

$$\begin{aligned}
&= \left[2 \text{ mol } \cancel{\text{HNO}_3} \times \frac{-207.4 \text{ kJ}}{\text{mol } \cancel{\text{HNO}_3\ (aq)}} + 1 \text{ mol } \cancel{\text{NO}\ (g)} \times \frac{+90.2 \text{ kJ}}{\text{mol } \cancel{\text{NO}\ (g)}}\right] \\
&- \left[3 \text{ mol } \cancel{\text{NO}_2\ (g)} \times \frac{+33.2 \text{ kJ}}{\text{mol } \cancel{\text{NO}_2\ (g)}} + 1 \text{ mol } \cancel{\text{H}_2\text{O}\ (l)} \times \frac{-285.8 \text{ kJ}}{\text{mol } \cancel{\text{H}_2\text{O}\ (l)}}\right] \\
&= 2(-207.4 \text{ kJ}) + 1(+90.2 \text{ kJ}) - 3(+33.2 \text{ kJ}) - 1(-285.8 \text{ kJ}) \\
&= -138.4 \text{ kJ}
\end{aligned}$$

Solution 2: Supporting Why the General Equation Is Valid

We can write this reaction as the sum of the decompositions of $3NO_2(g)$ and $1H_2O(l)$ into their constituent elements, and the formation of 2 $HNO_3(aq)$ and 1 $NO(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH_f° values for these compounds (from Tables T1 and T2), we have:

$$3\,\text{NO}_2(g) \longrightarrow \frac{3}{2}\text{N}_2(g) + 3\text{O}_2(g) \quad \Delta H_1^\circ = -99.6 \text{ kJ}$$

$$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \quad \Delta H_2^\circ = +285.8 \text{ kJ } [-1 \times \Delta H_f^\circ(\text{H}_2\text{O})]$$

$$\text{H}_2(g) + \text{N}_2(g) + 3\text{O}_2(g) \longrightarrow 2\,\text{HNO}_3(aq) \quad \Delta H_3^\circ = -414.8\ kJ\ [2 \times \Delta H_f^\circ(\text{HNO}_3)]$$

$$\frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}(g) \quad \Delta H_4^\circ = +90.2 \text{ kJ } [1 \times (\text{NO})]$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,\text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2\,\text{HNO}_3(aq) + \text{NO}(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}
\Delta H_{\text{rxn}}^\circ &= \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ = (-99.6 \text{ kJ}) + (+285.8 \text{ kJ}) + (-414.8 \text{ kJ}) + (+90.2 \text{ kJ}) \\
&= -138.4 \text{ kJ}
\end{aligned}$$

So the standard enthalpy change for this reaction is $\Delta H°$ = −138.4 kJ.

Note that this result was obtained by:

1. multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values,
2. multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then
3. subtracting the result found in step 2 from the result found in step 1.

This is also the procedure in using the general equation, as shown.

Exercise 3.4.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

Contributors and Attributions

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH_{298}° for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, $\Delta H_{\mathrm{f}}^{\circ}$, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Key Equations

- $\Delta U = q + w$
- $\Delta H^{\circ}_{\text{reaction}} = \sum n \times \Delta H_{\mathrm{f}}^{\circ}(\text{products}) - \sum n \times \Delta H_{\mathrm{f}}^{\circ}(\text{reactants})$

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

chemical thermodynamics

area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (*H*)

sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (Δ*H*)

heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)

work done as a system expands or contracts against external pressure

first law of thermodynamics

internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law

if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon

compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*)

total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH_c°)

heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation ($\Delta H_{\mathrm{f}}^{\circ}$)

enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state

set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function

property depending only on the state of a system, and not the path taken to reach that state

Contributors and Attributions

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3.5: Spontaneity

Learning Objectives

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

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure $3.5.1$).

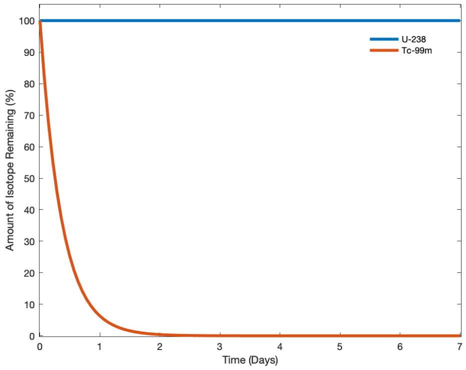


Figure $3.5.1$: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts) Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure $3.5.2$).

$$\mathrm{C(s, diamond)} \longrightarrow \mathrm{C(s, graphite)} \tag{3.5.1}$$

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

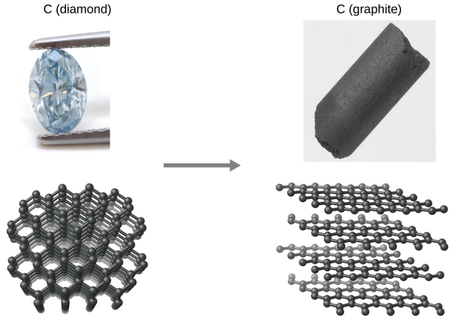


Figure $3.5.2$ The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php) Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure $3.5.3$). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{3.5.2}$$

$$= 0 \quad (\mathrm{P = 0 \; in \; a \; vaccum}) \tag{3.5.3}$$

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

$$\begin{aligned}\Delta U &= q + w && \text{(First Law of Thermodynamics)}\\ &= 0 + 0 = 0 && (3.5.4)\end{aligned}$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

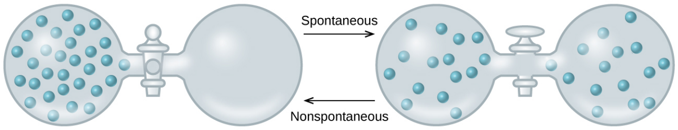


Figure $3.5.3$ An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks. When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure $3.5.4$). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{3.5.5}$$

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

Figure $3.5.4$When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object. Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

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

✓ Example $3.5.1$: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

Figure $3.5.5$(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa) This figure has three photos labeled, “a,” “b,” and “c.” Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

? Exercise $3.5.1$

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process	process that requires continual input of energy from an external source
spontaneous change	process that takes place without a continuous input of energy from an external source

3.6: Entropy

Learning Objectives

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

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure $3.6.2$) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot’s findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_rev) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be “reversed”) by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

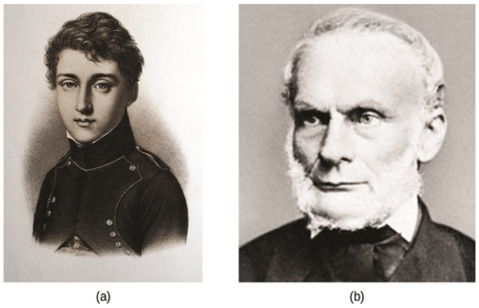


Figure $3.6.1$: (a) Nicholas Léonard Sadi Carnot’s research into steam-powered machinery and (b) Rudolf Clausius’s later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

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

$$\Delta S = \frac{q_\text{rev}}{T} \tag{3.6.1}$$

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

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{3.6.2}$$

Here k is the Boltzmann constant and has a value of $1.38 \times 10^{-23}\ J/K$.

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

$$\begin{aligned} \Delta S &= S_\text{f} - S_\text{i} \\ &= k \ln \Omega_\text{f} - k \ln \Omega_\text{i} \\ &= k \ln \frac{\Omega_\text{f}}{\Omega_\text{i}} \end{aligned} \tag{3.6.3}$$

For processes involving an increase in the number of microstates of the system, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $\Omega_f < \Omega_i$, yield a decrease in system entropy,

$\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

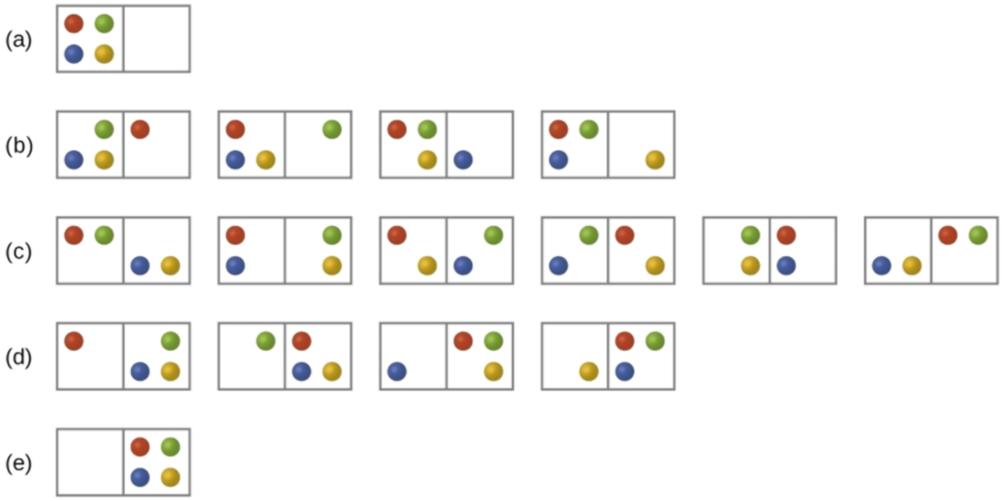


Figure $3.6.2$ The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box. Five rows of diagrams that look like dominoes are shown and labeled a, b, c, d, and e. Row a has one “domino” that has four dots on the left side, red, green, blue and yellow in a clockwise pattern from the top left, and no dots on the right. Row b has four “dominos,” each with three dots on the left and one dot on the right. The first shows a “domino” with green, yellow and blue on the left and red on the right. The second “domino” has yellow, blue and red on the left and green on the right. The third “domino” has red, green and yellow on the left and blue on the right while the fourth has red, green and blue on the left and yellow on the right. Row c has six “dominos”, each with two dots on either side. The first has a red and green on the left and a blue and yellow on the right. The second has a red and blue on the left and a green and yellow on the right while the third has a yellow and red on the left and a green and blue on the right. The fourth has a green and blue on the left and a red and yellow on the right. The fifth has a green and yellow on the left and a red and blue on the right. The sixth has a blue and yellow on the left and a green and red on the right. Row d has four “dominos,” each with one dot on the left and three on the right. The first “domino” has red on the left and a blue, green and yellow on the right. The second has a green on the left and a red, yellow and blue on the right. The third has a blue on the left and a red, green and yellow on the right. The fourth has a yellow on the left and a red, green and blue on the right. Row e has 1 “domino” with no dots on the left and four dots on the right that are red, green, blue and yellow.

Consider the general case of a system comprised of *N* particles distributed among *n* boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure $3.6.2$. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

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

$$\frac{6}{16} = \frac{3}{8}$$

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

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

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

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} = \frac{1}{8}$$

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

> *The most probable distribution is therefore the one of greatest entropy.*

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

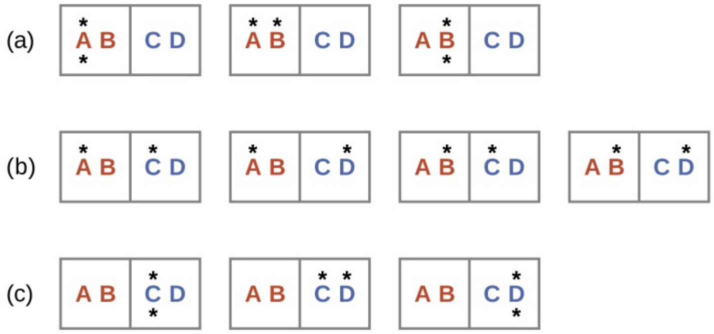
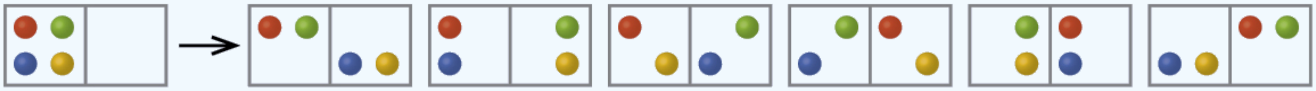


Figure $3.6.3$ This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates. Three rows labeled a, b, and c are shown and each contains rectangles with two sides where the left side is labeled, “A,” and “B,” and the right is labeled, “C,” and “D.” Row a has three rectangles where the first has a dot above and below the letter A, the second has a dot above the A and B, and the third which has a dot above and below the letter B. Row b has four rectangles; the first has a dot above A and C, the second has a dot above A and D, the third has a dot above B and C and the fourth has a dot above B and D. Row c has three rectangles; the first has a dot above and below the letter C, the second has a dot above C and D and the third has a dot above and below the letter D.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as “*”) in Figure $3.6.3$. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects’ temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

✓ Example 3.6.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



A diagram shows one rectangle with two sides that has four dots, red, green, yellow and blue written on the left side. A right-facing arrow leads to six more two-sided rectangles, each with two dots on the left and right sides. The first rectangle has a red and green dot on the left and a blue and yellow on the right, while the second shows a red and blue on the left and a green and yellow on the right. The third rectangle has a red and yellow dot on the left and a blue and green on the right, while the fourth shows a green and blue on the left and a red and yellow on the right. The fifth rectangle has a yellow and green dot on the left and a blue and red on the right, while the sixth shows a yellow and blue on the left and a green and red on the right.

Solution

We are interested in the following change:

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

$$\begin{aligned}\Delta S &= k \ln \frac{\Omega_c}{\Omega_a} \\ &= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1} \\ &= 2.47 \times 10^{-23}\ J/K\end{aligned}$$

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

? Exercise 3.6.1

Consider the system shown in Figure 3.6.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

Predicting the Sign of Δ*S*

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 3.6.4. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system’s component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

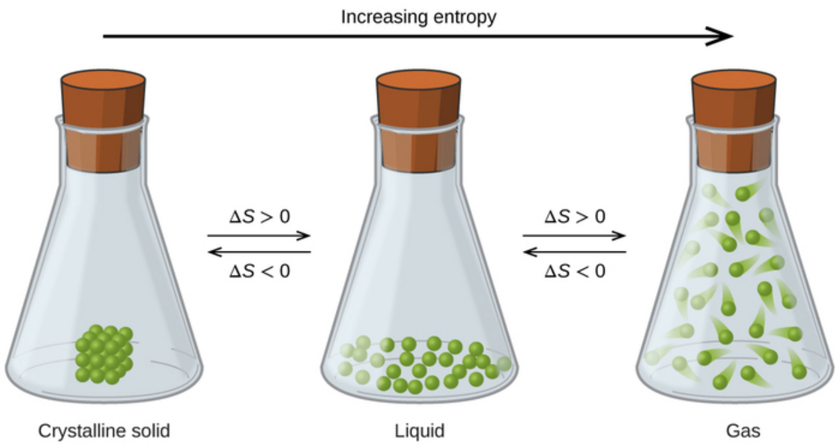


Figure 3.6.4 The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid. Three stoppered flasks are shown with right and left-facing arrows in between each; the first is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0,” while the second is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0.” A long, right-facing arrow is drawn above all the flasks and labeled, “Increasing entropy.” The left flask contains twenty-seven particles arranged in a cube in the bottom of the flask and is labeled, “Crystalline solid,” below. The middle flask contains twenty-seven particles dispersed randomly in the bottom of the flask and is labeled, “Liquid,” below. The right flask contains twenty-seven particles dispersed inside of the flask and moving rapidly and is labeled, “Gas,” below.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 3.6.5).

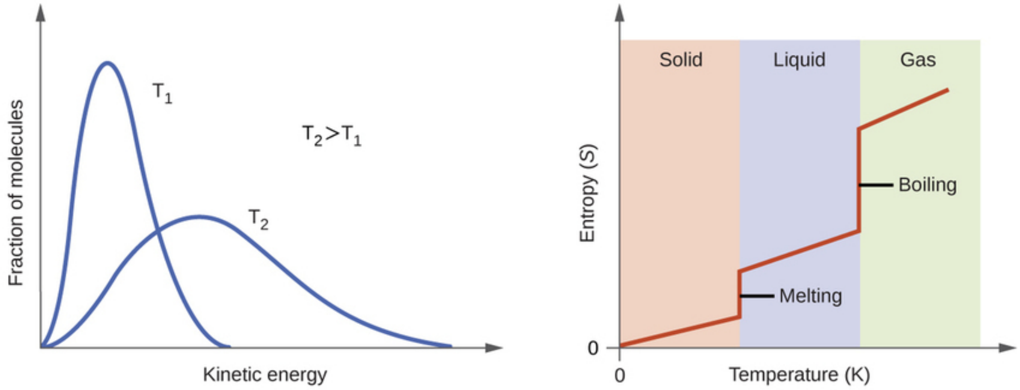


Figure 3.6.5 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy. Two graphs are shown. The y-axis of the left graph is labeled, “Fraction of molecules,” while the x-axis is labeled, “Velocity, v (m / s),” and has values of 0 through 1,500 along the axis with increments of 500. Four lines are plotted on this graph. The first, labeled, “100 K,” peaks around 200 m / s while the second, labeled, “200 K,” peaks near 300 m / s and is slightly lower on the y-axis than the first. The third line, labeled, “500 K,” peaks around 550 m / s and is lower than the first two on the y-axis. The fourth line, labeled, “1000 K,” peaks around 750 m / s and is the lowest of the four on the y-axis. Each line get increasingly broad. The second graph has a y-axis labeled, “Entropy, S,” with an upward-facing arrow and an x-axis labeled, “Temperature (K),” and a right-facing arrow. The graph has three equally spaced columns in the background, labeled, “Solid,” “Liquid,” and, “Gas,” from left to right. A line extends slightly upward through the first column in a slight upward direction, then goes straight up in the transition between the first two columns. In then progresses in a slight upward direction through the second column, then goes up dramatically between the second and third columns, then continues in a slight upward direction once more. The first vertical region of this line is labeled, “Melting,” and the second is labeled, “Boiling.”

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

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

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

✓ Example 3.6.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature ⟶ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6}(l) + \frac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\,\mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

? Exercise 3.6.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas

Answer d

Positive; There is a net production of one mole of gas.

Summary

Entropy (\(S\)) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$

Glossary

entropy (*S*)

state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (*W*)

possible configuration or arrangement of matter and energy within a system

reversible process

process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

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3.7: The Second and Third Laws of Thermodynamics

Learning Objectives

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

The Second Law of Thermodynamics

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

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{3.7.1}$$

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

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:
$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{3.7.2}$$
The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:
$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{3.7.3}$$
The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat flow is thermodynamically reversible. See the previous section’s discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 3.7.1.

Table 3.7.1: The Second Law of Thermodynamics

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

All spontaneous changes cause an increase in the entropy of the universe.

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{3.7.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 3.7.1.

✓ Example 3.7.1: Will Ice Spontaneously Melt?

The entropy change for the process

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

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

Solution

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

At −10.00 °C (263.15 K), the following is true:

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

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

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

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

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

? Exercise 3.7.1

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

Answer

> Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0 \tag{3.7.5}$$

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

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

We can make careful calorimetric measurements to determine the temperature dependence of a substance’s entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S°_{298} for values determined for one mole of substance, isolated in its pure form in its own container, at a pressure of 1 bar and a temperature of 298 K.

Definition: Term

The thermodynamic standard state of a substance refers to an isolated sample of that substance, in its own container, at 1.000 bar (0.9869 atm) pressure. If the substance is a solute, the most common standard state is one in which the concentration of the solute is 1.000 molal (sometimes approximated with 1.000 M). There is no defined temperature for the standard state, but most discussions about standard state assume that the temperature is 298.15 K (25ºC) unless otherwise noted.

This may seem like a strange definition, because it requires that each of the reactants and each of the products of a reaction are kept separate from one another, unmixed. The entropy of mixing must be determined separately.

The standard entropy change (Δ*S*°) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^\circ = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \tag{3.7.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, Δ*S*° for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{3.7.7}$$

is computed as the following:

$$= [xS^\circ_{298}(\text{C}) + yS^\circ_{298}(\text{D})] - [mS^\circ_{298}(\text{A}) + nS^\circ_{298}(\text{B})] \tag{3.7.8}$$

Table $3.7.2$ lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 or T2.

Table $3.7.2$: Standard Entropies (at 298.15 K, 1 atm)

Substance	$S^\circ_{298}\ \frac{J}{mol\ K}$
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
CO_2(*g*)	213.8
CH_4(*g*)	186.3
C_2H_4(*g*)	219.5
C_2H_6(*g*)	229.5
CH_3OH(*l*)	126.8
C_2H_5OH(*l*)	160.7
hydrogen	
H_2(*g*)	130.57
H(*g*)	114.6

Substance	$S^\circ_{298}\ \frac{J}{mol\ K}$
$H_2O(g)$	188.71
$H_2O(l)$	69.91
$HCI(g)$	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 3.7.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

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

Solution

The value of the standard entropy change at room temperature, ΔS°_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^\circ_{298} &= S^\circ_{298}(\mathrm{H_2O}(l)) - S^\circ_{298}(\mathrm{H_2O}(g)) \\ &= (70.0\ J\ mol^{-1} K^{-1}) - (188.8\ Jmol^{-1} K^{-1}) = -118.8\ J\ mol^{-1} K^{-1}\end{aligned}$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 3.7.2

Calculate the standard entropy change for the following process:

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

Answer

$-120.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$

Example 3.7.3: Determination of ΔS°

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

$$2\,\mathrm{CH_3OH}(l) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients.

$$\begin{aligned}\Delta S^\circ &= \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \\ &= [2S^\circ_{298}(\mathrm{CO_2}(g)) + 4S^\circ_{298}(\mathrm{H_2O}(l))] - [2S^\circ_{298}(\mathrm{CH_3OH}(l)) + 3S^\circ_{298}(\mathrm{O_2}(g))] \\ &= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1\ J/mol \cdot K\end{aligned}$$

Exercise 3.7.3

Calculate the standard entropy change for the following reaction:

$$\mathrm{Ca(OH)_2}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{H_2O}(l)$$

Answer

24.7 J/mol•K

Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

Glossary

second law of thermodynamics

entropy of the universe increases for a spontaneous process

standard entropy ($S°$)

entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

standard entropy change ($\Delta S°$)

change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

third law of thermodynamics

entropy of a perfect crystal at absolute zero (0 K) is zero

3.8: Gibbs Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the standard free energy change for a process using standard free energies of formation for its reactants and products
- Calculate standard free energy change for a process using senthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a chemical reaction is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. A second challenge when working with a chemical reaction is that we need to take into account the mixing of the substances, an issue that does not occur when observing the phase change if a pure substance. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

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

$$\Delta G^{\circ}_{\text{sys}} = \Delta H^{\circ}_{\text{sys}} - T\Delta S^{\circ}_{\text{sys}}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

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

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

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

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

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

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

$$\Delta G = -T\Delta S_{\text{univ}} \tag{3.8.1}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table $3.8.1$ summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table $3.8.1$: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium
$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical changes and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 3.8.1.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3.8.2}$$

It is important to understand that for phase changes, ΔG° tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG° tells you the **extent** of a reaction. In other words, ΔG° for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^\circ < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^\circ > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

✓ Example 3.8.1: Evaluation of ΔG° for a Phase Change of a Pure Substance

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this physical change for a pure substance?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{3.8.3}$$

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

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ \tag{3.8.4}$$

From Tables T1 or T2, here are the data:

Data from Tables T1 or T2

Substance	$\Delta H^\circ_\mathrm{f}$ (kJ/mol)	S°_{298} (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ_{298} = \Delta H^\circ_\mathrm{f}(\mathrm{H_2O}(g)) - \Delta H^\circ_\mathrm{f}(\mathrm{H_2O}(l)) \\ &= [-241.82\ kJ - (-285.83)]\ kJ/mol \\ &= 44.01\ kJ/mol \\ \Delta S^\circ &= \Delta S^\circ_{298} = S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l)) \\ &= 188.8\ J/mol\cdot K - 70.0\ J/K \\ &= 118.8\ J/mol\cdot K \end{aligned}$$

then use Equation 3.8.2:

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

Converting everything into kJ and combining at 298 K:

$$\begin{aligned}\Delta G^\circ_{298} &= \Delta H^\circ - T\Delta S^\circ \\ &= 44.01\ kJ/mol - (298\ K \times 118.8\ J/mol \cdot K) \times \frac{1\ kJ}{1000\ J} \\ & 44.01\ \mathrm{kJ/mol} - 35.4\ \mathrm{kJ/mol} = 8.6\ \mathrm{kJ/mol}\end{aligned}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous) at 298 K.

? Exercise 3.8.1: Evaluation of ΔG° for a Chemical Reaction

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the extent of this reaction at 298 K?

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

Answer

$\Delta G^\circ_{298} = 102.0\ \mathrm{kJ/mol}$; the reaction is reactant-favored at equilibrium at 25 °C. There will be more $\mathrm{C_2H_6}(g)$ than $\mathrm{H_2}(g)$ and $\mathrm{C_2H_4}(g)$ at equilibrium

Free energy changes may also use the standard free energy of formation $(\Delta G^\circ_\mathrm{f})$, for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, $(\Delta G^\circ_\mathrm{f})$ is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

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

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

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{3.8.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \tag{3.8.6}$$

$$= [x\Delta G^\circ_\mathrm{f}(\mathrm{C}) + y\Delta G^\circ_\mathrm{f}(\mathrm{D})] - [m\Delta G^\circ_\mathrm{f}(\mathrm{A}) + n\Delta G^\circ_\mathrm{f}(\mathrm{B})]. \tag{3.8.7}$$

✓ Example 3.8.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

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

Calculate the standard free energy change at room temperature, ΔG°_{298}, using:

a. standard free energies of formation and
b. standard enthalpies of formation and standard entropies.

Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium?

Solution

The required data are available in Tables T1 or T2 and are shown here.

Required data for Tables T1 or T2

Compound	$\Delta G^\circ_\mathrm{f}$ **(kJ/mol)**	$\Delta H^\circ_\mathrm{f}$ **(kJ/mol)**	S°_{298} (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ_{298} &= \sum \nu GS^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta G^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\text{O}_2(g)\right] - 1\Delta G^\circ_{298}\text{HgO}(s,\ \text{yellow}) \\ &= \left[1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\text{mol}(0\ \text{kJ/mol})\right] - 1\ \text{mol}(-58.43\ \text{kJ/mol}) = 58.43\ \text{kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ_{298} &= \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1\Delta H^\circ_{298}\text{HgO}(s,\ \text{yellow}) \\ &= [1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\text{mol}(0\ \text{kJ/mol})] - 1\ \text{mol}(-90.46\ \text{kJ/mol}) = 90.46\ \text{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{298} &= \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1\Delta S^\circ_{298}\text{HgO}(s,\ \text{yellow}) \\ &= \left[1\ \text{mol}(75.9\ \text{J/mol K}) + \frac{1}{2}\text{mol}(205.2\ \text{J/mol K})\right] - 1\ \text{mol}(71.13\ \text{J/mol K}) = 107.4\ \text{J/mol K}\end{aligned}$$

then we can use Equation \ref7} directly:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 90.46\ \text{kJ} - 298.15\ \text{K} \times 107.4\ \text{J/K}\cdot\text{mol} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \\ &= (90.46 - 32.01)\ \text{kJ/mol} = 58.45\ \text{kJ/mol}\end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is reactant-favored at equilibrium at room temperature.

? Exercise 3.8.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Tables T1 or T2). Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium at 25 °C?

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

Answer

141.5 kJ/mol, reactant-favored at equilibrium

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter’s section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

Note

The numerical value of ΔG° is always dependent on the temperature. In this section we are determining whether or not the **sign** of ΔG° is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

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

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

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

These four scenarios are summarized in Table 3.8.1

Table 3.8.1

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

✓ Example 3.8.3: Predicting the Temperature Dependence of Spontaneity

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

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

Does the sign of ΔG° of this process depend upon temperature?

Solution

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

Exercise 3.8.3

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

$$4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Fe_2O_3}(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer

ΔH^o and ΔS^o are both negative; the reaction is product-favored at equilibrium at low temperatures.

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

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

$$y = b + mx$$

Such a plot is shown in Figure 3.8.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which ΔG^o is zero:

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

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

Thus, saying a process is product-favored at equilibrium at "high" or "low" temperatures means the temperature is above or below, respectively, that temperature at which ΔG^o for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When ΔG^o < 0, K > 1, and the reaction will be product-favored at equilibrium. When ΔG^o > 0, K< 1, and the reaction is reactant-favored at equilibrium. When ΔG^o = 0, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and (essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔGº can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

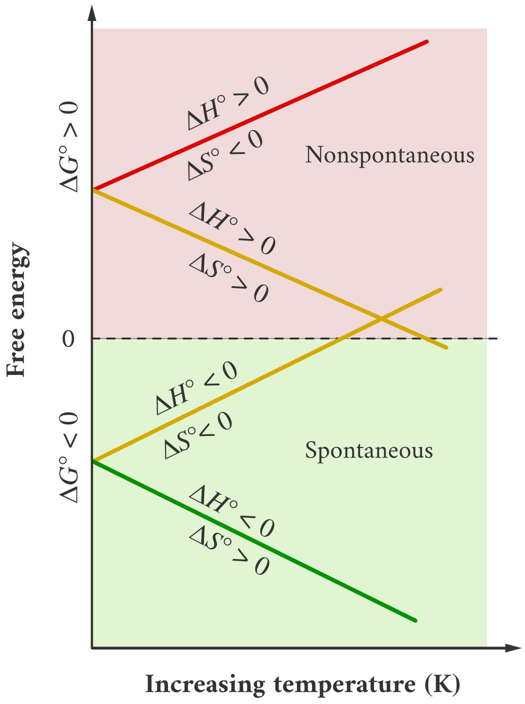

Figure 3.8.2 These plots show the variation in ΔGº with temperature for the four possible combinations of arithmetic sign for ΔHº and ΔSº. Note that in this graph of ΔGº, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

✓ Example 3.8.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

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

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{H}_2\text{O}(g)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) \\ &= -241.82\ \text{kJ/mol} - (-285.83\ \text{kJ/mol}) = 44.01\ \text{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\text{H}_2\text{O}(g)) - \Delta S_{298}^\circ(\text{H}_2\text{O}(l)) \\ &= 188.8\ \text{J/K}\cdot\text{mol} - 70.0\ \text{J/K}\cdot\text{mol} = 118.8\ \text{J/K}\cdot\text{mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \text{J/mol}}{118.8\ \text{J/K}\cdot\text{mol}} = 370.5\ \text{K} = 97.3\ ^\circ\text{C}$$

The accepted value for water’s normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

? Exercise 3.8.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for Δ*G* represents a finite driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When Δ*G* is zero, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, *Q*, was introduced as a convenient measure of the status of an equilibrium system. Recall that *Q* is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When *Q* is lesser than the equilibrium constant, *K*, the reaction will proceed in the forward direction until equilibrium is reached and *Q* = *K*. Conversely, if *Q* > *K*, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under nonstandard conditions, Δ*G*, is related to the standard free energy change, Δ*G*°, according to this equation:

$$\Delta G = \Delta G^\circ + RT\ln Q \tag{3.8.8}$$

R is the gas constant (8.314 J/K mol), *T* is the kelvin or absolute temperature, and *Q* is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in Example 3.8.1.

✓ Example 3.8.5: Calculating Δ*G* under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, $P_{\text{N}_2} = 0.870\ \text{atm}$, $P_{\text{H}_2} = 0.250\ \text{atm}$, and $P_{\text{NH}_3} = 12.9\ \text{atm}$

$$2\,\text{NH}_3(g) \longrightarrow 3\,\text{H}_2(g) + \text{N}_2(g) \qquad \Delta G^\circ = 33.0\ \text{kJ/mol}$$

Solution

Equation 3.8.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= 33.0\,\frac{\text{kJ}}{\text{mol}} + \left(8.314\,\frac{\text{J}}{\text{mol K}} \times 298\text{ K} \times \ln\frac{(0.250^3)\times 0.870}{12.9^2}\right) \\ &= 9680\,\frac{\text{J}}{\text{mol}} \text{ or } 9.68\text{ kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions. The reaction will proceed in the reverse direction to reach equilibrium.

? Exercise 3.8.5

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

$\Delta G = -47$ kJ; yes, the reaction proceeds in the forward direction, as written, to reach equilibrium.

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the Equation 3.8.8 may be written as

$$\underbrace{0 = \Delta G^\circ + RT\ln K}_{\text{at equilibrium}}$$

$$\Delta G^\circ = -RT\ln K \tag{3.8.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{3.8.10}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 3.8.1.

Table 3.8.1: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.
> 1	< 0	Products are more abundant at equilibrium.

✓ Example 3.8.6: Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \quad K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G^\circ = \Delta G^\circ_{298} &= [\Delta G^\circ_\mathrm{f}(\mathrm{Ag}^+(aq)) + \Delta G^\circ_\mathrm{f}(\mathrm{Cl}^-(aq))] - [\Delta G^\circ_\mathrm{f}(\mathrm{AgCl}(s))] \\ &= [77.1\ kJ/mol - 131.2\ kJ/mol] - [-109.8\ kJ/mol] \\ &= 55.7\ kJ/mol\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 3.8.10:

$$\begin{aligned}K_\mathrm{sp} = e^{-\frac{\Delta G^\circ}{RT}} &= \exp\left(-\frac{\Delta G^\circ}{RT}\right) \\ &= \exp\left(-\frac{55.7\times10^3\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol\cdot K}\times 298.15\ \mathrm{K}}\right) \\ &= \exp(-22.470) = \mathrm{e}^{-22.470} = 1.74\times10^{-10}\end{aligned}$$

? Exercise 3.8.6: dissociation of dinitrogen tetroxide

Use the thermodynamic data provided in Tables T1 or T2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)}$$

Answer

K = 6.9

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 3.8.3). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

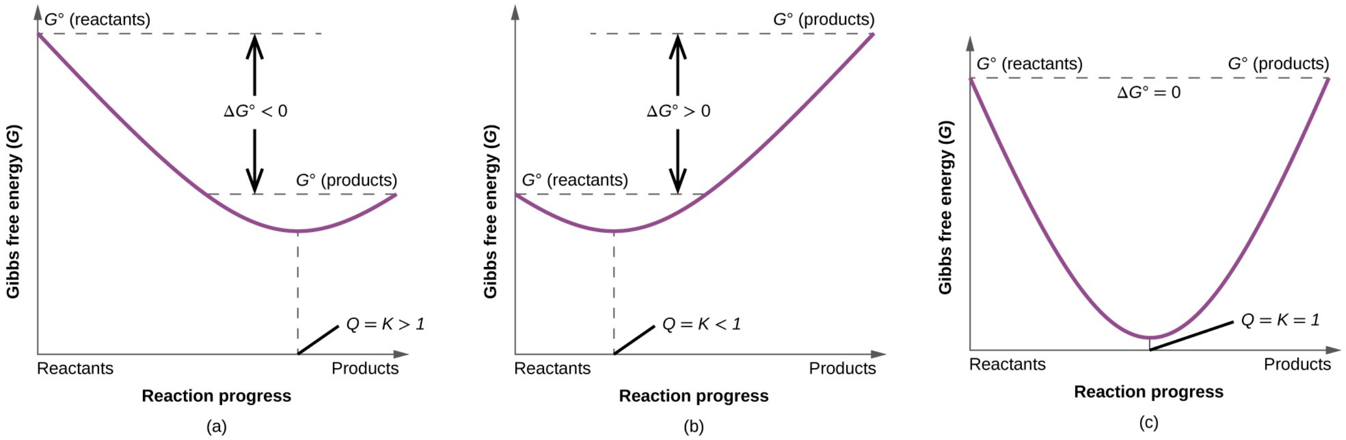

Figure 3.8.3 These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note that reactions with K equal to exactly 1.000 are rare.

Summary

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates that the process will proceed in the forward direction to reach equilibrium; a positive ΔG indicates that the process will proceed in the reverse direction to reach equilibrium ; and a ΔG of zero indicates that the system is at equilibrium. A negative value for ΔG^o means that the reaction is product-favored at equilibrium. A positive value for ΔG^o means that the reaction is reactant-favored at equilibrium. If ΔG^o equals 0 (a rare occurrence), the reaction has roughly equal amounts of reactants and products at equilibrium.A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Glossary

Gibbs free energy change (*G*)

thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

standard free energy change ($\Delta G°$)

change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)

change in free energy accompanying the formation of one mole of substance from its elements in their standard states

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CHAPTER OVERVIEW

4: Activity and Ionic Strength

The parameters we have been studying so far help to characterize the energetics and spontaneity of reversible reactions. In general, if we assume that the likelihood of two molecules reacting with one another is based on the probability that they will 'collide,' then the 'reactivity' of that substance is directly proportional to its concentration - the more molecules of a substance that are present in a system, the more likely that collisions will take place between that substance and another reactant. However, there are situations where additional factors influence the reactivity of compounds. Either the substance itself is at such a high concentration that molecules of the same substance interact with one another to affect its reactivity, or molecules of one substance are interacting with molecules of one or more other substances to influence reactivity. In this section, we will examine terms such as 'activity,' define the reference state for quantifying activity, and then adjust activity using activity coefficients, as calculated using the ionic strength of a solution.

4.1: 4.1. Reactivity and The Standard State

Before examining chemical reactivity and activity it is useful to revisit chemical energy. The chemical energy of a system is known as the Gibbs energy and is denoted by G. Suppose we wanted to think about the simplest chemical reaction possible – a situation in which A reacts to produce B.

$$\mathrm{A} \Leftrightarrow \mathrm{B} \tag{4.1.1}$$

A bottle of pure A has some amount of chemical energy. A bottle of pure B has some amount of chemical energy. A solution of A in water that is 2 Molar has some amount of chemical energy. A solution of B in water that is 2 Molar has some amount of chemical energy.

Do all four examples listed above (pure A, pure B, [A] = 2 M, B = [2 M]) have the same or different chemical energy?

Hopefully it will seem reasonable or intuitive to think that all four of these systems will have different chemical energies. Since the two compounds are different from each other, in their pure forms they likely have different chemical energies. Similarly, a chemical species dissolved in a solvent is now different than the pure compound and the two will have different chemical energies.

How would you measure or determine the absolute chemical energy of those four systems?

This is actually a trick question. We do not have methods available to determine the absolute chemical energy for a system. In reality the best that we can do is measure the difference in chemical energies between two systems. This difference is denoted as ΔG, which you have already studied in the preceding weeks and in other prior coursework.

Let’s continue to examine the situation in which A reacts to produce B.

$$\mathrm{A} \Leftrightarrow \mathrm{B} \tag{4.1.2}$$

When will the chemical energy (G) of this system achieve its lowest value?

The lowest value of chemical energy for a reaction occurs when it is at equilibrium. For the example above, this means that pure A and pure B must have a higher chemical energy than the equilibrium state of the reaction. It is important to note that chemical systems strive to have the lowest chemical energy as that will be their most stable state.

We will next consider what a plot of G versus the mole fraction of A and B in which the situation

$$[\mathrm{A}] + [\mathrm{B}] = 2 \text{ Molar} \tag{4.1.3}$$

is always satisfied. We can consider what the plot would look like for two different situations:

The reaction of A to produce B has a fairly large equilibrium constant.

The reaction of A to produce B has a fairly small equilibrium constant.

Remember that the equilibrium constant expression is:

$$\mathrm{K} = \frac{[\mathrm{B}]}{[\mathrm{A}]} \tag{4.1.4}$$

Since the equilibrium situation will have some concentration of both A and B, the system at equilibrium must have a lower chemical energy than either a 2 M solution of A or a 2M solution of B. That would allow us to draw two possible representations for the situation: one in which Keq is large (there is a much higher concentration of B than A), shown in the left panel of Figure 1; and one in which Keq is small (there is a much higher concentration of A than B), shown in the right panel of Figure 1.

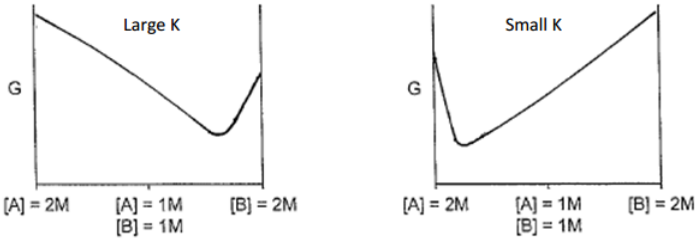

Figure 1. Plot of G versus molar quantities of reactant and product for a reaction with a large (left) and small (right) equilibrium constant (Keq).

Remember that we do not know how to calculate the true, absolute value of G. What we can do is quantify the difference in chemical energy (ΔG) between two different states (e.g., we could possibly measure the difference in chemical energy between a solution in which [A] = 2 M and equilibrium). The plot in Figure 2 illustrates the observed ΔG for such a situation (using the example of when Keq is large).

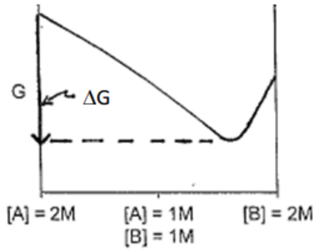

Figure 2. Magnitude of ΔG between [A] = 2 M and equilibrium.

Why do we need to define something called the standard state?

Consider an example where every student in a class was asked to perform a laboratory measurement of ΔG for the reaction of A to produce B. If we consider the example where K is large, you could imagine a situation in which one student starts with a solution where the concentration of A is 2 M and B is 0 while another starts with a solution where the concentration of B is 2 M and A is 0. Looking at the plot in Figure 2, both students may measure accurate and correct values for ΔG but the values that the students report will be different. As seen by the plot in Figure 2, the value one would measure for ΔG is dependent on the particular starting point, since each starting point has a different initial value of G. In order to record ΔG values that can be tabulated and compared, everyone must agree in advance to a uniform set of starting conditions. These agreed upon starting conditions are known as the standard state.

What conditions constitute the standard state?

The standard state is the situation where every reactant and product in the reaction has an **activity** of 1. Since there are many conditions where we are unable to determine the exact activity of a substance, an approximation is made where the standard state has the concentration of all soluble species in the reaction at 1 Molar, gases at a pressure of 1 atmosphere and a temperature of 25ºC (298 K). In addition, the standard state assumes that each of the soluble species behave as if they are the only compound present in the solution. This is called the assumption of a dilute solution, or an infinite dilution.

For A reacting to produce B, the standard state would be a solution in which [A] = 1 M and [B] = 1 M. The plot in Figure 3 shows the difference in chemical energy between the standard state and equilibrium for the situation in which Keq is large. The difference in chemical energy between the standard state and equilibrium is given a special designation: ΔG^o.

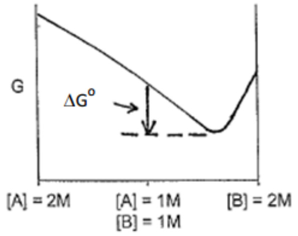

Figure 3. Difference in chemical energy between the standard state and equilibrium (ΔG^o) for a reaction with a large equilibrium constant.

You can imagine that it might be difficult to think about how you could actually make a standard state solution and somehow hold it in a suspended state before allowing it to react and achieve equilibrium, thereby allowing a measurement of ΔG^o. Meaning, it is difficult to prepare a solution of species A and species B that are both at 1 M concentration but in which both species behave as if they are the only compounds present in solution (the dilute solution, or infinite dilution assumption). [As an aside, electrochemical cells are actually ideal systems for measurements of ΔG^o because it is possible to prepare the two half reactions in separate chambers but prevent the reaction from taking place by not completing all of the circuitry between the two chambers.]

What does it mean for the difference in chemical energy (ΔG or ΔG^o) to be positive or negative?

In considering this, it is important to examine the two different plots of G for the reaction with a large Keq and small Keq. These are shown in Figure 4 and the value of ΔG^o is indicated in each plot.

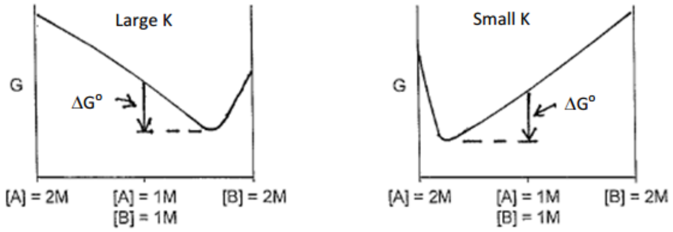

Figure 4. ΔG^o for a reaction with a large (left) and small (right) equilibrium constant.

Note that in both cases the chemical energy drops as the system goes from the standard state to equilibrium. However, when we think about carrying out a chemical reaction, our usual goal is to have the reaction form products. For this reason, we adopt a convention that says that ΔG^o is less than 0 (negative) for a reaction that favors the formation of products. ΔG^o is greater than 0 (positive) for a reaction that favors the formation of reactants.

The following equation is something you should have seen before in a unit on thermodynamics in either a general or physical chemistry course.

$$\Delta G^o = -RT \ln K \tag{4.1.5}$$

This equation provides the difference in chemical energy between the standard state and equilibrium. Note that if Keq is large (favors products), lnKeq is positive and ΔG^o is negative. Similarly if Keq is small (favors reactants), lnKeq is negative and ΔG^o is positive.

Suppose the Starting Conditions are not at the Standard State

There are many situations where you do not want to examine reactions that begin with standard state conditions but instead want to start with a set of non-standard state conditions. The difference in chemical energy between non-standard state conditions and equilibrium is designated as ΔG. The equation that allows us to calculate ΔG is as follows:

$$\Delta G = -RT \ln K + RT \ln Q \text{ or } \Delta G = \Delta G^o + RT \ln Q \tag{4.1.6}$$

As seen previously, the term Q is an expression that looks exactly like the equilibrium constant expression except that it is evaluated using the starting non-standard state concentrations. It is important to recognize what each part of this equation is providing.

–RTLnKeq (denoted as ΔG^o) is the difference in chemical energy between the standard state and equilibrium.

RTlnQ is the difference in chemical energy between the non-standard state starting conditions and the standard state.

The plot in Figure 5 shows the placement of these two terms for the example of A reacting to produce B that we have been examining. In this case the non-standard state conditions are further removed from chemical equilibrium than the standard state. Note that with [A] = 1.50 M and [B] = 0.50 M, the value of Q is 0.33.

$$Q = \frac{[B]}{[A]} = \frac{(0.50)}{(1.50)} = 0.33 \tag{4.1.7}$$

With the value of Q below 1, lnQ will be negative and the value of ΔG is more negative than the value of ΔG^o.

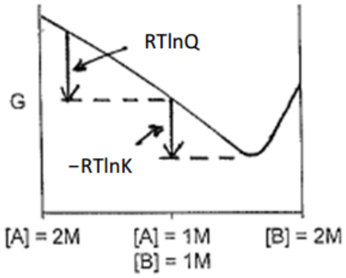

Figure 5. Representation of RTlnQ and –RTlnK for a reaction starting in non-standard state conditions. Non-standard state conditions are further from equilibrium than the standard state conditions.

The plot in Figure 6 shows starting non-standard state conditions that are closer to equilibrium than those of the standard state: [A] = 0.50 M; [B] = 1.50 M. In this case the value of Q is 3.0.

$$\mathrm{Q}=\frac{[\mathrm{B}]}{[\mathrm{A}]}=\frac{(1.50)}{(0.50)}=3.0 \tag{4.1.8}$$

With the value of Q above 1, lnQ is positive and the value of ΔG is less negative than the value of ΔG^o.

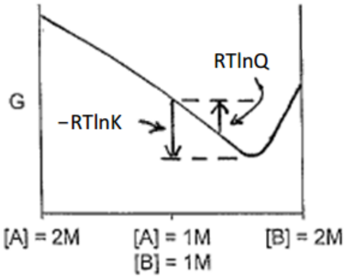

Figure 6. Representation of RTlnQ and –RTlnK for a reaction starting in non-standard state conditions. Non-standard state conditions are closer to equilibrium than the standard state conditions.

4.2: Ionic Strength

The properties of electrolyte solutions can significantly deviate from the laws used to derive chemical potential of solutions. In nonelectrolyte solutions, the intermolecular forces are mostly comprised of weak Van der Waals interactions, which have a r^{-7} dependence - as distance between molecules increases, the forces weaken by that distance raised to the 7th power. For practical purposes this can be considered ideal. In ionic solutions, however, there are significant electrostatic interactions between solute-solvent as well as solute-solute molecules. These electrostatic forces are governed by Coulomb's law, which has a r^{-2} dependence - as distance between molecules increases, forces weaken by a factor of distance squared. Consequently, the behavior of an electrolyte solution deviates considerably from that of an ideal solution. Indeed, this is why, when solutions have a significant abundance of ions (as determined by judgment and experience) we utilize the activities of the individual components and not their concentrations to calculate deviations from ideal behavior. Examples in environmental engineering when we might need to use non-ideal solution approaches include when we are working with seawater, brackish water, brines from desalination processes or oil and gas exploration, and other solutions that result in high concentrations of electrolytes and charged solutes.

The Debye-Hückel Limiting Law

In 1923, Peter Debye and Erich Hückel developed a theory that would allow us to calculate the mean ionic activity coefficient of the solution, $\gamma_{\pm}$, and could explain how the behavior of ions in solution contribute to this constant.

Assumptions of Debye-Hückel Theory

The Debye-Hückel theory is based on three assumptions of how ions act in solution:

1. Electrolytes completely dissociate into ions in solution.
2. Solutions of Electrolytes are very dilute, on the order of 0.01 M.
3. Each ion is surrounded by ions of the opposite charge, on average.

Debye and Hückel developed the following equation to calculate the mean ionic activity coefficient $\gamma_{\pm}$:

$$\log_{10} \gamma_{\pm} = -\frac{1.824 \times 10^6}{(\varepsilon T)^{3/2}} z^2 \sqrt{I} \tag{4.2.1}$$

where

- ε is the dielectric constant of the medium, such as water for an aqueous solution,
- z is the charge of the cation or anion, respectively, and
- I is the ionic strength of the solution.

The Equation 4.2.1 is known as the **Debye-Hückel Limiting Law**. The ionic strength is calculated using the following relation for all the ions in solution:

$$I = \frac{1}{2} \sum_i C_i z_i^2 \tag{4.2.2}$$

where C_i and z_i are the molar concentration and the charge of the ith ion in the electrolyte, respectively. Since most of the electrolyte solutions we study are aqueous $(\varepsilon = 78.54)$ and have a temperature of 298 K, the Limiting Law in Equation 4.2.1 reduces to

$$\log_{10} \gamma_{\pm} = -0.509 z^2 \sqrt{I} \tag{4.2.3}$$

The Debye-Hückel Limiting Law has been stated to be useful and valid for solutions with an ionic strength below 0.005 M.

The Extended Debye-Hückel Limiting Law

A modified form of the above law takes into account additional spatial effects on the forces between between molecules, due to the sizes of the ions. This modified equation is:

$$\log_{10} \gamma_{\pm} = -0.509 z^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \tag{4.2.4}$$

where all previous parameters are the same, and a is the ion size parameter, an integer typically between 3 and 9. The extended D-H equation is stated to be useful and valid for solutions with an ionic strength below 0.1 M, and particularly when one compound dominates the ionic strength

The Davies Equation

A final equation presented here for estimating activity coefficient is the Davies Equation, and it uses similar parameters and form as the two D-H models:

$$\log_{10} \gamma_{\pm} = -0.509 z^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3 I \right) \tag{4.2.5}$$

The Davies equation is stated to be useful at ionic strengths up to 0.5 M, making it a better choice than the D-H models for estimating gamma values in more concentrated solutions.

Additional models exist, such as the Pitzer Equation, also known as the Specific Interaction Model. However, we will stop our treatment of the topic at this point. Examples in class and in the homework will give you an opportunity to calculate I and gamma values.

References

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2. Chang, Raymond. Physical Chemistry for the Biosciences. Sausalito, California: University Science Books, 2005.

Contributors and Attributions

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4.3: Activity and Activity Coefficients

Up to this point in the course we have assumed that the solutions with which we are dealing are what are called ideal solutions. However, real solutions will deviate from this kind of behavior. In the case of gases, fugacity is a parameter that can be used to accommodate for deviations from ideal models. Likewise, in solutions, the parameter called **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute A is related to its concentration by

$$a_A = \gamma \frac{m_A}{m^o} \tag{4.3.1}$$

where γ is the **activity coefficient**, m_A is the molality of the solute A, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, meanng that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_A = \mu_A^o + RT \ln a_A \tag{4.3.2}$$

In *Water Chemistry*, Mark Benjamin defines activity coefficient, via a rearrangement of the first equation above, as the ratio of two activities: the activity per mole or per molecule in the actual state of interest, divided by the activity per mole or per molecule in the reference state (standard state). Because the activities are expressed per mole or per molecule, they could be expressed as 'per concentration.' Likewise, the activity of a solute in the standard state is defined as 1. So, the activity coefficient expression simplifies to:

$$\gamma_A = \frac{activity_A}{C_{A-real} / C_{A-stdstate}} \tag{4.3.3}$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration. Fortunately, some theoretical and empirical relationships have been developed to estimate activity coefficients based on the charge of an ion, the abundance of other ions in the solution (termed ionic strength), and the properties of the solvent (often water). Some of these methods are presented in the next section.

Contributors and Attributions

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CHAPTER OVERVIEW

5: Gas Laws

5.1: Gas Pressure

Learning Objectives

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth’s atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears “pop” during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure $5.1.1$). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

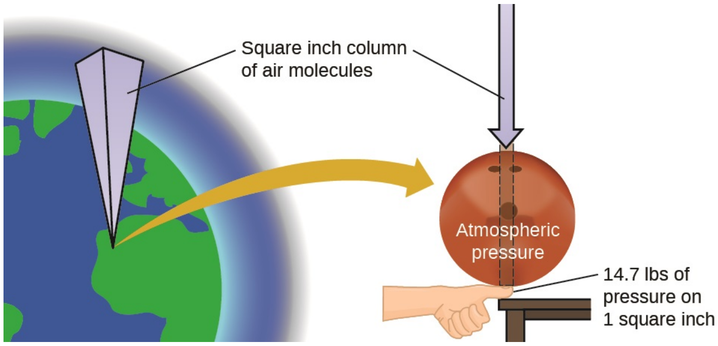


Figure $5.1.1$: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail. Diagram of Earth with a square inch column of air molecules extending to the atmosphere. This column points to an arrow pointing down on a bowling ball resting on a human thumbnail placed on top of a table.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.

A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

Pressure is defined as the force exerted on a given area:

$$P=\frac{F}{A} \tag{5.1.1}$$

> Since pressure is directly proportional to force and inversely proportional to area (Equation 5.1.1), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 5.1.1) to determine which would be more likely to fall through thin ice in Figure 5.1.2.—the elephant or the figure skater?


(a) (b)

Figure 5.1.2 Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi). Figure a is a photo of a large gray elephant on grassy, beige terrain. Figure b is a photo of a figure skater with her right skate on the ice, upper torso lowered, arms extended upward behind her chest, and left leg extended upward behind her.

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000\frac{\text{lb}}{\text{elephant}} \times \frac{1\text{ elephant}}{4\text{ feet}} \times \frac{1\text{ foot}}{250\text{ in}^2} = 14\text{ lb/in}^2 \tag{5.1.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ blades}} \times \frac{1\text{ blade}}{2\text{ in}^2} = 30\text{ lb/in}^2 \tag{5.1.3}$$

Even though the elephant is more than one hundred times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ feet}} \times \frac{1\text{ foot}}{30\text{ in}^2} = 2\text{ lb/in}^2 \tag{5.1.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 5.1.1 provides some information on these and a few other common units for pressure measurements

Table 5.1.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
millibar (mbar, or mb)	1000 mbar = 1 bar	
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1\ \text{torr} = \frac{1}{760}\ \text{atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

✓ Example 5.1.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2\ \text{in}\ \cancel{\text{Hg}} \times \frac{25.4\ \cancel{\text{mm}}}{1\ \cancel{\text{in}}} \times \frac{1\ \text{torr}}{1\ \text{mm}\ \cancel{\text{Hg}}} = 742\ \text{torr}$

b. $742\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.976\ \text{atm}$

c. $742\ \cancel{\text{torr}} \times \frac{101.325\ \text{kPa}}{760\ \cancel{\text{torr}}} = 98.9\ \text{kPa}$

d. $98.9\ \cancel{\text{kPa}} \times \frac{1000\ \cancel{\text{Pa}}}{1\ \cancel{\text{kPa}}} \times \frac{1\ \cancel{\text{bar}}}{100,000\ \cancel{\text{Pa}}} \times \frac{1000\ \text{mbar}}{1\ \cancel{\text{bar}}} = 989\ \text{mbar}$

? Exercise 5.1.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth’s surface, with a barometer (Figure 5.1.3). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

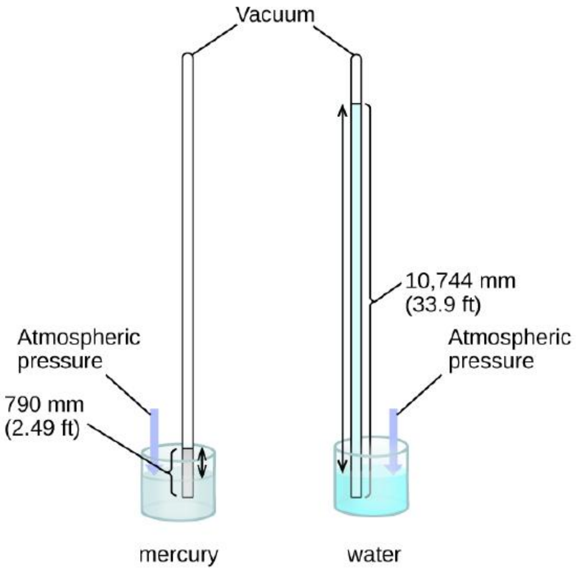


Figure $5.1.3$ In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall. Two barometers are in vacuum. One utilizes mercury while the other uses water in the capillary tube. Both barometers are exposed to atmospheric pressure. The barometer with mercury shows mercury levels of 2.49 feet. The barometer with water has a much greater level of 33.9 feet.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, *p*:

$$p = h\rho g \tag{5.1.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

✓ Example $5.1.2$: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = $13.6\ g/cm^3$.

Solution

The hydrostatic pressure is given by Equation 5.1.5, with $h = 760\ mm$, $\rho = 13.6\ g/cm^3$, and $g = 9.81\ m/s^2$. Plugging these values into the Equation 5.1.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\mathrm{m}^2 = 101,325\ \frac{\mathrm{kg}\cdot\mathrm{m/s}^2}{\mathrm{m}^2} = 101,325\ \frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}^2}$$

$$\begin{aligned} p &= \left(760\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right) \times \left(\frac{13.6\ \mathrm{g}}{1\ \mathrm{cm}^3} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{(100\ \mathrm{cm})^3}{(1\ \mathrm{m})^3}\right) \times \left(\frac{9.81\ \mathrm{m}}{1\ \mathrm{s}^2}\right) \\ &= (0.760\ \mathrm{m})(13,600\ \mathrm{kg/m}^3)(9.81\ \mathrm{m/s}^2) = 1.01 \times 10^5\ \mathrm{kg/ms}^2 = 1.01 \times 10^5\ N/\mathrm{m}^2 \\ &= 1.01 \times 10^5\ \mathrm{Pa} \end{aligned}$$

Exercise 5.1.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

A manometer is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 5.1.3) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

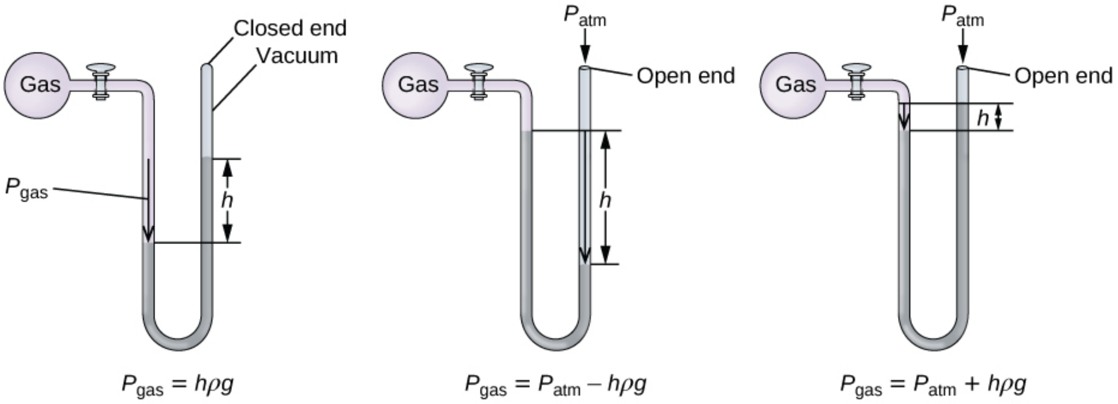
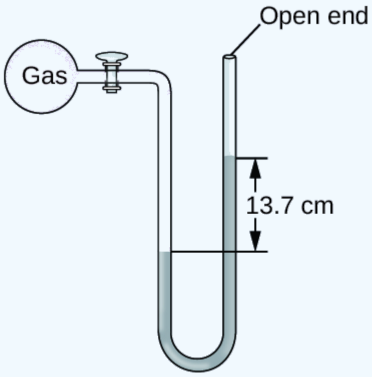


Figure 5.1.4 A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density. The first manometer is closed end. The gas in the bulb exerts a certain pressure on the liquid in the tube so that the height, h, between the two levels of liquid on both sides of the U tube is proportional to the pressure. The equation is P subscript gas equals to h rho g. The second manometer has an open end. The equation for P subscript gas is equals to P subscript atm minus h rho g. The final manometer is also open ended and has equation of P subscript gas equals to P subscript atm plus h rho g for cases where pressure of the gas is greater than atmospheric pressure.

Example 5.1.3: Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown below. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 13.7 centimeters. The level on the right side is higher than the left.

Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

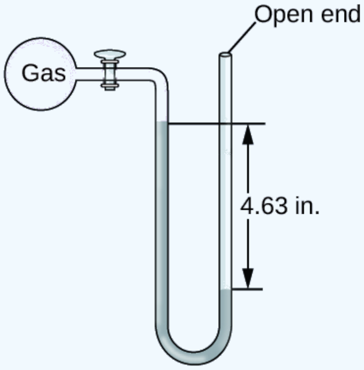
b. $897\ \cancel{\text{mmHg}} \times \frac{1\text{ atm}}{760\ \cancel{\text{mmHg}}} = 1.18\text{ atm}$

c. $1.18\ \cancel{\text{atm}} \times \frac{101.325\text{ kPa}}{1\ \cancel{\text{atm}}} = 1.20 \times 10^2\text{ kPa}$

? Exercise 5.1.3

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 4.63 inches. The level on the left side is higher than the right.

Answer a

642 mm Hg

Answer b

0.845 atm

Answer c

85.6 kPa

Application: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 5.1.5). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).

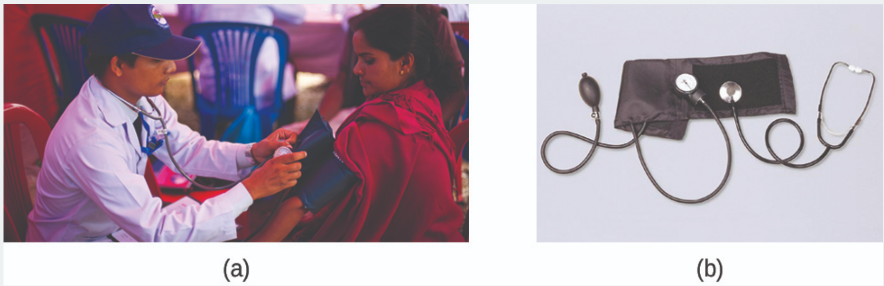


Figure 5.1.5 (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure 5.1.5) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

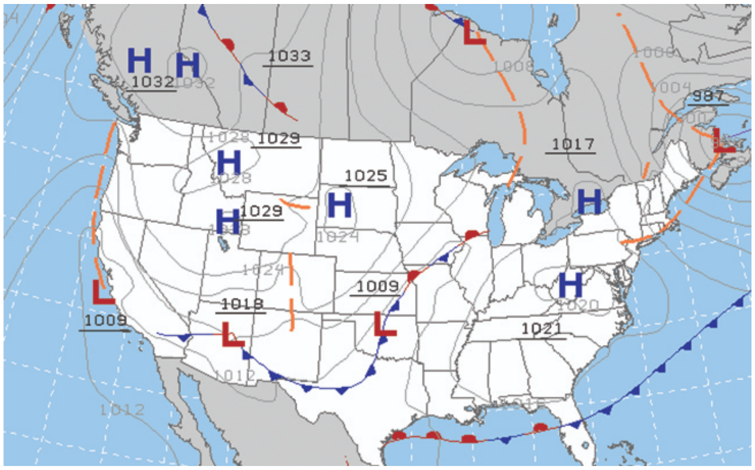


Figure 5.1.6: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration) A weather map of the United States is shown which points out areas of high and low pressure with the letters H in blue and L in red. There are curved grey lines throughout the United States region as well as beyond it around area of Canada and the oceans.

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 5.1.7: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

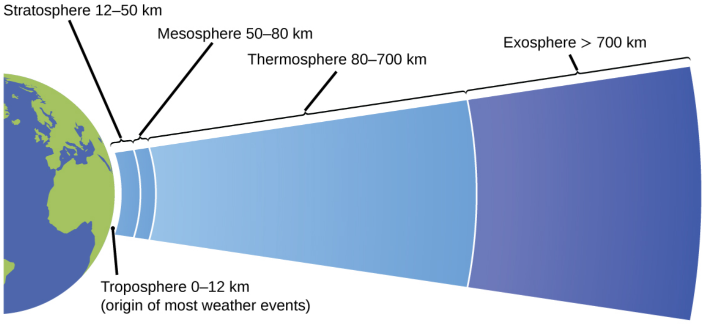


Figure 5.1.7: Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere. The different layers of the atmosphere is illustrated as a cross sectional slice of the Earth's atmosphere. The different thickness of each layer is shown. The thermosphere has the largest portion, followed by the exosphere, stratosphere, mesosphere, and troposphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Glossary

atmosphere (atm)

unit of pressure; 1 atm = 101,325 Pa

bar

(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer

device used to measure atmospheric pressure

hydrostatic pressure

pressure exerted by a fluid due to gravity

manometer

device used to measure the pressure of a gas trapped in a container

pascal (Pa)

SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)

unit of pressure common in the US

pressure

force exerted per unit area

torr

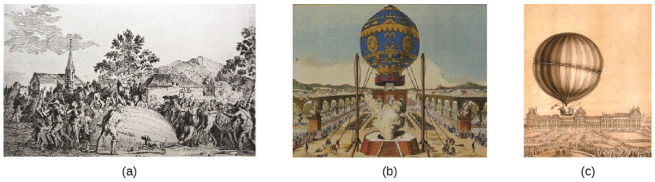
unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

5.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

Learning Objectives

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 5.2.1), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



(a) (b) (c)

Figure 5.2.1: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris. This figure includes three images. Image a is a black and white image of a hydrogen balloon apparently being deflated by a mob of people. In image b, a blue, gold, and red balloon is being held to the ground with ropes while positioned above a platform from which smoke is rising beneath the balloon. In c, an image is shown in grey on a peach-colored background of an inflated balloon with vertical striping in the air. It appears to have a basket attached to its lower side. A large stately building appears in the background.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 5.2.2) and the pressure increases.

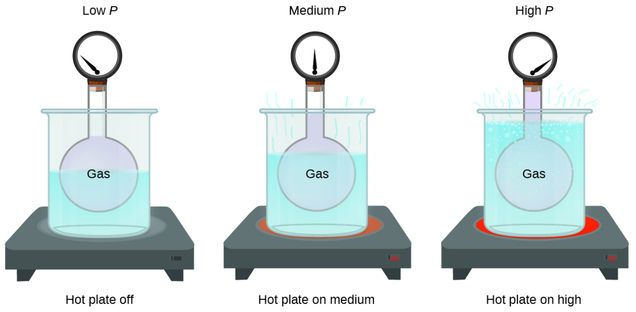


Figure 5.2.2 The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases. This figure includes three similar diagrams. In the first diagram to the left, a rigid spherical container of a gas to which a pressure gauge is attached at the top is placed in a large beaker of water, indicated in light blue, atop a hot plate. The needle on the pressure gauge points to the far left on the gauge. The diagram is labeled "low P" above and "hot plate off" below. The second similar diagram also has the rigid spherical container of gas placed in a large beaker from which light blue wavy line segments extend from the top of the liquid in the beaker. The beaker is situated on top of a slightly reddened circular area. The needle on the pressure gauge points straight up, or to the middle on the gauge. The diagram is labeled "medium P" above and "hot plate on medium" below. The third diagram also has the rigid spherical container of gas placed in a large beaker in which bubbles appear near the liquid surface and several wavy light blue line segments extend from the surface out of the beaker. The beaker is situated on top of a bright red circular area. The needle on the pressure gauge points to the far right on the gauge. The diagram is labeled "high P" above and "hot plate on high" below.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure 5.2.3. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then *P* and *T* are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
–150	173	36.0
–100	223	46.4
–50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0

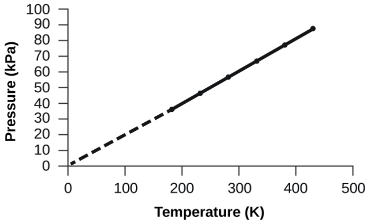


Figure 5.2.3 For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero. This figure includes a table and a graph. The table has 3 columns and 7 rows. The first row is a header, which labels the columns "Temperature, degrees C," "Temperature, K," and "Pressure, k P a." The first column contains the values from top to bottom negative 150, negative 100, negative 50, 0, 50, and 100. The second column contains the values from top to bottom 173, 223, 273, 323, 373, and 423. The third column contains the values 36.0, 46.4, 56.7, 67.1, 77.5, and 88.0. A graph appears to the right of the table. The horizontal axis is labeled "Temperature (K)." with markings and labels provided for multiples of 100 beginning at 0 and ending at 500. The vertical axis is labeled "Pressure (k P a)" with markings and labels provided for multiples of 10, beginning at 0 and ending at 100. Six data points from the table are plotted on the graph with black dots. These dots are connected with a solid black line. A dashed line extends from the data point furthest to the left to the origin. The graph shows a positive linear trend.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P*-*T* relationship for gases is known as either Amontons's law or Gay-Lussac's law. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where ∝ means “is proportional to,” and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in “Condition 1” (with $P = P_1$ and $T = T_1$), and then changes to “Condition 2” (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

✓ Example 5.2.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning “Store only at temperatures below 120 °F (48.8 °C). Do not incinerate.” Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

a. The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)
b. We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons’s/Gay-Lussac’s law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360\text{ kPa}}{297\text{ K}} = \frac{P_2}{323\text{ K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360\text{ kPa} \times 323\ \cancel{\text{K}}}{297\ \cancel{\text{K}}} = 390\text{ kPa}$$

? Exercise 5.2.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 torr

Volume and Temperature: Charles’s Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let’s say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

Video 5.2.1: This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure 5.2.2.

Temperature (°C)	Temperature (K)	Volume (L)
–3	270	22
–23	250	21
–53	220	18
–162	111	9

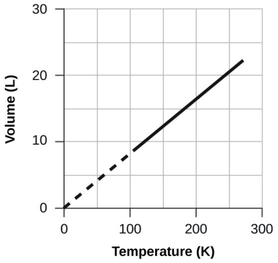


Figure 5.2.4 The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph’s origin, representing a temperature of absolute zero. This figure includes a table and a graph. The table has 3 columns and 6 rows. The first row is a header, which labels the columns “Temperature, degrees C,” “Temperature, K,” and “Pressure, k P a.” The first column contains the values from top to bottom negative 100, negative 50, 0, 100, and 200. The second column contains the values from top to bottom 173, 223, 273, 373, and 473. The third column contains the values 14.10, 18.26, 22.40, 30.65, and 38.88. A graph appears to the right of the table. The horizontal axis is labeled “Temperature (K).” with markings and labels provided for multiples of 100 beginning at 0 and ending at 300. The vertical axis is labeled “Volume (L)”

with marking and labels provided for multiples of 10, beginning at 0 and ending at 30. Five data points from the table are plotted on the graph with black dots. These dots are connected with a solid black line. The graph shows a positive linear trend.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. Charles's law states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \alpha T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T$$

with k being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = k), and as seen with the *P*-*T* relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

✓ Example 5.2.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives: $V_2 = \frac{0.300 \text{ L} \times 303 \cancel{\text{K}}}{283 \cancel{\text{K}}} = 0.321 \text{ L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

? Exercise 5.2.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

✓ Example 5.2.3: Measuring Temperature with a Volume

Change Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

Rearrangement gives $T_2 = \frac{131.7 \cancel{\text{cm}^3} \times 273.15 \text{ K}}{150.0 \text{ cm}^3} = 239.8 \text{ K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

? Exercise 5.2.3

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure 5.2.5.

Figure 5.2.5 When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear. This figure contains a diagram and two graphs. The diagram shows a syringe labeled with a scale in m l or c c with multiples of 5 labeled beginning at 5 and ending at 30. The markings halfway between these measurements are also provided. Attached at the top of the syringe is a pressure gauge with a scale marked by fives from 40 on the left to 5 on the right. The gauge needle rests between 10 and 15, slightly closer to 15. The syringe plunger position indicates a volume measurement about halfway between 10 and 15 m l or c c. The first graph is labeled "V (m L)" on the horizontal axis and "P (p s i)" on the vertical axis. Points are labeled at 5, 10, 15, 20, and 25 m L with corresponding values of 39.0, 19.5, 13.0, 9.8, and 6.5 p s i. The points are connected with a smooth curve that is declining at a decreasing rate of change. The second graph is labeled "V (m L)" on the horizontal axis and "1 divided by P (p s i)" on the vertical axis. The horizontal axis is labeled at multiples of 5, beginning at zero and extending up to 35 m L. The vertical axis is labeled by multiples of 0.02, beginning at 0 and extending up to 0.18. Six points indicated by black dots on this graph are connected with a black line segment showing a positive linear trend.

Unlike the *P*-*T* and *V*-*T* relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto \frac{1}{V}$$

or

$$P = k \cdot \frac{1}{V}$$

or

$$PV = k$$

or

$$P_1V_1 = P_2V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure $\left(\frac{1}{P}\right)$ versus the volume (V), or the inverse of volume $\left(\frac{1}{V}\right)$ versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to "linearize" their data. If we plot *P* versus *V*, we obtain a hyperbola (Figure $5.2.6$).

Figure $5.2.6$ The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $\left(\frac{1}{P}\right)$ vs. V is linear. This diagram shows two graphs. In a, a graph is shown with volume on the horizontal axis and pressure on the vertical axis. A curved line is shown on the graph showing a decreasing trend with a decreasing rate of change. In b, a graph is shown with volume on the horizontal axis and one divided by pressure on the vertical axis. A line segment, beginning at the origin of the graph, shows a positive, linear trend.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

✓ Example $5.2.4$: Volume of a Gas Sample

The sample of gas has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the *P*-*V* graph in Figure $5.2.6a$
b. the $\frac{1}{P}$ vs. *V* graph in Figure $5.2.6b$
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

a. Estimating from the *P*-*V* graph gives a value for *P* somewhere around 27 psi.
b. Estimating from the $\frac{1}{P}$ versus *V* graph give a value of about 26 psi.
c. From Boyle's law, we know that the product of pressure and volume (*PV*) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ m}\cancel{\text{L}}}{7.5 \text{ m}\cancel{\text{L}}} = 26 \text{ psi}$$

It was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

? Exercise $5.2.4$

The sample of gas has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure $5.2.6a$
b. the $\frac{1}{P}$ vs. *V* graph in Figure $5.2.6b$
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Answer a

about 17–18 mL

Answer b

~18 mL

Answer c

17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure $5.2.7$).

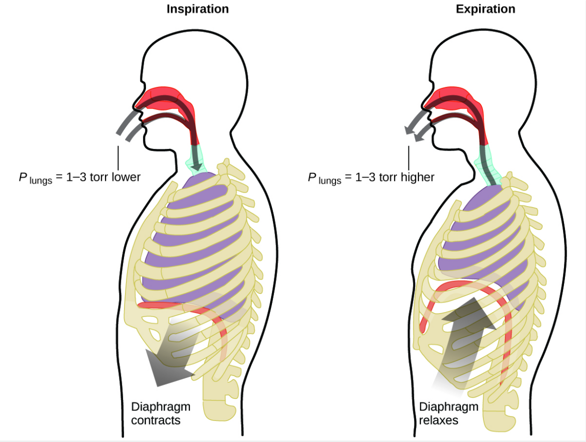


Figure 5.2.7 Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs. This figure contains two diagrams of a cross section of the human head and torso. The first diagram on the left is labeled "Inspiration." It shows curved arrows in gray proceeding through the nasal passages and mouth to the lungs. An arrow points downward from the diaphragm, which is relatively flat, just beneath the lungs. This arrow is labeled "Diaphragm contracts." At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr lower" is provided. The second, similar diagram, which is labeled "Expiration," reverses the direction of both arrows. Arrows extend from the lungs out through the nasal passages and mouth. Similarly, an arrow points up to the diaphragm, showing a curved diaphragm and lungs reduced in size from the previous image. This arrow is labeled "Diaphragm relaxes." At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr higher" is provided.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by Avogadro's law: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T.

> *Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).*

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's law: $\frac{P}{T}$ = constant at constant V and n
- Charles's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the ideal gas law, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the ideal gas constant or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.3145 kPa L mol^{-1} K^{-1}.

> *The ideal gas law is easy to remember and apply in solving problems, as long as you use the **proper values**and units for the gas constant, R.*

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an ideal gas. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

✓ Example 5.2.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

? Exercise 5.2.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of *n* × *R* (where *n* = the number of moles of the gas and *R* is the ideal gas law constant).

✓ Example 5.2.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 5.2.8). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?

Figure 5.2.8 Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild) This photograph shows a scuba diver underwater with a tank on his or her back and bubbles ascending from the breathing apparatus.

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}\longrightarrow\frac{(153\text{ atm})(13.2\text{ L})}{(300\text{ K})}=\frac{(3.13\text{ atm})(V_2)}{(310\text{ K})}$$

Solving for V_2:

$$V_2=\frac{(153\ \cancel{\text{atm}})(13.2\text{ L})(310\ \cancel{\text{K}})}{(300\ \cancel{\text{K}})(3.13\ \cancel{\text{atm}})}=667\text{ L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

? Exercise 5.2.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 5.2.9) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.

Figure 5.2.9 Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor). This picture shows colorful underwater corals and anemones in hues of yellow, orange, green, and brown, surrounded by water that appears blue in color.

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a standard temperature and pressure (STP) for reporting properties of gases: 273.15 K (0.00 °C) and 1 atm (101.325 kPa). At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the standard molar volume (Figure 5.2.10).

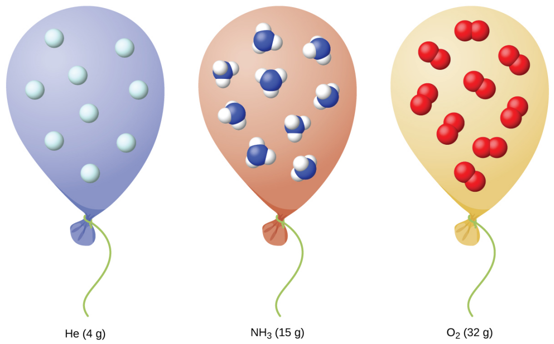


Figure 5.2.10: Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases. This figure shows three balloons each filled with H e, N H subscript 2, and O subscript 2 respectively. Beneath the first balloon is the label "4 g of He" Beneath the second balloon is the label, "15 g of N H subscript 2." Beneath the third balloon is the label "32 g of O subscript 2." Each balloon contains the same number of molecules of their respective gases.

Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

Key Equations

- $PV = nRT$

Summary

absolute zero
temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law
(also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Avogadro's law
volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Boyle's law
volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law
volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

ideal gas
hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant (*R*)
constant derived from the ideal gas equation $R = 0.08226$ L atm mol^{-1} K^{-1} or 8.314 L kPa mol^{-1} K^{-1}

ideal gas law
relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)
273.15 K (0 °C) and 1 atm (101.325 kPa)

standard molar volume
volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

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5.3: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton’s law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, “It took the mob only a moment to remove his head; a century will not suffice to reproduce it."

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask “How much?” We can answer the question with masses of substances or volumes of solutions. However, we can also answer this question another way: with volumes of gases. We can use the ideal gas equation to relate the pressure, volume, temperature, and number of moles of a gas. Here we will combine the ideal gas equation with other equations to find gas density and molar mass. We will deal with mixtures of different gases, and calculate amounts of substances in reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can used to determine its molar mass and thereby assist in its identification. The ideal gas law, $PV = nRT$, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in Example $5.3.1$.

Example $5.3.1$: Derivation of a Density Formula from the Ideal Gas Law

Use $PV = nRT$ to derive a formula for the density of gas in g/L

Solution

$$PV = nRT \tag{5.3.1}$$

Rearrange to get (mol/L):

$$\frac{n}{v} = \frac{P}{RT} \tag{5.3.2}$$

Multiply each side of the equation by the molar mass (or molecular weight), $\mathcal{M}$. When moles are multiplied by $\mathcal{M}$ in g/mol, g are obtained:

$$(\mathscr{M})\left(\frac{n}{V}\right) = \left(\frac{P}{RT}\right)(\mathscr{M}) \tag{5.3.3}$$

$$\mathscr{M}/V = \rho = \frac{P\mathscr{M}}{RT} \tag{5.3.4}$$

Exercise $5.3.1$

A gas was found to have a density of 0.0847 g/L at 17.0 °C and a pressure of 760 torr. What is its molar mass? What is the gas?

Answer

$$\rho = \frac{P\mathscr{M}}{RT} \tag{5.3.5}$$

$$0.0847\text{ g/L} = 760\,\cancel{\text{torr}} \times \frac{1\,\cancel{\text{atm}}}{760\,\cancel{\text{torr}}} \times \frac{\mathscr{M}}{0.0821\text{ L}\,\cancel{\text{atm}}/\text{mol K}} \times 290\text{ K} \tag{5.3.6}$$

$\mathcal{M}$ = 2.02 g/mol; therefore, the gas must be hydrogen (H_2, 2.02 g/mol)

We must specify both the temperature and the pressure of a gas when calculating its density because the number of moles of a gas (and thus the mass of the gas) in a liter changes with temperature or pressure. Gas densities are often reported at STP.

Molar Mass of a Gas

Another useful application of the ideal gas law involves the determination of molar mass. By definition, the molar mass of a substance is the ratio of its mass in grams, m, to its amount in moles, n:

$$\mathscr{M} = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n} \tag{5.3.7}$$

The ideal gas equation can be rearranged to isolate n:

$$n = \frac{PV}{RT} \tag{5.3.8}$$

and then combined with the molar mass equation to yield:

$$\mathscr{M} = \frac{mRT}{PV} \tag{5.3.9}$$

This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.

The Pressure of a Mixture of Gases: Dalton’s Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other’s pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 5.3.2). The pressure exerted by each individual gas in a mixture is called its partial pressure. This observation is summarized by Dalton’s law of partial pressures: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{Total} = P_A + P_B + P_C + \ldots = \sum_i P_i \tag{5.3.10}$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

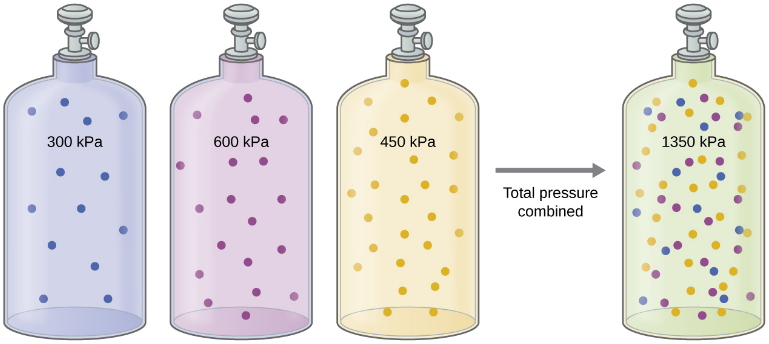


Figure 5.3.2: If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its mole fraction (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}} \tag{5.3.11}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example 5.3.2: The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H_2, 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{\mathrm{H_2}} = \frac{(2.50 \times 10^{-3}\ \mathrm{mol})(0.08206\ \cancel{\mathrm{L}}\,\mathrm{atm}\ \cancel{\mathrm{mol^{-1}\ K^{-1}}})(308\ \cancel{\mathrm{K}})}{10.0\ \cancel{\mathrm{L}}} = 6.32 \times 10^{-3}\ \mathrm{atm} \tag{5.3.12}$$

$$P_{\mathrm{He}} = \frac{(1.00 \times 10^{-3}\ \cancel{\mathrm{mol}})(0.08206\ \cancel{\mathrm{L}}\,\mathrm{atm}\ \cancel{\mathrm{mol^{-1}\ K^{-1}}})(308\ \cancel{\mathrm{K}})}{10.0\ \cancel{\mathrm{L}}} = 2.53 \times 10^{-3}\ \mathrm{atm} \tag{5.3.13}$$

$$P_{\mathrm{Ne}} = \frac{(3.00 \times 10^{-4}\ \cancel{\mathrm{mol}})(0.08206\ \cancel{\mathrm{L}}\ \mathrm{atm}\ \cancel{\mathrm{mol^{-1}\ K^{-1}}})(308\ \cancel{\mathrm{K}})}{10.0\ \cancel{\mathrm{L}}} = 7.58 \times 10^{-4}\ \mathrm{atm} \tag{5.3.14}$$

The total pressure is given by the sum of the partial pressures:

$$P_{\mathrm{T}} = P_{\mathrm{H_2}} + P_{\mathrm{He}} + P_{\mathrm{Ne}} = (0.00632 + 0.00253 + 0.00076)\ \mathrm{atm} = 9.61 \times 10^{-3}\ \mathrm{atm} \tag{5.3.15}$$

Exercise 5.3.2

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 5.3.3), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

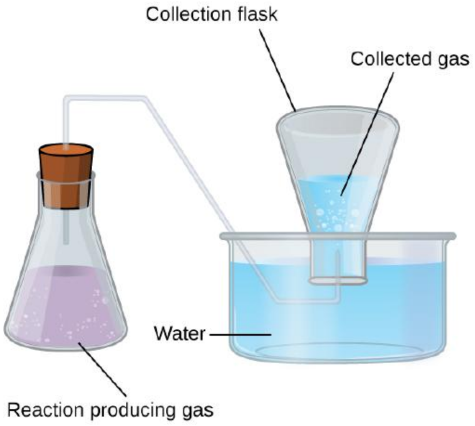


Figure 5.3.3: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the "dry" gas pressure, that is, the pressure of the gas only, without water vapor.

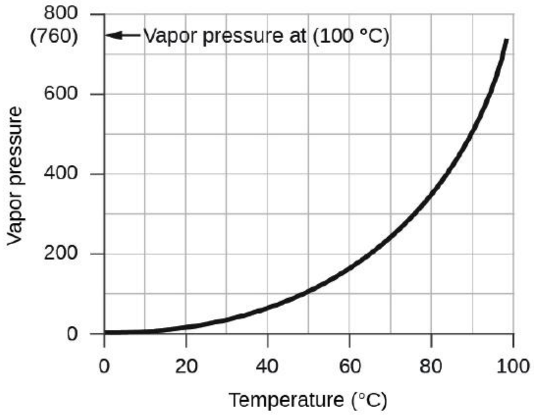


Figure 5.3.4: This graph shows the vapor pressure of water at sea level as a function of temperature.

The vapor pressure of water, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 5.3.4); more detailed information on the temperature dependence of water vapor can be found in Table 5.3.1, and vapor pressure will be discussed in more detail in the next chapter on liquids.

Table **5.3.1**: *Vapor Pressure of Ice and Water in Various Temperatures at Sea Level*

Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)
–10	1.95		18	15.5		30	31.8
–5	3.0		19	16.5		35	42.2
–2	3.9		20	17.5		40	55.3
0	4.6		21	18.7		50	92.5
2	5.3		22	19.8		60	149.4
4	6.1		23	21.1		70	233.7
6	7.0		24	22.4		80	355.1
8	8.0		25	23.8		90	525.8

Temperature (°C)	Pressure (torr)
10	9.2
12	10.5
14	12.0
16	13.6
26	25.2
27	26.7
28	28.3
29	30.0
95	633.9
99	733.2
100.0	760.0
101.0	787.6

Example 5.3.4: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 5.3.3, what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_{\mathrm{T}} = P_{\mathrm{Ar}} + P_{\mathrm{H_2O}} \tag{5.3.16}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{\mathrm{Ar}} = P_{\mathrm{T}} - P_{\mathrm{H_2O}} \tag{5.3.17}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{\mathrm{Ar}} = 750\ \mathrm{torr} - 25.2\ \mathrm{torr} = 725\ \mathrm{torr} \tag{5.3.18}$$

Exercise 5.3.4

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Answer

0.583 L

Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions. We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g) \tag{5.3.19}$$

a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 5.3.4. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

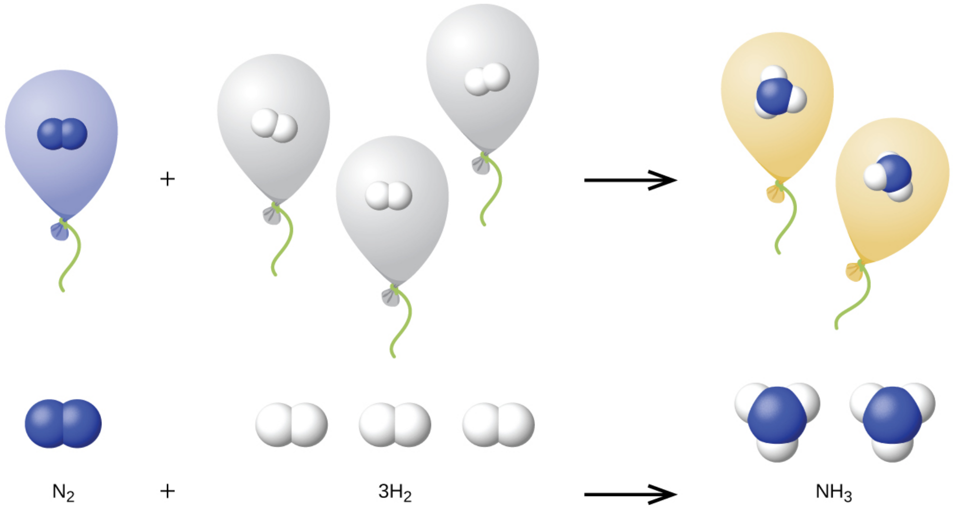


Figure 5.3.5: *One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.*

Example 5.3.5: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\begin{aligned} \mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \longrightarrow &\quad 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l) \qquad (5.3.20) \\ 1\ \text{volume} + 5\ \text{volumes} &\quad 3\ \text{volumes} + 4\ \text{volumes} \qquad (5.3.21) \end{aligned}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \mathrm{L}\ \cancel{\mathrm{C_3H_8}} \times \frac{5\ \mathrm{L}\ \mathrm{O_2}}{1\ \mathrm{L}\ \cancel{\mathrm{C_3H_8}}} = 13.5\ \mathrm{L}\ \mathrm{O_2} \tag{5.3.22}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 5.3.5

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2\,\mathrm{C_2H_2} + 5\,\mathrm{O_2} \longrightarrow 4\,\mathrm{CO_2} + 2\,\mathrm{H_2O} \tag{5.3.23}$$

Answer

3.34 tanks (2.34×10^4 L)

Example 5.3.6: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g) \tag{5.3.24}$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683\ \cancel{\text{billion ft}^3\ \mathrm{NH_3}} \times \frac{3\ \text{billion ft}^3\ \mathrm{H_2}}{2\ \cancel{\text{billion ft}^3\ \mathrm{NH_3}}} = 1.02 \times 10^3\ \text{billion ft}^3\ \mathrm{H_2} \tag{5.3.25}$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Exercise 5.3.6

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer

51.0 L

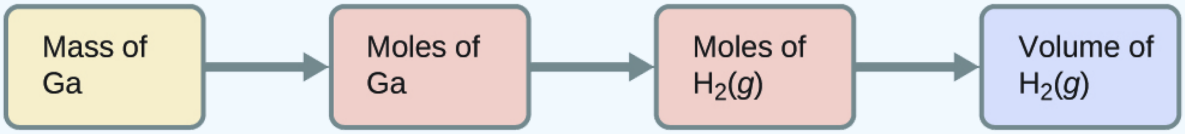
Example 5.3.7: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\,\mathrm{Ga}(s) + 6\,\mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{GaCl_3}(aq) + 3\,\mathrm{H_2}(g) \tag{5.3.26}$$

Solution

To convert from the mass of gallium to the volume of $H_2(g)$, we need to do something like this:



The first two conversions are:

$$8.88\ \cancel{\text{g Ga}} \times \frac{1\ \cancel{\text{mol Ga}}}{69.723\ \cancel{\text{g Ga}}} \times \frac{3\ \text{mol H}_2}{2\ \cancel{\text{mol Ga}}} = 0.191\ \text{mol H}_2 \tag{5.3.27}$$

Finally, we can use the ideal gas law:

$$V_{\mathrm{H_2}} = \left(\frac{nRT}{P}\right)_{\mathrm{H_2}} = \frac{0.191\ \cancel{\text{mol}} \times 0.08206\ \text{L atm}\ \cancel{\text{mol}^{-1}\ \text{K}^{-1}} \times 300\ \text{K}}{0.951\ \text{atm}} = 4.94\ \text{L} \tag{5.3.28}$$

Exercise 5.3.7

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in oxygen?

Answer

1.30×10^3 L

Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favorable living conditions—without atmosphere, the average global average temperature of 14 °C (57 °F) would be about –19 °C (–2 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 5.3.6).

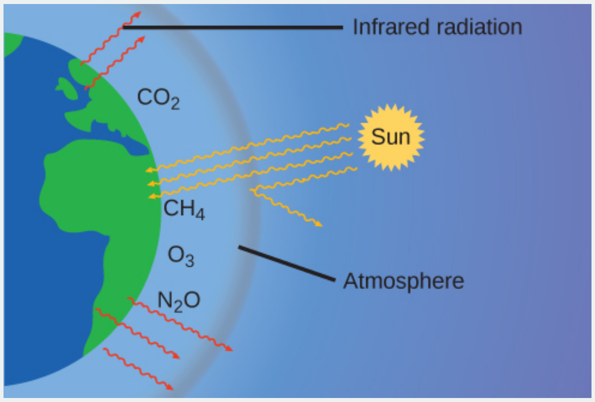


Figure 5.3.6: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO_2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO_2. Reliable data from ice cores reveals that CO_2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO_2 concentration has increased from historical levels of below 300 ppm to almost 400 ppm today (Figure 5.3.7).

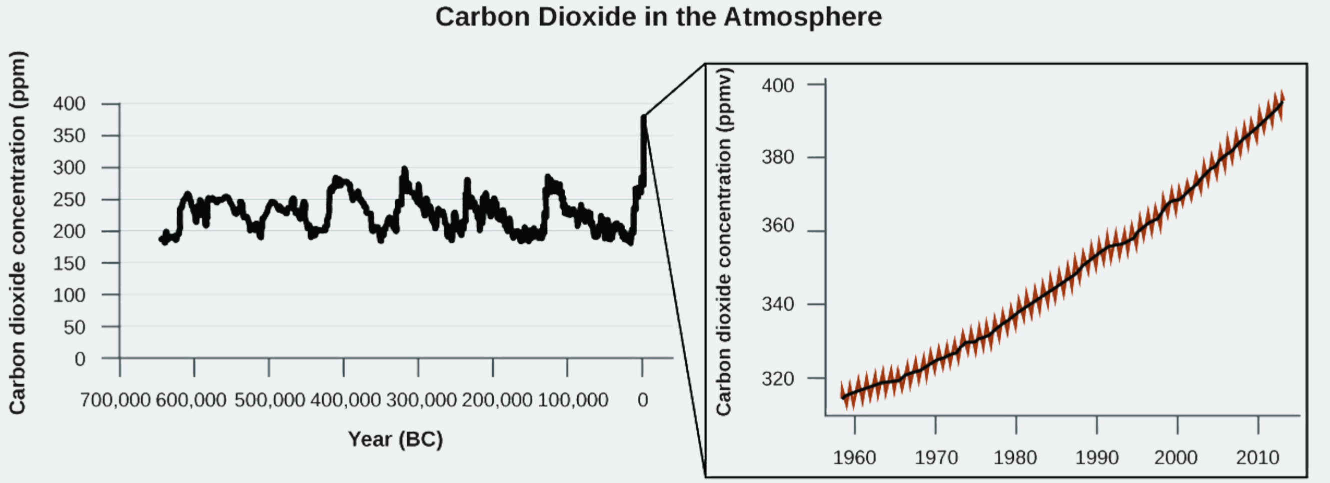


Figure 5.3.7: Figure CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Contributors and Attributions

Summary

Contributors and Attributions

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton’s law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro’s law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

Key Equations

- $P_{Total} = P_A + P_B + P_C + \ldots = \Sigma_i P_i$
- $P_A = X_A P_{Total}$
- $X_A = \frac{n_A}{n_{Total}}$

Footnotes

1. “Quotations by Joseph-Louis Lagrange,” last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.../Lagrange.html

Summary

Dalton’s law of partial pressures

total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

mole fraction (X)

concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

partial pressure

pressure exerted by an individual gas in a mixture

vapor pressure of water

pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

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- Template:ContribOpenStax

CHAPTER OVERVIEW

6: Acid-Base Chemistry

Topic hierarchy

Acids and bases are ubiquitous in our natural and manufactured environments and in our lives. These types of reactions govern not only the behavior of acids and bases themselves but the behaviors of other chemicals of environmental relevance. Examples include muriatic acid (cleaner), acetylsalicylic acid (aspirin), hypochlorous acid (bleach), ascorbic acid (vitamin C), carbonic acid, phosphoric acid, and ammonia/ammonium.

6.1: 6.1 Dissociation of Water and the pH Scale

> This page is a draft and is under active development.

An understanding of acid and base chemistry principles, as well as the ability to solve quantitative problems, requires first learning how water behaves and relates to these concepts. We know the formula for water is $H_2O_{(l)}$, and that it is a permanent dipole due to the electronegativity of the oxygen atom. The oxygen draws the two pairs of shared electrons closer to it and slightly away from the hydrogen atoms, creating a slightly negative charge around the oxygen atom.

Because the electrons are nearer the oxygen atom, a hydrogen atom can actually 'pivot' away from the rest of the molecule and reorient itself in solution, either towards the oxygen atom in another water molecule, associate with another anion, or combine with a hydroxide ion to form a new water molecule. While these reactions are transient and continuous, they are significant enough to be of relevance. We write this reaction, simplified, as:

$$\mathrm{H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)}$$

For most of our discussion of acid base chemistry, we will drop the phase designations and generally work with aqueous phase ions:

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-}$$

In this reaction, one hydrogen ion is "dis-associating" with the rest of the molecule. So, this and other acid reactions like it are called ***dissociation*** reactions. For water it is also sometimes called hydrolysis. ('hydro' and lysis') The hydrogen ion, H^+ is called a ***proton.*** The OH^- ion is ***hydroxide***.

Just like other reactions we studied in thermodynamics, this reaction is reversible and has an equilibrium that is sensitive to temperature, etc. So, acid base chemistry is really just, you guessed it, more thermodynamics.

Using the ideal, dilute solution assumption (meaning we can use concentration instead of activity), we can write the expression for the equilibrium constant for this reaction as:

$$K_{eq} = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]}$$

Because this Keq is for the dissociation of water, we call it K_w. And, because the activity of water is ~1.0, we can re-write the equation:

Using our equation $\Delta G = -RT\ln K_{eq}$, we can calculate ***the value of*** $K_{w,298K} = 1\times10^{-14}$.

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}]$$

Now, this equilibrium of water is usually responding to changes in system pH that are caused by other species – strong or weak acids and bases. So, we wouldn't have a case with pure water where the protons from water had to exactly match the hydroxide ions from water. In fact this is rarely the case. Instead we have solutions that are acidic and basic all the time. There will be other stuff in solution that will take care of conservation of mass and electroneutrality.

K_w is sensitive to temperature, as are all equilibrium constants. We already know how to adjust this value for temperature.

In the term pH, the H refers to the concentrations of protons, H^+. The p is a mathematical shorthand, referring to the negative base-10 logarithm. So,

$pH = -\log[H^+]$

Although not as common, you could just as easily (and legitimately) us the term 'pOH':

$pOH = -\log[OH^-]$

Because K_w is an equilibrium constant (or, an equilibrium coefficient, if you consider that it is not truly constant but can change with temperature), we can always relate pH and pOH, or $[H^+_{(aq)}]$ and $[OH^-_{(aq)}]$. Let's do an example.

Example 6.1.1

What is pH when $[H^+] = [OH^-]$?

Solution

$K_w = [H^+]\,[OH^-] = 1\times10^{-14}$,   and $[H^+] = [OH^-] = x$,   so $x^2 = 1\times10^{-14}$

$x = [H^+] = 1\times10^{-7}$ $-\log_{10}[H^+] = -\log_{10}(1\times10^{-7}) = pH$ $pH = 7$

Neutral pH is when $[OH^-] = [H^+] = 1\times10^{-7}$. Acidic solutions have $[H^+] > 1\times10^{-7}$, or $pH < 7$. Basic, or alkaline, solutions have $[H^+] < 1\times10^{-7}$, or pH >

Exercise 6.1.1

For these other solutions, fill in the missing values.

Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
pH =	pH =	pH = 7	pH =	pH =
pOH =	pOH = 10	pOH =	pOH =	pOH =
$[H^+] = 1x10^{-1}$ M	$[H^+] =$	$[H^+] =$	$[H^+] = 1x10^{-9}$ M	$[H^+] =$
$[OH^-] =$	$[OH^-] =$	$[OH^-] =$	$[OH^-] =$	$[OH^-] = 1x10^{-11}$ M

Answer

The table is repeated below, with missing values filled in.

Solution 1	Solution 2	Solution 3	Solution 4	Solution 5
pH = 1	pH = 4	pH = 7	pH = 9	pH = 3
pOH = 13	pOH = 10	pOH = 7	pOH = 5	pOH = 11
$[H^+] = 1x10^{-1}$ M	$[H^+] = 1x10^{-4}$ M	$[H^+] = 1x10^{-7}$ M	$[H^+] = 1x10^{-9}$ M	$[H^+] = 1x10^{-3}$ M
$[OH^-] = 1x10^{-13}$ M	$[OH^-] = 1x10^{-10}$ M	$[OH^-] = 1x10^{-7}$ M	$[OH^-] = 1x10^{-5}$ M	$[OH^-] = 1x10^{-11}$ M

.

Another useful relationship follows from these:

$$pH + pOH \quad = \quad -\log[H^+] + -\log[OH^-] \quad = \quad -\log 10^{-14} \quad = \quad 14$$

An additional example using temperature adjustment of Keq:

Thinking about corrosivity of water to plumbing materials: If we were to heat up water in a hot water heater to a temperature of 50C, will that water become more corrosive or less corrosive (based on its pH) to plumbing materials? Assume that the water is still neutral: $[H^+_{(aq)}] = [OH^-_{(aq)}]$, and assume that lower pH translates into more corrosive water.

6.2: 6.2 Acids, Bases, and Salts

> This page is a draft and is under active development.

Beyond Water: Structure of Acids and Bases

To define acids and bases, we'll use the definitions below:

Acid – A substance that can, to at least some extent, donate a proton into solution.

Base – A compound that can, to at least some extent, accept a proton from solution.

Acids and bases are generally categorized into either ***strong acids*** or ***weak acids***. Although this is a continuum rather than a hard definition, it is a useful one for understanding aqueous chemistry. Also, the categories are more often applied to acids than bases. So, some examples of strong acids and weak acids are shown below:

Strong Acids	Weak Acids
Nitric Acid, HNO_3	Acetic Acid, $HC_2H_3O_2$
Sulfuric Acid, H_2SO_4	Ammonium ion, NH_4^+
Hydrochloric Acid, HCl	...many others

For these three strong acids, we will assume that there is 100% complete dissociation into proton and conjugate base.

For all weak acids, we cannot assume that there is 100% dissociation. Instead, there will be some partitioning between the acid and base forms.

We use the equilibrium constant to quantify the tendency of an acid to dissociate, and we call that equilibrium constant K_a. A weak acid (the form with the proton) and its conjugate base (the form without the proton) can have very different properties. So, it is important that we can quantify the amount or concentration of the compound in both the ***protonated*** and ***unprotonated*** forms.

Some examples that we'll show in class include:

Hypochlorous Acid, HOCl:

$$\mathrm{HOCl(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{OCl^-(aq)}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{OCl^-}]}{[\mathrm{HOCl}]}$$

Bicarbonate Ion, HCO_3-

$$\mathrm{HCO_3^-(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{CO_3^{-2}(aq)}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{CO_3^{-2}}]}{[\mathrm{HCO_3^-}]}$$

Acetic Acid, CH_3COOH

$$\mathrm{CH_3COOH(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{CH_3COO^-(aq)}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

Ammonium Ion, NH_4^+

$$\mathrm{NH_4^+(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{NH_3(aq)}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{NH_3}]}{[\mathrm{NH_4^+}]}$$

In these Ka equations I have left off the phase designations for now, since we will be working primarily in the aqueous phase.

Because the numeric values of most acid dissociation equilibrium constantsare <0.1, we usually tabulate them as pKa values, or, -logKa. For example, if Ka = 1×10^{-6}, pKa = 6.

Salts of Acids and Bases

Species that participate in acid/base reactions don't always start out as acids or bases. For instance, sodium can be combined with phosphate in dry chemical form to make sodium phosphate, $Na_3PO_{4(s)}$. If we dissolve it in water at some concentration below its solubility, it will generally all dissolve, right?

$$\mathrm{Na_3PO_4}(s) \longrightarrow 3\,\mathrm{Na^+}(aq) + \mathrm{PO_4^{-3}}(aq) \tag{6.2.1}$$

But, phosphoric acid is a weak acid. In solution, it behaves according to the reactions below:

$$\mathrm{H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \rightleftharpoons 2\,H^+(aq) + HPO_4^{-2}(aq) \rightleftharpoons 3\,H^+(aq) + PO_4^{-3}(aq)}$$

In our system of interest here we have water, some of which has dissociated into H^+ and OH^-.

$$\mathrm{H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)}$$

So, some of that PO_4^{3-} from the sodium phosphate salt will react with H^+ back up the phosphoric acid dissociation reaction pathway:

$$\mathrm{H^+(aq) + PO_4^{-3}(aq) \rightleftharpoons HPO_4^{-2}(aq) + H^+(aq) \rightleftharpoons H_2PO_4^-(aq) + H^+(aq) \rightleftharpoons H_3PO_4(aq)}$$

In essence, we have created a weak acid system by adding the sodium salt of the acid.

Common clues that you are dealing with a salt:

The cation is **sodium or potassium**, and its associated anion is a component of a weak acid/base system.

The anion is **chloride**, and its associated cation is a component of a weak acid/base system

For the problems we will be doing, we will usually be working with salts in which the cations are sodium or potassium. These are monovalent cations, so their salt compounds are very soluble in water and will result in that salt completely dissolving. Sometimes calcium and magnesium salts will come into play, as well, and we'll also assume they completely dissolve. If the salt is an anion, it will usually be chloride that we are looking at. Chloride salts of acids and bases are highly soluble in water and completely dissociate.

Learn to recognize the salts of acids and basis, so that you can determine when a compound will completely dissociate into its constituent ions. This will make it much easier to solve acid and base equilibria.

6.3: 6.3 Numerical Solutions to Acid-Base Chemistry Problems

> This page is a draft and is under active development.

Weak acid/base systems exist within broader systems, usually aqueous phase. Sometimes the weak acid/base pair dominates the system and controls the pH of that solution. Other times, there are other constituents or characteristics of the system that control the pH to a certain condition. In the latter, we can use the Henderson-Hasselbach equation, or just the Ka equation, to determine the partitioning between the weak acid and weak base pair(s).

In the former case, we may not know the pH of the solution or the partitioning of the acid/base forms. In those cases, we can use equilibrium chemistry to predict or model what the expected pH and partitioning will be. We will use a four step process to set up these problems and will find exact solutions by solving what usually ends up being a 2nd or 3rd order polynomial. The four-step process is described below. We will illustrate the process using an example of a solution.

6.3.1 Write all reactions; list all unknowns:

6.3.2 Write all equations of equiliubrium

6.3.3 Write a mass balance for the primary acid/base species of interest

6.3.4 Write a charge balance assuming electroneutrality

CHAPTER OVERVIEW

7: Solubility and Precipitation

7.1: Precipitation and Dissolution

Learning Objectives

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $Ca_5(PO_4)_3(OH)$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Chatelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a solution.

The Solubility Product Constant

Silver chloride is what's known as a sparingly soluble ionic solid (Figure 7.1.1). Halides of Ag^+ are not normally soluble. However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and $Cl^−$ ions in equilibrium with undissolved silver chloride:

$$\mathrm{AgCl}(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \tag{7.1.1}$$

This equilibrium, like other equilibria, is dynamic; some of the solid AgCl continues to dissolve, but at the same time, Ag^+ and $Cl^−$ ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.

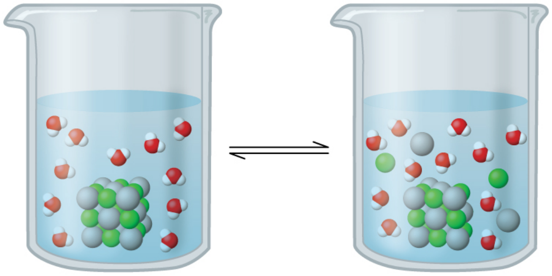


Figure 7.1.1: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and $Cl^−$ ions in equilibrium with undissolved silver chloride.

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the solubility product (K_{sp}) of the solid. Recall that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \tag{7.1.2}$$

with

$$K_{\mathrm{sp}} = [\mathrm{Ag}^+(aq)][\mathrm{Cl}^-(aq)] \tag{7.1.3}$$

When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. In other words, **always write these reactions as dissolution reactions!** The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of the ions, raised to the power of their stoichiometric coefficients from the balanced reaction. Here, the solubility product constant is equal to the product of $[Ag^+]$ and $[Cl^−]$ when a solution of silver chloride is in equilibrium with undissolved AgCl. There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore [AgCl] does not appear in the expression for K_{sp} (the activity of a pure solid is defined as 1).

Table 7.1.1: Common Solubility Products by Decreasing Equilibrium Constants

Substance	K_{sp} at 25 °C
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}

Some common solubility products are listed in Table 7.1.1 according to their K_{sp} values. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left (the solid form), so that relatively few hydrated ions would be present in a saturated solution.

Example 7.1.1: Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

a. AgI, silver iodide, a solid with antiseptic properties
b. $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids
c. $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
d. $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
e. $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

(For d. and e., common ions such as ammonium, phosphate, and hydroxide will remain intact after dissolution of the parent compound.)

Solution

a. $\mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{I^-}(aq) \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{I^-}]$
b. $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]$
c. $\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2$
d. $\mathrm{Mg(NH_4)PO_4}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + \mathrm{NH_4^+}(aq) + \mathrm{PO_4^{3-}}(aq) \quad K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{NH_4^+}][\mathrm{PO_4^{3-}}]$
e. $\mathrm{Ca_5(PO_4)_3OH}(s) \rightleftharpoons 5\,\mathrm{Ca^{2+}}(aq) + 3\,\mathrm{PO_4^{3-}}(aq) + \mathrm{OH^-}(aq) \quad K_{sp} = [\mathrm{Ca^{2+}}]^5[\mathrm{PO_4^{3-}}]^3[\mathrm{OH^-}]$

Exercise 7.1.1

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

a. $BaSO_4$
b. Ag_2SO_4
c. $Al(OH)_3$
d. Pb(OH)Cl

Answer a

$$\mathrm{BaSO_4}(s) \rightleftharpoons \mathrm{Ba^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}]$$

Answer b

$$\mathrm{Ag_2SO_4}(s) \rightleftharpoons 2\,\mathrm{Ag^+}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_{sp} = [\mathrm{Ag^+}]^2[\mathrm{SO_4^{2-}}]$$

Answer c

$$\mathrm{Al(OH)_3}(s) \rightleftharpoons \mathrm{Al^{2+}}(aq) + 3\,\mathrm{OH^-}(aq) \qquad K_\mathrm{sp} = [\mathrm{Al^{3+}}][\mathrm{OH^-}]^3$$

Answer d

$$\mathrm{Pb(OH)Cl}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + \mathrm{OH^-}(aq) + \mathrm{Cl^-}(aq) \qquad K_\mathrm{sp} = [\mathrm{Pb^{2+}}][\mathrm{OH^-}][\mathrm{Cl^-}]$$

Now we will extend the discussion of K_{sp} and show how the solubility product constant is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

K_{sp} and Solubility

The definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M^{m+}}(aq) + q\mathrm{X^{n-}}(aq) \tag{7.1.4}$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its molar solubility.

Example 7.1.2: Calculation of K_{sp} from Equilibrium Concentrations

We began the chapter with an informal discussion of how the mineral fluorite is formed. Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{F^-}(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.1 × 10^{-4} *M*; therefore, that of F^- is 4.2 × 10^{-4} *M*, that is, twice the concentration of Ca^{2+}. What is the solubility product of fluorite?

Solution

A saturated solution is a solution at equilibrium with the solid. Thus the reaction, as above, is:

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{F^-}(aq)$$

Write out the K_{sp} expression, then substitute in concentrations and solve for $K_{sp.}$

$$K_\mathrm{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = 3.7 \times 10^{-11}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 7.1.2

In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 3.7 × 10^{-5} *M*. What is the solubility product for $Mg(OH)_2$?

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

Answer

2.0 × 10^{-13}

Example 7.1.3: Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3 × 10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3 × 10^{-9}.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu}^{+}(aq) + \mathrm{Br}^{-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\mathrm{sp}} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$

At equilibrium:

$$\begin{gathered} K_{\mathrm{sp}} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}] \\ 6.3 \times 10^{-9} = (x)(x) = x^2 \\ x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5} \end{gathered}$$

Therefore, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Exercise 7.1.3

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

1.2×10^{-8} *M*

Example 7.1.4: Determination of Molar Solubility from K_{sp}, Part II

Determination of Molar Solubility from K_{sp}, Part II The K_{sp} of calcium hydroxide, $\mathrm{Ca(OH)_2}$, is 8.0×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product constant of calcium hydroxide is 1.3×10^{-6}.

The reaction is:

$$\mathrm{Ca(OH)_2}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + 2\,\mathrm{OH}^{-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{OH}^{-}]^2$$

At equilibrium:

$$\begin{aligned} &K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{OH}^{-}]^2 \\ &1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3 \\ &x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3} \end{aligned}$$

Therefore, the molar solubility of $\mathrm{Ca(OH)_2}$ is 6.9×10^{-3} *M*.

Exercise 7.1.4

The K_{sp} of $\mathrm{PbI_2}$ is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer

1.5×10^{-3} *M*

Note that solubility is not always given as a molar value. When the solubility of a compound is given in some unit other than moles per liter, we must convert the solubility into moles per liter (i.e., molarity) in order to use it in the solubility product constant expression. Example 7.1.5 shows how to perform those unit conversions before determining the solubility product equilibrium.

Example 7.1.5: Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 7.1.2) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product equilibrium constant for $PbCrO_4$.

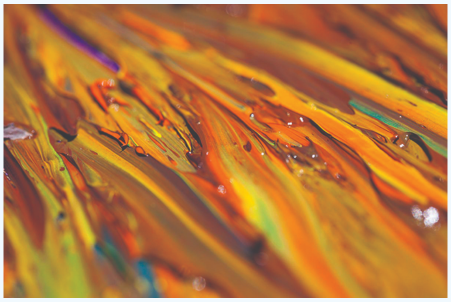
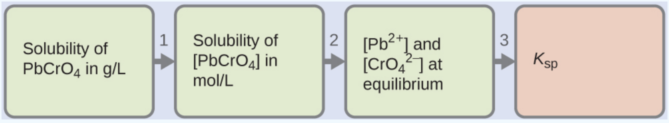


Figure 7.1.2: Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

We are given the solubility of $PbCrO_4$ in grams per liter. If we convert this solubility into moles per liter, we can find the equilibrium concentrations of Pb^{2+} and CrO_4^{2-}, then K_{sp}:



1. *Use the molar mass of $PbCrO_4$ $\left(\frac{323.2\text{ g}}{1\text{ mol}}\right)$ to convert the solubility of $PbCrO_4$ in grams per liter into moles per liter:*

$$[\mathrm{PbCrO_4}] = \frac{4.6 \times 10^{-6}\text{ g PbCrO}_4}{1\text{ L}} \times \frac{1\text{ mol PbCrO}_4}{323.2\text{ g PbCrO}_4}$$
$$= \frac{1.4 \times 10^{-8}\text{ mol PbCrO}_4}{1\text{ L}}$$
$$= 1.4 \times 10^{-8}\ M$$

2. *The chemical equation for the dissolution indicates that 1 mol of $PbCrO_4$ gives 1 mol of $Pb^{2+}(aq)$ and 1 mol of* $CrO_4^{2-}(aq)$:

$$\mathrm{PbCrO_4}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + \mathrm{CrO_4^{2-}}(aq)$$

Thus, both $[Pb^{2+}]$ and $[CrO_4^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

$$[\mathrm{Pb^{2+}}] = [\mathrm{CrO_4^{2-}}] = 1.4 \times 10^{-8}\ M$$

3. *Solve.* $K_{sp} = [Pb^{2+}]\,[CrO_4^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

Exercise 7.1.5

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.46 grams per liter at 20 °C. What is its solubility product?

Answer

2.08×10^{-4}

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 1.1 × 10^{-10}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 7.1.3).

Figure 7.1.3: The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons).

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Predicting Precipitation

Tabulated K_{sp} values can also be compared to reaction quotients calculated from experimental data to tell whether a solid will precipitate in a reaction under specific conditions: Q equals K_{sp} at equilibrium; if Q is less than K_{sp}, the solid will dissolve until Q equals K_{sp}; if Q is greater than K_{sp}, precipitation will occur at a given temperature until Q equals K_{sp}.

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \tag{7.1.5}$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient $(Q = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}])$ is equal to the solubility product (K_{sp} = 4.8 × 10^{-9}). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains $\mathrm{CO_3^{2-}}$ ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and $\mathrm{CO_3^{2-}}$ ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example 7.1.7 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example 7.1.7: Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = 8.9 \times 10^{-12} \tag{7.1.6}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \tag{7.1.7}$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}]$ = 0.0537 *M* and $[OH^-]$ = 0.0010 *M*. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$\mathrm{Q} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8} \tag{7.1.8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

Exercise 7.1.7

Use the solubility products in Table E3 to determine whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}]$ = 0.0001 *M* and $[\mathrm{HPO_4^{2-}}]$ = 0.001 *M*.

Answer

No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp}

Example 7.1.8: Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-*M* solution of $AgNO_3$ and a 2.0×10^{-4}-*M* solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

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

The solubility product is 1.8×10^{-10} (Table E3).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[Ag^+]$ and $[Cl^-]$ are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4})\ M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, Q, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\mathrm{Ag^+}][\mathrm{Cl^-}] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp}.

Exercise 7.1.8

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Example 7.1.9: Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 7.1.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?

Figure 7.1.4: Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq) \tag{7.1.9}$$

For this reaction (Table E3):

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8} \tag{7.1.10}$$

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $C_2O_4^{2-}$ that is necessary to produce the first trace of solid:

$$Q = K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8}$$
$$(2.2 \times 10^{-3})[C_2O_4^{2-}] = 1.96 \times 10^{-8}$$
$$[C_2O_4^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}$$

A concentration of $[C_2O_4^{2-}]$ = 8.9 × 10^{-6} M is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 7.1.9

If a solution contains 0.0020 mol of CrO_4^{2-} per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer

4.5 × 10^{-9} M

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example 7.1.8—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Example 7.1.10: Concentrations Following Precipitation

Clothing washed in water that has a manganese [Mn^{2+}(*aq*)] concentration exceeding 0.1 mg/L (1.8 × 10^{-6} M) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep [Mn^{2+}] equal to 1.8 × 10^{-6} M?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{\mathrm{sp}} = 2 \times 10^{-13} \tag{7.1.11}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is 1.8 × 10^{-6} M. From that, we calculate the pH. At equilibrium:

$$K_{\mathrm{sp}} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2 \tag{7.1.12}$$

or

$$(1.8 \times 10^{-6})[\mathrm{OH^-}]^2 = 2 \times 10^{-13} \tag{7.1.13}$$

so

$$[\mathrm{OH^-}] = 3.3 \times 10^{-4}\ M \tag{7.1.14}$$

Now we calculate the pH from the pOH:

$$\begin{aligned} \mathrm{pOH} &= -\log[\mathrm{OH^-}] = -\log(3.3 \times 10^{-4}) = 3.48 \\ \mathrm{pH} &= 14.00 - \mathrm{pOH} = 14.00 - 3.48 = 10.52 \end{aligned}$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of 1.8 × 10^{-6} M; at that concentration or less, the ion will not stain clothing.

Exercise 7.1.10

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of Mg^{2+}(*aq*) in sea water is 5.37 × 10^{-2} M. Calculate the pH at which [Mg^{2+}] is diminished to 1.0 × 10^{-5} M by the addition of $Ca(OH)_2$.

Answer

10.97

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl (K_{sp} = 1.6 × 10^{-10}), AgBr (K_{sp} = 5.0 × 10^{-13}), and AgI (K_{sp} = 1.5 × 10^{-16}) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure $7.1.5$). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{2-}) are often present in both municipal and industrial wastewaters. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure $7.1.5$: Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from wastewater is by the addition of calcium hydroxide, known as lime, $Ca(OH)_2$. The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3(OH)$, which then precipitates out of the solution:

$$5\,Ca^{2+} + 3\,PO_4^{3-} + OH^- \rightleftharpoons Ca_{10}(PO_4)_6 \cdot (OH)_2(s) \tag{7.1.15}$$

The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate ("alum").

Contributors and Attributions

Summary

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp}, of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions M^{m+} and X^{n-}:

$$M_pX_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$$

We write the solubility product expression as:

$$K_{\mathrm{sp}} = [\mathrm{M}^{\mathrm{m+}}]^p[\mathrm{X}^{\mathrm{n-}}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp}, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions. A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution.

Glossary

molar solubility

solubility of a compound expressed in units of moles per liter (mol/L)

olubility product (K_{sp})

equilibrium constant for the dissolution of a slightly soluble electrolyte

Contributors and Attributions

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7.2: Graphical Representations of Metal Solubility

This page is a draft and is under active development.

Metal-Hydroxide Precipitation

Solubility and precipitation reactions typically involve a metal cation in solution bonding with a corresponding counter anion, which could be monatomic (Cl-, F-) or polyatomic (CO3-2, PO4-3). One anion commonly involved in precipitation is the hydroxide ion, OH-. We also know that hydroxide is a key player in acid-base equilibria and the pH scale. So, it comes to reason that the solubility of metals is influenced by the pH state of an aqueous system.

A metal cation of charge +n will generally react with n hydroxide ions to form a neutral precipitate of the form

$$\mathrm{Me(OH)}_{\mathrm{n(s)}} \tag{7.2.1}$$

which can be represented with the following equation:

$$\mathrm{Me}_{\mathrm{n(s)}} \rightleftharpoons \mathrm{Me}^{+\mathrm{n}}_{\mathrm{(aq)}} + \mathrm{nOH}^{-}_{\mathrm{(aq)}}$$

If we use the equation for Ksp in combination with the equation for Kw, we can reveal the relationship between metal hydroxide solubility and pH. Let’s use an example of magnesium hydroxide,

$$\mathrm{Mg(OH)}_2 \tag{7.2.2}$$

...for which Ksp = 5.61x10^-12 (engineeringtoolbox.com). Starting with the solubility equilibrium expression for Ksp:

$$K_{sp} = [\mathrm{Mg}^{+2}_{\mathrm{(aq)}}][\mathrm{OH}^{-}_{\mathrm{(aq)}}]^2$$

If we take the log_10 of both sides of the equation and rearrange:

$$log(K_{sp}) = log[\mathrm{Mg}^{+2}] + 2log[\mathrm{OH}^{-}]$$

$$log[\mathrm{Mg}^{+2}] = log(K_{sp}) - 2log[\mathrm{OH}^{-}]$$

$$log[\mathrm{Mg}^{+2}] = log(K_{sp}) + 2pOH$$

We know that pH + pOH = 14, so pOH = 14-pH. Also, the log_10 of Ksp = -11.25. Substituting those into the equation below yields

$$log[\mathrm{Mg}^{+2}] = -11.25 + 2(14 - pH)$$

$$log[\mathrm{Mg}^{+2}] = -11.25 + 28 - 2pH$$

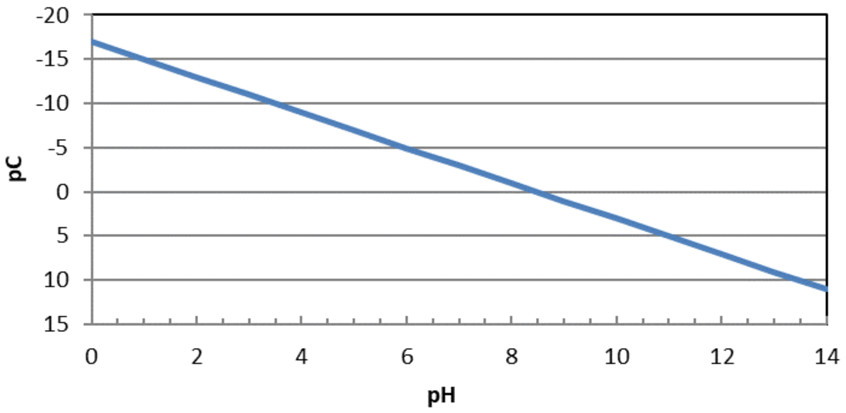
$$log[\mathrm{Mg}^{+2}] = 16.75 - 2pH$$

Or, if we multiply by -1, the left hand side is -log[Mg+2], or pC for Mg+2.

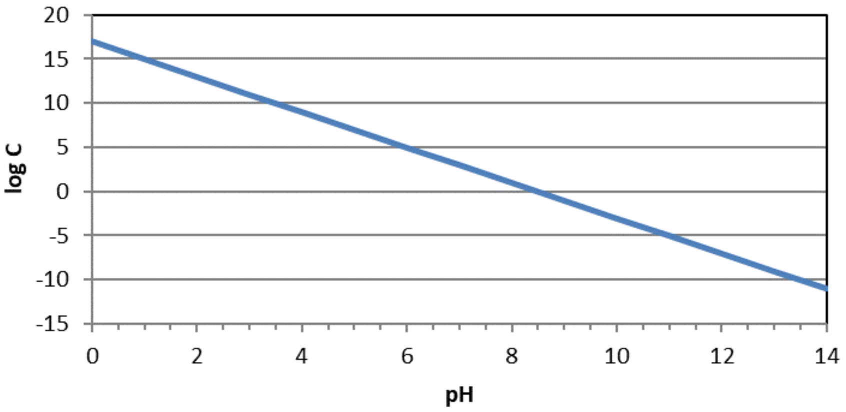
$$-log[\mathrm{Mg}^{+2}] = -16.75 + 2pH$$

This equation shows the relationship between the maximum concentration of dissolved magnesium in aqueous solution as a function of pH. The concentration is a maximum because it was derived from the Ksp equation, which represents the limit of solubility. It should be noted that this equation does not consider the presence of other anions that might precipitate with magnesium, only hydroxide ion.

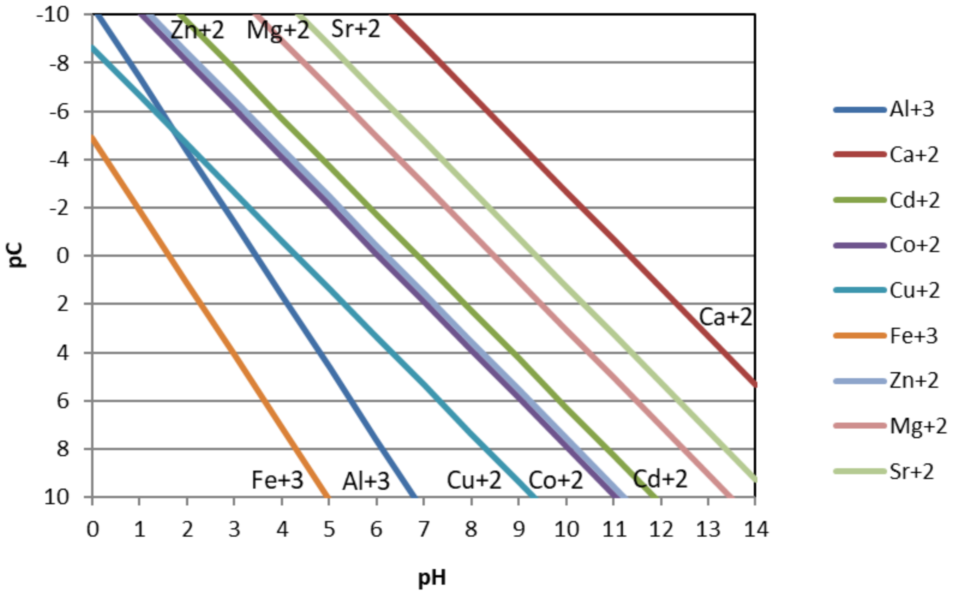
We can show this relationship graphically by plotting the concentration against pH as the independent variable. With acids and bases, we plotted pC-pH diagrams, or the -log of the concentration on the y-axis. Then, we flipped the y-axis so that it preserved the concept of high concentrations being high on the y-axis and low concentrations low on that axis.



You may also see these figures plotted as logC-pH diagrams. However, they should look exactly the same except for the numeric quantities on the y-axis. In logC-pH diagrams, the y-axis will appear as it would on a normal figure – with higher numbers at the top and lower at the bottom. Because those are logC values instead of pC (-logC) values, concentrations are still higher at the top of the diagram and lower at the bottom of the diagram.



If we follow this approach for multiple metal ions, we can compare the relative solubilities of metal hydroxides as a function of pH. Examining the figure below, we see two general observations. First, metal hydroxides can be present at much higher concentrations at lower pH. In other words, metal hydroxides are more soluble under acidic conditions. This makes sense when we consider Le Chatelier's principle: at low pH values, hydroxide ion (one of the products of the dissolution reaction) is very scarce in solution. So, the dissolution equilibrium should 'want' to shift to the right towards the products of hydroxide and the dissolve metal ion. A second observation from the figure is that, at a given pH, trivalent metal ions (aluminum and ferric iron) are less soluble than divalent metal ions.


pC
-10
-8
-6
-4
-2
0
2
4
6
8
10
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Zn+2
Mg+2
Sr+2
Ca+2
Fe+3
Al+3
Cu+2
Co+2
Cd+2
Al+3
Ca+2
Cd+2
Co+2
Cu+2
Fe+3
Zn+2
Mg+2
Sr+2

CHAPTER OVERVIEW

8: Complexation

8.1: Metals Complexation in Aqueous Solution

Learning Objectives

- Define the terms *coordination complex*, *ligand*, *polydentate*, and *chelate*.
- Explain the origins of *d*-orbital splitting; that is, why the energies of certain atomic-*d* orbitals are more affected by some ligands than others in an octahedral complex.
- Why are many coordination complexes highly *colored*?

Complexes such as $Cu(NH_3)_6^{2+}$ have been known and studied since the mid-nineteenth century, and their structures had been mostly worked out by 1900. Although the hybrid orbital model was able to explain how neutral molecules such as water or ammonia could bond to a transition metal ion, it failed to explain many of the special properties of these complexes. Finally, in 1940-60, a model known as *ligand field theory* was developed that is able to organize and explain most of the observed properties of these compounds. Since that time, coordination complexes have played major roles in cellular biochemistry, inorganic catalysis, and metal speciation in environmental systems.

What is a Complex?

If you have taken a lab course in chemistry, you have very likely admired the deep blue color of **copper sulfate** crystals, $CuSO_4{\cdot}5H_2O$. The proper name of this substance is copper(II) sulfate pentahydrate, and it is typical of many salts that incorporate *waters of hydration* into their crystal structures. It is also a *complex*, a term used by chemists to describe a substance composed of two other substances (in this case, $CuSO_4$ and H_2O) each of which is capable of an independent existence.

Figure 8.1.1: (left) Crystals of $\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}$. from Stephanb (via Wikipedia). (right) Anhydrous CuSO_4 after the water was removed.

The binding between the components of a complex is usually weaker than a regular chemical bond; thus most solid hydrates can be decomposed by heating, driving off the water and yielding the *anhydrous* salt:

$$\underbrace{\text{CuSO}_4 \cdot 5\,\text{H}_2\text{O}}_{\text{blue}} \rightarrow \underbrace{\text{CuSO}_{4\,(s)}}_{\text{white}} + 5H_2O \tag{8.1.1}$$

Driving off the water in this way also destroys the color, turning it from a beautiful deep blue to a nondescript white. If the anhydrous salt is now dissolved in water, the blue color now pervades the entire solution. It is apparent that the presence of water is somehow necessary for the copper(II) ion to take on a blue color, but why should this be?

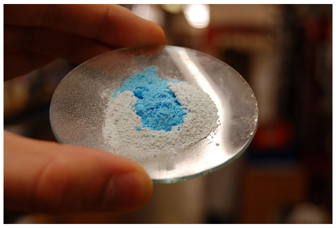


Figure 8.1.2: Difference between anhydrous and hydrated copper sulfate after a few drops of water was added to anhydrous $CuSO_4$.

A very common lab experiment that most students carry out is to add some dilute ammonia to a copper sulfate solution. At first, the solution turns milky as the alkaline ammonia causes the precipitation of copper hydroxide:

$$\text{Cu}^{2+} + 2\,\text{OH}^- \rightarrow \text{Cu(OH)}_2\text{(s)} \tag{8.1.2}$$

(The same precipitation could be carried out by adding a strong base such as NaOH, as shown in the video below.)

However, if more ammonia is added, the cloudiness disappears and the solution assumes an intense deep blue color that makes the original solution seem pale by comparison. The equation for this reaction is usually given as

$$Cu^{2+} + 6\,NH_3 \rightarrow Cu(NH_3)_6^{2+} \tag{8.1.3}$$

The new product is commonly known as the *copper-ammonia complex ion*, or more officially, hexamminecopper(II) complex ion.

Equation 8.1.3 is somewhat misleading, however, in that it implies the formation of a new complex where none existed before. In fact, since about 1895, it has been known that the ions of most transition metals dissolve in water to form complexes with water itself, so a better representation of the reaction of dissolved copper with ammonia would be

$$Cu(H_2O)_6^{2+} + 6\,NH_3 \rightarrow Cu(NH_3)_6^{2+} + 6\,H_2O \tag{8.1.4}$$

In effect, the ammonia binds more tightly to the copper ion than does water, and it thus displaces the latter when it comes into contact with the hexaaquocopper(II) ion, as the dissolved form of Cu^{2+} is properly known.

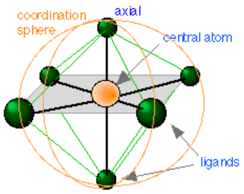
> *Most transition metals dissolve in water to form complexes with water itself.*

The basics of Coordination Complexes

Although our primary focus in this unit is on bonding, the topic of coordination complexes is so important in chemistry and biochemistry that some of their basic features are worth knowing about, even if their detailed chemistry is beyond the scope of this course. These complexes play an especially crucial role in physiology and biochemistry. Thus heme, the oxygen-carrying component of red blood cells (and the source of the red color) is basically a complex of iron, and the part of chlorophyll that converts sunlight into chemical energy within green plants is a magnesium complex.

Some Definitions

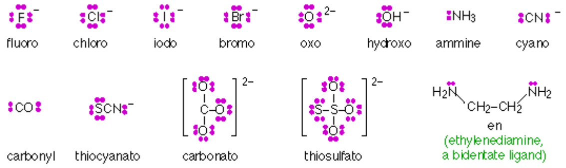
We have already defined a *complex* as a substance composed of two or more components capable of an independent existence. A *coordination complex* is one in which a *central atom* or ion is joined to one or more *ligands* (Latin *ligare*, to tie) through what is called a *coordinate covalent bond* in which both of the bonding electrons are supplied by the ligand. In such a complex the central atom acts as an electron-pair acceptor (*Lewis acid* — think of H^+ which has no electrons at all, but can accept a pair from something like Cl^-) and the ligand as an electron-pair donor (*Lewis base*). The central atom and the ligands coordinated to it constitute the *coordination sphere*. Thus the salt $[Co(NH_3)_5Cl]Cl_2$ is composed of the complex ion $[Co(NH_3)_5Cl]^{2+}$ and two Cl^- ions; components within the square brackets are inside the coordination sphere, whereas the two chloride ions are situated outside the coordination sphere. These latter two ions could be replaced by other ions such as NO_3^- without otherwise materially changing the nature of the complex.



The central atoms of coordination complexes are most often *cations* (positive ions), but may in some cases be neutral atoms, as in nickel carbonyl $Ni(CO)_4$.

Ligands composed of ions such as $F^–$ or small molecules such as H_2O or $CN^–$ possess more than one set of lone pair electrons, but only one of these pairs can coordinate with a central ion. Such ligands are said to be *monodentate* ("one tooth".) Larger ligands may contain more than one atom capable of coordinating with a single central ion, and are described as *polydentate*. Thus ethylenediamine (shown below) is a *bidentate* ligand. Polydentate ligands whose geometry enables them to occupy more than one coordinating position of a central ion act as *chelating agents* (Greek χελος, *chelos*, claw) and tend to form extremely stable complexes known as *chelates*.

Chelation is widely employed in medicine, water-treatment, analytical chemistry and industry for binding and removing metal ions of particular kinds. Some of the more common ligands (chelating agents) are shown here:



Structure and bonding in transition metal complexes

Complexes such as $Cu(NH_3)_6^{2+}$ have been known and studied since the mid-nineteenth century. Why they should form, or what their structures might be, were complete mysteries. At that time all inorganic compounds were thought to be held together by ionic charges, but ligands such as water or ammonia are of course electrically neutral. A variety of theories such as the existence of "secondary valences" were concocted, and various chain-like structures such as $CuNH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3$ were proposed. Finally, in the mid-1890s, after a series of painstaking experiments, the chemist Alfred Werner (Swiss, 1866-1919) presented the first workable theory of complex ion structures.

Werner claimed that his theory first came to him in a flash after a night of fitful sleep; by the end of the next day he had written his landmark paper that eventually won him the 1913 Nobel Prize in Chemistry.

What holds them together?

An understanding of the nature of the bond between the central ion and its ligands would have to await the development of Lewis' *shared-electron pair theory* and Pauling's *valence-bond* picture. *Hybridization* of the *d* orbitals of the central ion creates vacancies able to accommodate one or more pairs of unshared electrons on the ligands. Although these models correctly predict the structures of many transition metal complexes, they are by themselves unable to account for several of their special properties:

- The metal-to-ligand bonds are generally much weaker than ordinary covalent bonds;
- Some complexes utilize "inner" *d* orbitals of the central ion, while others are "outer-orbital" complexes;
- Transition metal ions tend to be intensely colored.

Paramagnetism of coordination complexes

Unpaired electrons act as tiny magnets; if a substance that contains unpaired electrons is placed near an external magnet, it will undergo an attraction that tends to draw it into the field. Such substances are said to be *paramagnetic*, and the degree of paramagnetism is directly proportional to the number of unpaired electrons in the molecule. Magnetic studies have played an especially prominent role in determining how electrons are distributed among the various orbitals in transition metal complexes.

Studies of this kind are carried out by placing a sample consisting of a solution of the complex between the poles of an electromagnet. The sample is suspended from the arm of a sensitive balance, and the change in apparent weight is measured with the magnet turned on and off. An increase in the weight when the magnet is turned on indicates that the sample is attracted to the magnet (*paramagnetism*) and must therefore possess one or more unpaired electrons. The precise number can be determined by calibrating the system with a substance whose electron configuration is known.

Supplemental (Optional) Background Reading: Crystal field theory

The current model of bonding in coordination complexes developed gradually between 1930-1950. In its initial stages, the model was a purely electrostatic one known as *crystal field theory* which treats the ligand ions as simple point charges that interact with the five atomic *d* orbitals of the central ion. It is this theory which we describe below.

It is remarkable that this rather primitive model, quite innocent of quantum mechanics, has worked so well. However, an improved and more complete model that incorporates molecular orbital theory is known as *ligand field theory*. In an isolated transition metal atom the five outermost *d* orbitals all have the same energy which depends solely on the spherically symmetric electric field due to the nuclear charge and the other electrons of the atom. Suppose now that this atom is made into a *cation* and is placed in solution, where it forms a hydrated species in which six H_2O molecules are coordinated to the central ion in an *octahedral*arrangement. An example of such an ion might be **hexaaquotitanium(III), $Ti(H_2O)_6^{3+}$**.

The ligands (H_2O in this example) are bound to the central ion by electron pairs contributed by each ligand. Because the six ligands are located at the corners of an octahedron centered around the metal ion, these electron pairs are equivalent to clouds of negative charge that are directed from near the central ion out toward the corners of the octahedron. We will call this an octahedral electric field, or the *ligand field*.

d-orbital splitting

The differing shapes of the five kinds of d orbitals cause them to interact differently with the electric fields created by the coordinated ligands. This diagram (from a Purdue U. chemistry site) shows outlines of five kinds of d orbitals.

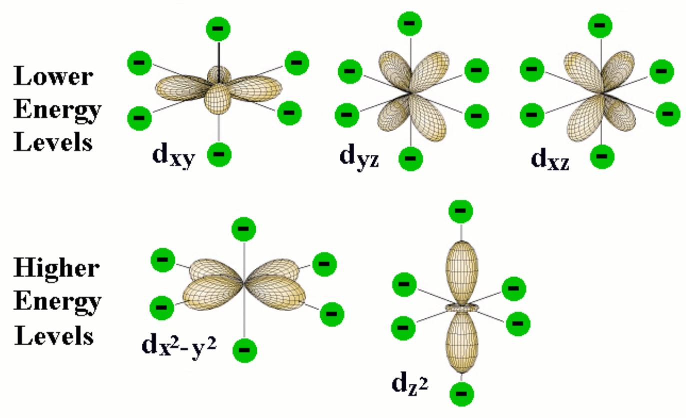


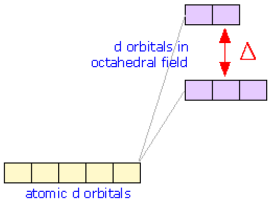
Figure 8.1.3:

The green circles represent the coordinating electron-pairs of the ligands located at the six corners of the octahedron around the central atom. The two d orbitals at the bottom have regions of high electron density pointing directly toward the ligand orbitals; the resulting electron-electron repulsion raises the energy of these *d* orbitals.

Although the five *d* orbitals of the central atom all have the same energy in a spherically symmetric field, their energies will not all be the same in the octahedral field imposed by the presence of the ligands. The reason for this is apparent when we consider the different geometrical properties of the five d orbitals. Two of the *d* orbitals, designated d_x2 and $d_x2_{-y}2$, have their electron clouds pointing directly toward ligand atoms. We would expect that any electrons that occupy these orbitals would be subject to repulsion by the electron pairs that bind the ligands that are situated at corresponding corners of the octahedron. As a consequence, the energies of these two *d* orbitals will be raised in relation to the three other *d* orbitals whose lobes are not directed toward the octahedral positions.

d1	d2	d3	d4	d5	d6	d7	d8	d9	d10
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
3	4	5	6	7	8	9	10	11	12

The number of electrons in the *d* orbital of the central atom is easily determined from the location of the element in the periodic table, taking in account, of course, of the number of electrons removed in order to form the positive ion.



The effect of the octahedral ligand field due to the ligand electron pairs is to split the *d* orbitals into two sets whose energies differ by a quantity denoted by *Δ* ("delta") which is known as the *d orbital splitting energy*. Note that both sets of central-ion *d* orbitals are repelled by the ligands and are both raised in energy; the upper set is simply raised by a greater amount. Both the total energy shift and Δ are strongly dependent on the particular ligands.

Why are transition metal complexes often highly colored?

Returning to our example of $Ti(H_2O)_6^{3+}$, we note that Ti has an outer configuration of $4s^23d^2$, so that Ti^{3+} will be a d^1 ion. This means that in its ground state, one electron will occupy the lower group of *d* orbitals, and the upper group will be empty. The *d*-orbital splitting in this case is 240 kJ per mole which corresponds to light of blue-green color; absorption of this light promotes the electron to the upper set of *d* orbitals, which represents the *exited state* of the complex. If we illuminate a solution of $Ti(H_2O)_6^{3+}$ with white light, the blue-green light is absorbed and the solution appears violet in color.

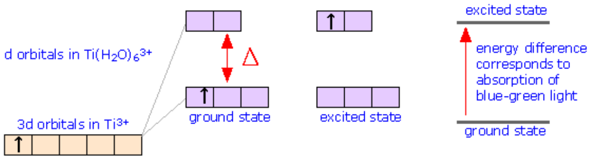
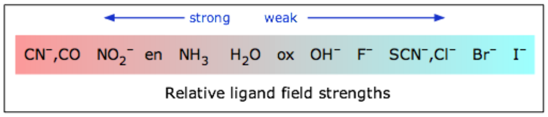


Figure 8.1.4 shows how the colors of hexaamminenickel II complexes are affected by different ligands.

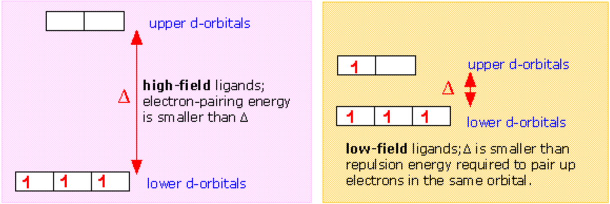
Figure 8.1.4: Color of various Ni(II) complexes in aqueous solution. From left to right, hexaamminenickel(II), tris(ethylenediamine)nickel(II), tetrachloronickelate(II) and hexaaquanickel(II). from LHcheM (via Wikipedia)

High- and low spin complexes

The magnitude of the *d* orbital splitting depends strongly on the nature of the ligand and in particular on how strong an electrostatic field is produced by its electron pair bond to the central ion.



If Δ is not too large then the electrons that occupy the *d* orbitals do so with their spins unpaired until a d^5 configuration is reached, just as occurs in the normal *Aufbau* sequence for atomic electron configurations. Thus a weak-field ligand such as H_2O leads to a “high spin” complex with Fe(II).



In contrast to this, the cyanide ion acts as a strong-field ligand; the *d* orbital splitting is so great that it is energetically more favorable for the electrons to pair up in the lower group of *d* orbitals rather than to enter the upper group with unpaired spins. Thus hexacyanoiron(II) is a “low spin” complex— actually zero spin, in this particular case.

Different *d* orbital splitting patterns occur in square planar and tetrahedral coordination geometries, so a very large number of arrangements are possible. In most complexes the value of Δ corresponds to the absorption of visible light, accounting for the colored nature of many such compounds in solution and in solids such as $CuSO_4 \cdot 5\,H_2O$ ()Figure 8.1.1.

Approximately one-third of the chemical elements are present in living organisms. Many of these are metallic ions whose function within the cell depends on the formation of *d*-orbital coordination complexes with small molecules such as *porphyrins* (see below). These complexes are themselves bound within proteins (*metalloproteins*) which provide a local environment that is essential for their function, which is either to transport or store diatomic molecule (oxygen or nitric oxide), to transfer electrons in oxidation-reduction processes, or to catalyze a chemical reaction. The most common of these utilize complexes of Fe and Mg, but other micronutrient metals including Cu, Mn, Mo, Ni, Se, and Zn are also important.

Hemoglobin

Hemoglobin is one of a group of heme proteins that includes myoglobin, cytochrome-c, and catalase. Hemoglobin performs the essential task of transporting dioxygen molecules from the lungs to the tissues in which it is used to oxidize glucose, this oxidation serving as the source of energy required for cellular metabolic processes.

Hemoglobin consists of four *globin* protein subunits (depicted by different colors in this diagram) joined together by weak intermolecular forces. Each of these subunits contains, buried within it, a molecule of *heme*, which serves as the active site of oxygen transport. The presence of hemoglobin increases the oxygen carrying capacity of 1 liter of blood from 5 to 250 ml. Hemoglobin is also involved in blood pH regulation and CO_2 transport.

Heme itself consists of an iron atom coordinated to a tetradentate *porphyrin*. When in the ferrous (Fe^{2+} state) the iron binds to oxygen and is converted into Fe^{3+}. Because a bare heme molecule would become oxidized by the oxygen without binding to it, the adduct must be stabilized by the surrounding globin protein. In this environment, the iron becomes octahedrally-coordinated through binding to a component of the protein in a fifth position, and in the sixth position either by an oxygen molecule or by a water molecule, depending on whether the hemoglobin is in its oxygenated state (in arteries) or deoxygenated state (in veins).

The heme molecule (purple) is enfolded within the polypeptide chain as shown here. The complete hemoglobin molecule contains four of these subunits, and all four must be present for it to function. The binding of O_2 to heme in hemoglobin is not a simple chemical equilibrium; the binding efficiency is regulated by the concentrations of H^+, CO_2, and organic phosphates. It is remarkable that the binding sites for these substances are on the outer parts of the globin units, far removed from the heme. The mechanism of this exquisite molecular-remote-control arises from the fact that the Fe^{2+}ion is too large to fit inside the porphyrin, so it sits slightly out of the porphyrin plane. This Fe radius diminishes when it is oxygenated, allowing it to move into the plane. In doing so, it pulls the protein component to which it is bound with it, triggering a sequence of structural changes that extend throughout the protein.

Myoglobin is another important heme protein that is found in muscles. Unlike hemoglobin, which consists of four protein subunits, myoglobin is made up of only one unit. Its principal function is to act as an oxygen storage reservoir, enabling vigorous muscle activity at a rate that could not be sustained by delivery of oxygen through the bloodstream. Myoglobin is responsible for the red color of meat. Cooking of meat releases the O_2 and oxidizes the iron to the +3 state, changing the color to brown.

Carbon monoxide poisoning

Other ligands, notably cyanide ion and **carbon monoxide**, are able to bind to hemoglobin much more strongly than does iron, thereby displacing it and rendering hemoglobin unable to transport oxygen. Air containing as little as 1 percent CO will convert hemoglobin to carboxyhemoglobin in a few hours, leading to loss of consciousness and death. Even small amounts of carbon monoxide can lead to substantial reductions in the availability of oxygen. The 400-ppm concentration of CO in cigarette smoke will tie up about 6% of the hemoglobin in heavy smokers; the increased stress this places on the heart as it works harder to compensate for the oxygen deficit is believed to be one reason why smokers are at higher risk for heart attacks. CO binds to hemoglobin 200 times more tightly than does O_2.

Chlorophyll

Chlorophyll is the light-harvesting pigment present in green plants. Its name comes from the Greek word χλορος (*chloros*), meaning "green"- the same root from which chlorine gets its name. Chlorophyll consists of a ring-shaped tetradentate ligand known as a *porphin* coordinated to a central magnesium ion. A histidine residue from one of several types of associated proteins forms a fifth coordinate bond to the Mg atom.

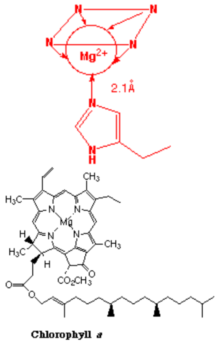


Figure 8.1.5: Left: detail of Mg coordination; notice that the metal is slightly out of the plane of the porphin ring. Right: plan view of Mg within the porphin ligand. A histidine residue from an associated protein forms the fifth coordination point to the Mg atom.

The light energy trapped by chlorophyll is utilized to drive a sequence of reactions whose net effect is to bring about the reduction of CO_2 to glucose ($C_6H_{12}O_6$) in a process known as photosynthesis which serves as the fuel for all life processes in both plants and animals.

Contributors and Attributions

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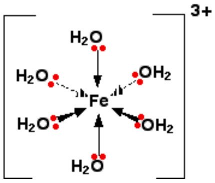
8.2: Acidity of the Hexaaqua Ions

This page explains why complex ions of the type $[M(H_2O)_6]^{n+}$ are acidic.

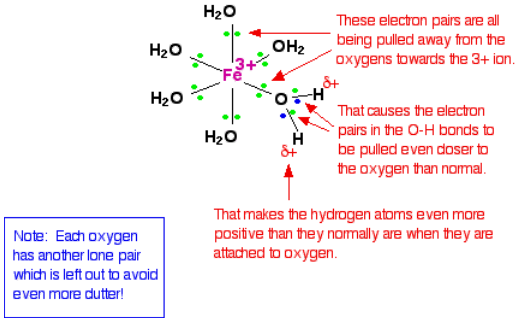
The Charge Distribution within Complex Ion

Hexaaqua ions are what they sound like: a metal-ligand complex in which a central metal ion is surrounded by six water molecules acting as ligands, with each oxygen atom sharing one of its unshared pairs of electrons with the central metal ion. While the pH's of solutions containing such ions vary a lot from one metal to another (assuming you are comparing solutions of equal concentrations), they all tend to exhibit properties of an acid. The underlying explanation is the same for all of them.

We'll take the hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$ as typical. The structure of the ion is:



Each of the six water molecules are attached to the central iron(III) ion via a co-ordinate bond using one of the two lone pairs on the oxygen. We'll choose one of these water molecules at random and look at the bonding in a bit more detail - showing all the bonds around the oxygen including its two hydrogen atoms. Imagine for the moment that the 3+ charge is located entirely on the iron.



These electron pairs are all being pulled away from the oxygens towards the 3+ ion.

That causes the electron pairs in the O-H bonds to be pulled even closer to the oxygen than normal.

That makes the hydrogen atoms even more positive than they normally are when they are attached to oxygen.

Note: Each oxygen has another lone pair which is left out to avoid even more clutter!

When the lone pairs on the oxygens form co-ordinate bonds with the iron, there is obviously a movement of electrons towards the iron atom. That has an effect on the O-H bond's electrons, which in turn get pulled towards the oxygen even more than usual. That leaves the hydrogen nuclei more exposed than normal. The overall effect is that each of the hydrogen atoms is more positive than it is in ordinary water molecules. The 3+ charge is no longer located entirely on the iron but spread out over the whole ion - much of it on the hydrogen atoms at the edge of the coordination sphere.

The behavior of this ion in water

The hydrogen atoms attached to the water ligands are sufficiently positive that they can be pulled off in a reaction involving water molecules in the solution. The first stage of this process is:

$$\mathrm{Fe(H_2O)_6^{+3} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{+2} + H_3O^+} \tag{8.2.1}$$

The complex ion is acting as an (Arrhenius) acid by donating a hydrogen ion to water molecules in the solution to form hydronium ions. The water is, of course, acting as a (Arrhenius) base by accepting the hydrogen ion. Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify Equation 8.2.1:

$$\mathrm{[Fe(H_2O)_6]^{+3}_{(aq)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+2}_{(aq)} + H^+_{(aq)}} \tag{8.2.2}$$

However, if you write it like this, remember that the hydrogen ion is not just falling off the complex ion. It is being pulled off by a water molecule in the solution. Whenever you write "$H^+(aq)$" what you really mean is a hydroxonium ion, H_3O^+.

Finally, these reactions are sometimes written as if the water molecules surrounding the central metal ion are not there, and that instead of donating protons, they are picking up hydroxide ions as ligands. For example:

$$Fe^{+3}_{(aq)} + OH^-_{(aq)} \rightleftharpoons Fe(OH)^{+2}_{(aq)} \tag{8.2.3}$$

The hexaaquairon(III) ion is quite strongly acidic giving solutions with pH's around 1.5, depending on concentration. You can get further loss of hydrogen ions as well, from a second and a third water molecule since the complex ion is a polyprotic acid. So, the central iron atom appears to be surrounded by an increasing number of hydroxide ions instead of the water molecules originally present. We would represent these additional reactions as follows:

$$Fe(OH)^{+2}_{(aq)} + OH^-_{(aq)} \rightleftharpoons Fe(OH)^{+}_{2(aq)} \tag{8.2.4}$$

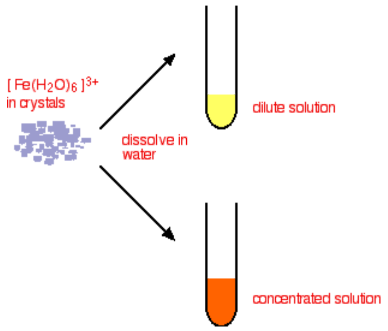
$$Fe(OH)^{+}_{2(aq)} + OH^-_{(aq)} \rightleftharpoons Fe(OH)_{3\ (aq)} \tag{8.2.5}$$

In the final case, we are left with a neutral complex. It may persist to some extent in water, but because it has no charge, it may be sparingly soluble and will be in equilibrium with its solid-phase precipitate form.

In practice

What do you actually get in solution if you dissolve an iron(III) salt in water? In fact you get a mixture of all the complexes that you have seen in the equations above. These reactions are all equilibria, so everything will be present. The proportions depend on how concentrated the solution is and whether the pH is controlled by other molecules in solution.

The color of an iron(III) salt solution is variable and depends in part on the concentration of the solution; dilute solutions can be pale yellow, while more concentrated ones are much more orange and may even produce some orange precipitate. None of these colors represents the true color of the $[Fe(H_2O)_6]^{3+}$ ion - which is a very pale lilac color and is only really easy to see in solids containing the ion.

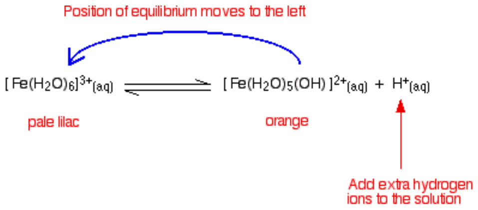


Looking at the equilibrium showing the loss of the first hydrogen ion:

$$\underbrace{Fe(H_2O)_6^{3+}}_{\text{pale lilac}} + H_2O \rightleftharpoons \underbrace{Fe(H_2O)_5(OH)^{2+}}_{\text{orange}} + H_3O^+ \tag{8.2.6}$$

The color of the new complex ion on the right-hand side is so strong that it completely masks the color of the hexaaqua ion. In concentrated solutions, the equilibrium position will be even further to the right-hand side (Le Chatelier's Principle), and so the color darkens. You will also get significant loss of other hydrogen ions (Equation 8.2.4 and 8.2.5) leading to some formation of the neutral complex and thus some precipitate.

The position of this equilibrium can be shifted by adding extra hydrogen ions from a concentrated acid (e.g., by adding concentrated nitric acid to a solution of iron(III) nitrate). The new hydrogen ions push the position of the equilibrium to the left so that you can see the color of the hexaaqua ion. This is slightly easier to follow if you write the simplified version of the equilibrium (Equation 8.2.2).



3+ Ions are More Acidic than 2+ ions

Solutions containing 3+ hexaaqua ions tend to have pH's in the range from 1 to 3. Solutions containing 2+ ions have higher pH's - typically around 5 - 6, although they can go down to about 3. Remember that the reason that these ions are acidic is because of the pull of the electrons towards the positive central ion. An ion with 3+ charges on it is going to pull the electrons more strongly than one with only 2+ charges.

In 3+ ions, the electrons in the O-H bonds will be pulled further away from the hydrogens than in 2+ ions. That means that the hydrogen atoms in the ligand water molecules will have a greater positive charge in a 3+ ion, and so will be more attracted to water molecules in the solution. If they are more attracted, they will be more readily lost - and so the 3+ ions are more acidic.

Contributors and Attributions

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8.3: Chelation

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it.

Introduction

Many complexes are relatively unreactive species remaining unchanged throughout a sequence of chemical or physical operations and can often be isolated as stable solids or liquid compounds. Other complexes have a much more transient existence and may exist only in solution or be highly reactive and easily converted to other species. All metals form complexes, although the extent of formation and nature of these depend very largely on the electronic structure of the metal. The concept of a metal complex originated in the work of Alfred Werner, who in 1913 was awarded the first Nobel Prize in Inorganic chemistry.

Complexes may be non-ionic (neutral) or cationic or anionic, depending on the charges carried by the central metal ion and the coordinated groups. The total number of points of attachment to the central element is termed the coordination number and this can vary from 2 to greater than 12, but is usually 6. The term ligand come from the latin word *ligare*, which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. The first use of the term in a British journal was by H. Irving and R.J.P. Williams in *Nature*, 1948, 162, 746 in their paper describing what is now called the Irving-Williams series.

Ligands can be further characterised as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. The term **chelate** was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew [*J. Chem. Soc.*, 1920, 117, 1456], who stated: "The adjective chelate, derived from the great claw or **chela (chely- Greek)** of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings."

Metal complexation is of widespread interest. It is studied not only by inorganic chemists, but by physical and organic chemists, biochemists, pharmacologists, molecular biologists and environmentalists.

Thermodynamic Stability

The "stability of a complex in solution" refers to the degree of association between the two species involved in the state of equilibrium. Qualitatively, the greater the association, the greater the stability of the compound. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightarrow ML_4 \tag{8.3.1}$$

then the larger the stability constant, the higher the proportion of ML_4 that exists in the solution. Free metal ions rarely exist in solution so that M, will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For example in water:

$$M(H_2O)_4 + L \rightleftharpoons M(H_2O)_3L + H_2O \tag{8.3.2}$$

$$M(H_2O)_3L + L \rightleftharpoons M(H_2O)_2L_2 + H_2O \tag{8.3.3}$$

However, for simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

$M + L \rightarrow ML$ with

$$K_1 = \frac{[ML]}{[M][L]} \tag{8.3.4}$$

$ML + L \rightarrow ML_2$ with

$$K_2 = \frac{[ML_2]}{[ML][L]} \tag{8.3.5}$$

$ML_2 + L \rightarrow ML_3$ with

$$K_3 = \frac{[ML3]}{[ML_2][L]} \tag{8.3.6}$$

$ML_3 + L \rightarrow ML_4$ with

$$K_4 = \frac{[ML_4]}{[ML_3][L]} \tag{8.3.7}$$

where K_1, K_2 etc. are referred to as "stepwise stability constants." Alternatively, the "Overall Stability Constant" can be constructed

$$M + 4L \rightarrow ML_4 \beta_4 = \frac{[ML_4]}{[M][L]^4} \tag{8.3.8}$$

The stepwise and overall stability constants are therefore related as follows:

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \tag{8.3.9}$$

or more generally,

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \times \ldots K_n \tag{8.3.10}$$

Table E4 outlines the sequential formation constants for a range of metal-ligand complexes.

Example 8.3.1: The Cuprammonium Ion

Consider the four steps involved in the formation of the cuprammonium ion $Cu(NH_3)_4^{2+}$:

STEP 1:

$$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+} \tag{8.3.11}$$

with

$$K_1 = \frac{[Cu(NH_3)^{2+}]}{[Cu^{2+}][NH_3]} \tag{8.3.12}$$

STEP 2:

$$CuNH_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+} \tag{8.3.13}$$

with

$$K_2 = \frac{[Cu(NH_3)_2^{2+}]}{[Cu(NH_3)^{2+}][NH_3]} \tag{8.3.14}$$

STEP 3:

$$Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{2+} \tag{8.3.15}$$

with

$$K_3 = \frac{[Cu(NH_3)_3^{2+}]}{[Cu(NH_3)_2^{2+}][NH_3]} \tag{8.3.16}$$

STEP 4:

$$Cu(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} \tag{8.3.17}$$

with

$$K_4 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu(NH_3)_3^{2+}][NH_3]} \tag{8.3.18}$$

where the $\{K\}$ constants are the *stepwise stability constants*. Also:

$$\beta_4 = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} \tag{8.3.19}$$

The addition of the four ammine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

$$\log K_1 = 4.0, \tag{8.3.20}$$

$$\log K_2 = 3.2, \tag{8.3.21}$$

$$\log K_3 = 2.7, \tag{8.3.22}$$

$$\log K_4 = 2.0 \text{ or } \log \beta_4 = 11.9 \tag{8.3.23}$$

Pay attention to definitions: a number of texts may refer to β_4 as the **instability constant** or the **dissociation constant** of coordination complexes (e.g., termed β_4' below) , which corresponds to the **reciprocal** of the formation constant (K_4), since the reactions referred to are those where fully formed complexes break down to the aqua ion and free ligands. For example,

$$\beta_4' = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]} \tag{8.3.24}$$

However, this is not definition use here (Table E4) and should be compared with the equation for the formation constant given earlier.

It is usual to represent the metal-binding process by a series of stepwise equilibria which lead to stability constants that may vary numerically from hundreds to enormous values such as 10^{35} and more. That is

100,000,000,000,000,000,000,000,000,000,000,000.0

For this reason, they are commonly reported as logarithms. So $\log_{10}$ (β) = $\log_{10}$ (10^{35}) = 35. It is additionally useful to use logarithms, since log(K) is directly proportional to the free energy of the reaction.

$$\Delta G^o = -RT\ln(\beta) \tag{8.3.25}$$

$$\Delta G^o = -2.303RT\log_{10}(\beta) \tag{8.3.26}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{8.3.27}$$

Below are three tables of the formation constants and thermodynamics properties of example ligand-metal complexes; a more complete table can be found in Table E4.

Table 8.3.1: Reaction of ammonia and 1,2-diaminoethane with Cd^{2+}.

# of ligands	ΔG° ($kJmol^{-1}$)	ΔH° ($kJmol^{-1}$)	ΔS° (JK-1mol^{-1})	log β
2 NH_3(1 en)	-28.24 (-33.30)	-29.79 (-29.41)	-5.19 (+13.05)	4.95 (5.84)
4 NH_3(2 en)	-42.51 (-60.67)	-53.14 (-56.48)	-35.50 (+13.75)	7.44 (10.62)

Table 8.3.2: Reaction of pyridine and 2,2'-bipyridine with Ni^{2+}.

# of ligands	log β	ΔG° ($kJmol^{-1}$)
2 py (1 bipy)	3.5 (6.9)	-20 (-39)
4 py (2 bipy)	5.6 (13.6)	-32 (-78)
6 py (3 bipy)	9.8 (19.3)	-56 (-110)

Table 8.3.3: *Reaction of ammonia and 1,2-diaminoethane with* Ni^{2+}.

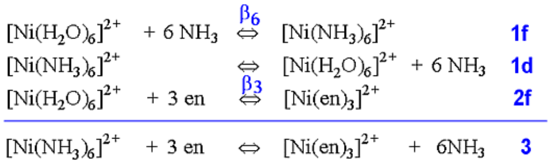
# of ligands	log β	ΔG° ($kJmol^{-1}$)
1 NH_3	2.8	-16
2 NH_3 (1 en)	5.0 (7.51)	-28.5 (-42.8)
3 NH_3	6.6	-37.7
4 NH_3 (2 en)	7.87 (13.86)	-44.9 (-79.1)
5 NH_3	8.6	-49.1
6 NH_3 (3 en)	8.61 (18.28)	-49.2 (-104.4)

The Chelate Effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia. It has been known for many years that a comparison of this type always shows that the complex resulting from coordination with the chelating ligand is **much more thermodynamically stable**. This can be seen by looking at the values for adding two monodentates compared with adding one bidentate, or adding four monodentates compared to two bidentates, or adding six monodentates compared to three bidentates.

A number of points should be highlighted from the formation constants in Table E4. In Table 8.3.1, it can be seen that the ΔH° values for the formation steps are almost identical, that is, heat is evolved to about the same extent whether forming a complex involving monodentate ligands or bidentate ligands. What is seen to vary significantly is the ΔS° term which changes from negative (unfavorable) to positive (favorable). Note as well that there is a dramatic increase in the size of the ΔS° term for adding two compared to adding four monodentate ligands. (-5 to -35 $JK^{-1}mol^{-1}$). What does this imply, if we consider ΔS° to give a measure of disorder?

In the case of complex formation of Ni^{2+} with ammonia or 1,2-diaminoethane, by rewriting the equilibria, the following equations are produced.



$$[Ni(H_2O)_6]^{2+} + 6\,NH_3 \overset{\beta_6}{\Leftrightarrow} [Ni(NH_3)_6]^{2+} \qquad \textbf{1f}$$
$$[Ni(NH_3)_6]^{2+} \Leftrightarrow [Ni(H_2O)_6]^{2+} + 6\,NH_3 \qquad \textbf{1d}$$
$$[Ni(H_2O)_6]^{2+} + 3\,en \overset{\beta_3}{\Leftrightarrow} [Ni(en)_3]^{2+} \qquad \textbf{2f}$$
$$[Ni(NH_3)_6]^{2+} + 3\,en \Leftrightarrow [Ni(en)_3]^{2+} + 6NH_3 \qquad \textbf{3}$$

Using the equilibrium constant for the reaction (3 above) where the *three* bidentate ligands replace the *six* monodentateligands, we find that at a temperature of 25° C:

$$\Delta G^{\circ} = -2.303\,RT\,\log_{10} K \tag{8.3.28}$$

$$= -2.303\,RT\,(18.28 - 8.61) \tag{8.3.29}$$

$$= -54\text{ kJ mol}^{-1} \tag{8.3.30}$$

Based on measurements made over a range of temperatures, it is possible to break down the ΔG° term into the enthalpy and entropy components.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{8.3.31}$$

The result is that: $\Delta H^{\circ} = -29 kJmol^{-1}$

- TΔS° = -25 kJ mol^{-1}
and at 25C (298K)
ΔS° = +88 J K^{-1} mol^{-1}

> For many years, these numbers have been **incorrectly recorded** in textbooks. For example, the third edition of "Basic Inorganic Chemistry" by F.A. Cotton, G. Wilkinson and P.L. Gaus, John Wiley & Sons, Inc, 1995, on page 186 gives the values as:

> $$\Delta G° = -67 \text{ kJ mol}^{-1}$$
> $$\Delta H° = -12 \text{ kJ mol}^{-1}$$
> $$-T\Delta S° = -55 \text{ kJ mol}^{-1}$$
>
> The conclusion they drew from these incorrect numbers was that the chelate effect was essentially an entropy effect, since the TΔS° contribution was nearly 5 times bigger than ΔH°.
>
> In fact, the breakdown of the ΔG° into ΔH° and TΔS° shows that the two terms are nearly equal (-29 and -25 kJ mol^{-1}, respectively) with the ΔH° term a little bigger! The entropy term found is still much larger than for reactions involving a non-chelating ligand substitution at a metal ion. How can we explain this enhanced contribution from entropy? One explanation is to count the number of species on the left and right hand side of the equation above.

It will be seen that on the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species, that is a net gain of 3 species occurs as the reaction proceeds. This can account for the increase in entropy since it represents an increase in the disorder of the system. An alternative view comes from trying to understand how the reactions might proceed. To form a complex with 6 monodentates requires 6 separate favorable collisions between the metal ion and the ligand molecules. To form the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm but remember that the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring.

If you consider dissociation steps, then when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again. **Both** conditions favor the formation of the complex with bidentate groups rather than monodentate groups.

References

1. For a fascinating review of the origin and dissemination of the term 'ligand' in chemistry see: W.H. Brock, K.A Jensen, C.K. Jorgensen and G.B. Kauffman, *Polyhedron*, 2, 1983, 1-7.
2. Gilbert T. Morgan and H.D.K. Drew, *J. Chem. Soc.*, 1920, 117, 1456
3. H. Irving and R.J.P. Williams, *Nature*, 1948, 162, 746
4. A description of his Alfred Werner's life and the influence his work played in the development of coordination chemistry is given by G.B. Kauffman in "*Inorganic Coordination Compounds*", Heyden & Son Ltd, 1981.

Problems

Calculate the entropy changes at 25°C, for the following reactions:

$$Zn^{2+} + 2NH_3 <=> [Zn(NH_3)_2]^{2+}$$

$$\Delta H = -28.03 \text{ kJ mol}^{-1} \text{ and } \log_{10} \beta_2 = 5.01$$

$$Zn^{2+} + en <=> [Zn(en)]^{2+}$$

$$\Delta H = -27.6 \text{ kJ mol}^{-1} \text{ and } \log_{10} \beta = 6.15 \text{ (NB R=8.314 JK}^{-1}\text{mol}^{-1})$$

Solution

The calculations make use of the equations:

$$\mathbf{\Delta G° = RT\ln\beta}$$
$$\mathbf{\Delta G° = 2.303RT\log_{10}\beta}$$
$$\mathbf{\Delta G° = \Delta H° - T\Delta S°}$$

First it is necessary to calculate the ΔG values from the given formation constants and temperature 25C = 298K.

For the ammonia complex, ΔG = -8.314 * 298 * 2.303 * 5.01 kJmol^{-1}, that is -28.6 kJmol^{-1}.

For the 1,2-diaminoethane complex, ΔG= -8.314 * 298 * 2.303 * 6.15 kJmol^{-1} which corresponds to -35.1 kJmol^{-1}.

This makes use of the relation between Ln and log10 such that ln(x) = 2.303 log10 (x).

Then using the second relationship above, ΔS can be found.

$$\Delta S=\frac{\Delta H-\Delta G}{T} \tag{8.3.32}$$

For the ammonia complex this gives 1.9 JK^{-1}mol^{-1} and for the 1,2-diaminoethane complex 25.2 JK^{-1}mol^{-1}, which are the values given as answer 2.

Contributors and Attributions

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8.4: Metals Complexes With Ligands Other Than Hydroxide

This page explains what is meant by a stability constant for a complex ion, and goes on to look at how the stability constant's magnitude is governed in part by the entropy change during a ligand exchange reaction.

Sequential Reactions

If you add ammonia solution to a solution containing hexaaquacopper(II) ions, $[Cu(H_2O)_6]^{2+}$, four of the water molecules are eventually replaced by ammonia molecules to give $[Cu(NH_3)_4(H_2O)_2]^{2+}$. This can be written as a single equilibrium reaction to show the overall effect:

$$[Cu(H_2O)_6]^{+2} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{+2} + 4\,H_2O \tag{8.4.1}$$

However, in fact the water molecules get replaced one at a time, and so this is made up of a series of sequential reactions:

$$[Cu(H_2O)_6]^{+2} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{+2} + H_2O \tag{8.4.2}$$

$$[Cu(NH_3)(H_2O)_5]^{+2} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{+2} + H_2O \tag{8.4.3}$$

$$[Cu(NH_3)_2(H_2O)_4]^{+2} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{+2} + H_2O \tag{8.4.4}$$

$$[Cu(NH_3)_3(H_2O)_3]^{+2} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{+2} + H_2O \tag{8.4.5}$$

Although this can look a bit daunting at first sight, all that is happening is that first you have one, then two, then three, then four water molecules in total replaced by four NH3 ligands. Using the approach from Section 9.2, in which we omit the water molecules, we could write these as:

$$Cu^{+2} + NH_3 \rightleftharpoons Cu(NH_3)^{+2} \tag{8.4.6}$$

$$Cu(NH_3)^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_2^{+2} \tag{8.4.7}$$

$$Cu(NH_3)_2^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_3^{+2} \tag{8.4.8}$$

$$Cu(NH_3)_3^{+2} + NH_3 \rightleftharpoons Cu(NH_3)_4^{+2} \tag{8.4.9}$$

Individual stability constants

Let's take a closer look at the first of these equilibria (Equation 8.4.6). Like any other equilibrium, this one has an equilibrium constant, K_{eq} - except that in this case, we call it a stability constant. Because this is the first water molecule to be replaced, we call it K_1 and is given by this expression:

$$K_1 = \frac{[Cu(NH_3)^{+2}]}{[Cu^{+2}][NH_3]} \tag{8.4.10}$$

Note that, at the top of this page, square brackets were used in the chemical reactions to illustrate that the charge on a molecule applied to the entire molecule. In the equation here for K_1, the square brackets [ ] are back to what we are used to them referring to: molar concentrations in aqueous solution.

K_1 for this reaction is 1.78x10^4. Compared to many equilibrium constants we have seen for acid-base reactions, solubility product reactions, and Henry's Law gas-aqueous partitioning, the magnitude of this K_1 is much, much larger. This suggests that there is a strong tendency to form the ion containing an ammonia molecule. A high value of a stability constant shows that the ion is easily formed. Each of the other equilibria above also has its own stability constant, K_2, K_3 and K_4. For example, K_2 is given by:

$$K_2 = \frac{[Cu(NH_3)_2^{+2}]}{[Cu(NH_3)^{+2}][NH_3]} \tag{8.4.11}$$

And K_2 has a value of 4.07x10^3. Again, this value of K is fairly high compared to other K_{eq} we have worked with previously. So, that suggests that this reaction also tends to be favorable.

The equations for K_3 and K_4 would be:

$$K_3 = \frac{[\mathrm{Cu(NH_3)_3^{+2}}]}{[\mathrm{Cu(NH_3)_2^{+2}}][\mathrm{NH_3}]} \tag{8.4.12}$$

$$K_4 = \frac{[\mathrm{Cu(NH_3)_4^{+2}}]}{[\mathrm{Cu(NH_3)_3^{+2}}][\mathrm{NH_3}]} \tag{8.4.13}$$

The following table shows all four of the stability constants. As with Ka and Ksp values, these are often expressed as log transformations. Because formation constants are generally greater than 10^0 (or 1), they are often expressed as logK values as opposed to pK values.

Metal-Ligand Complex	n = _; K_n	Value	log K_n
$Cu(NH_3)^{+2}$	1; K_1	1.78×10^4	4.25
$Cu(NH_3)_2{}^{+2}$	2; K_2	4.07×10^3	3.61
$Cu(NH_3)_3{}^{+2}$	3; K_3	9.55×10^2	2.98
$Cu(NH_3)_4{}^{+2}$	4; K_4	1.74×10^2	2.24

The fact that all the K values are greater than 1 generally reflects that the sequential metal-ligand complexes are each more favored than the prior complex. However, there are diminishing returns - notice that the incremental K values are declining as you replace more and more waters. This is common with individual stability constants.

Cumulative Reactions and Beta Values

Instead of writing individual sequential reactions in which one ligand molecule is added at a time, sometimes these reactions are written as cumulative reactions. In this approach, the starting point for each reaction is the central metal ion, and the other reactant is *n* ligand molecules. The next four reactions illustrate this approach:

$$\mathrm{Cu^{+2} + NH_3 \rightleftharpoons Cu(NH_3)^{+2}} \tag{8.4.14}$$

$$\mathrm{Cu^{+2} + 2\,NH_3 \rightleftharpoons Cu(NH_3)_2^{+2}} \tag{8.4.15}$$

$$\mathrm{Cu^{+2} + 3\,NH_3 \rightleftharpoons Cu(NH_3)_3^{+2}} \tag{8.4.16}$$

$$\mathrm{Cu^{+2} + 4\,NH_3 \rightleftharpoons Cu(NH_3)_4^{+2}} \tag{8.4.17}$$

And, their equilibrium constant equations are:

$$\beta_1 = \frac{[\mathrm{Cu(NH_3)^{+2}}]}{[\mathrm{Cu^{+2}}][\mathrm{NH_3}]} \tag{8.4.18}$$

$$\beta_2 = \frac{[\mathrm{Cu(NH_3)_2^{+2}}]}{[\mathrm{Cu^{+2}}][\mathrm{NH_3}]^2} \tag{8.4.19}$$

$$\beta_3 = \frac{[\mathrm{Cu(NH_3)_3^{+2}}]}{[\mathrm{Cu^{+2}}][\mathrm{NH_3}]^3} \tag{8.4.20}$$

$$\beta_4 = \frac{[\mathrm{Cu(NH_3)_4^{+2}}]}{[\mathrm{Cu^{+2}}][\mathrm{NH_3}]^4} \tag{8.4.21}$$

The first reaction and Keq equation look the same as the approach above. However, for subsequent reactions, note the differences due to the stoichiometric coefficient on the NH3 molecule in the chemical reaction. Also, instead of calling these stability constants 'K', the greek letter beta is used.

This approach is chemically and mathematically identical to the sequential approach, but it can have advantages when applying these concepts to engineering problems. We will do some of these problems in class and in lab. The next section in this reading shows that the beta value for each complex is the mathematical product of the preceding K values leading up to the formation of that complex.

Summary

Whether you are looking at the sequential replacement of individual water molecules with ligand molecules, or cumulative reactions producing the complex ions, a stability constant is simply the equilibrium constant for the reaction you are looking at. The **larger** the value of the stability constant, the further the reaction lies to the **right**. That implies that complex ions with large stability constants are more stable than ones with smaller ones. Stability constants tend to be very large numbers. In order to simplify the numbers a "log" scale is often used.

Contributors and Attributions

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8.5: Origin of Color in Complex Ions

This page is going to take a simple look at the origin of color in complex ions - in particular, why so many transition metal ions are colored.

White light and Colors

If you pass white light through a prism it splits into all the colors of the rainbow. Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred metersfor radio waves. Visible light has wavelengths from about 400 to 750 nm. (1 nanometer = 10-9 meters.)

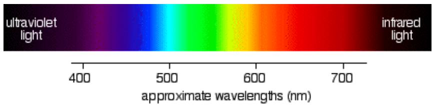
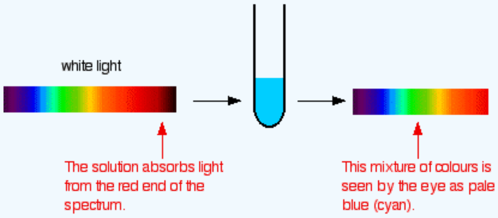


Figure: The diagram shows an approximation to the spectrum of visible light.

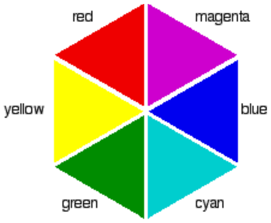
Example 1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan). The diagram gives an impression of what happens if you pass white light through copper(II) sulfate solution.

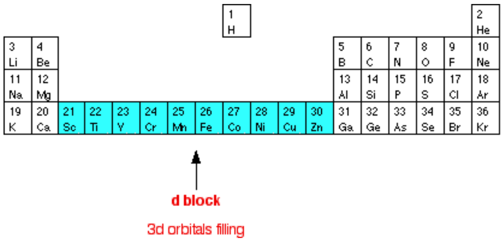


Working out what color you will see is not easy if you try to do it by imagining "mixing up" the remaining colors. You wouldn't have thought that all the other colors apart from some red would look cyan, for example. Sometimes what you actually see is quite unexpected. Mixing different wavelengths of light doesn't give you the same result as mixing paints or other pigments. You can, however, sometimes get some estimate of the color you would see using the idea of complementary colors.

If you arrange some colors in a circle, you get a "color wheel". The diagram shows one possible version of this.



colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum. Cyan is the complementary color of red.



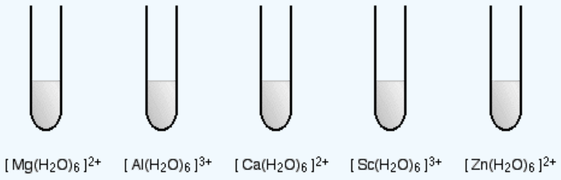
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). This shortened version of the Periodic Table shows the first row of the d block, where the 3d orbitals are being filled.

> *The usual definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] $3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^1 4s^2$) does not really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. Technically, the Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.*

✓ Example 2: Hexaaqua Metal Ions

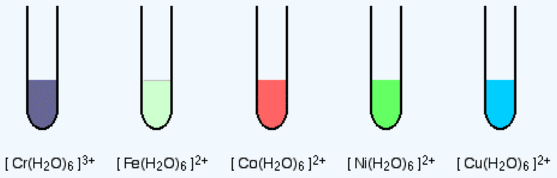
The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[M(H_2O)_6]^{n+}$. The charge on these ions is typically 2+ or 3+.

Non-transition metal ions



These ions are all colorless.

Transition metal ions



The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

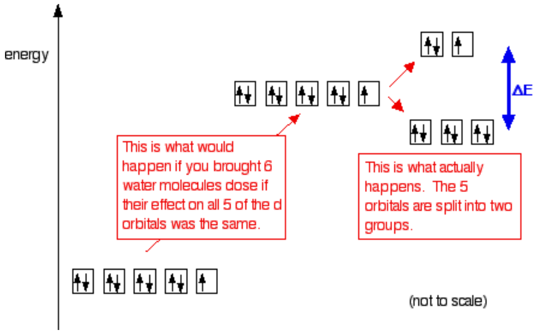
So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion?

The Origin of Color in Complex Ions containing transition metals

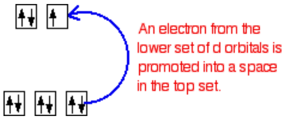
Complex ions containing transition metals are usually colored, whereas the similar ions from non-transition metals are not. That suggests that the partly filled d orbitals must be involved in generating the color in some way. Remember that transition metals are defined as having partly filled d orbitals.

Octahedral Complexes

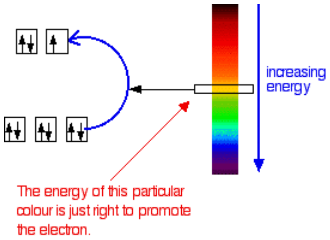
For simplicity we are going to look at the octahedral complexes which have six simple ligands arranged around the central metal ion. The argument is not really any different if you have multidentate ligands. When the ligands bond with the transition metal ion, there is repulsion between the electrons in the ligands and the electrons in the d orbitals of the metal ion. That raises the energy of the d orbitals. However, because of the way the d orbitals are arranged in space, it doesn't raise all their energies by the same amount. Instead, it splits them into two groups. The diagram shows the arrangement of the d electrons in a Cu^{2+} ion before and after six water molecules bond with it.



Whenever 6 ligands are arranged around a transition metal ion, the d orbitals are always split into 2 groups in this way - 2 with a higher energy than the other 3. The size of the energy gap between them (shown by the blue arrows on the diagram) varies with the nature of the transition metal ion, its oxidation state (whether it is 3+ or 2+, for example), and the nature of the ligands. When white light is passed through a solution of this ion, some of the energy in the light is used to promote an electron from the lower set of orbitals into a space in the upper set.



Each wavelength of light has a particular energy associated with it. Red light has the lowest energy in the visible region. Violet light has the greatest energy. Suppose that the energy gap in the d orbitals of the complex ion corresponded to the energy of yellow light.



The yellow light would be absorbed because its energy would be used in promoting the electron. That leaves the other colors. Your eye would see the light passing through as a dark blue, because blue is the complementary color of yellow.

Tetrahedral Complexes

Simple tetrahedral complexes have four ligands arranged around the central metal ion. Again the ligands have an effect on the energy of the d electrons in the metal ion. This time, of course, the ligands are arranged differently in space relative to the shapes of the d orbitals. The net effect is that when the d orbitals split into two groups, three of them have a greater energy, and the other two a lesser energy (the opposite of the arrangement in an octahedral complex). Apart from this difference of detail, the explanation for the origin of color in terms of the absorption of particular wavelengths of light is exactly the same as for octahedral complexes.

What about non-transition metal complex ions?

Non-transition metals do not have partly filled d orbitals. Visible light is only absorbed if some energy from the light is used to promote an electron over exactly the right energy gap. Non-transition metals do not have any electron transitions which can absorb wavelengths from visible light. For example, although scandium is a member of the d block, its ion (Sc^{3+}) hasn't got

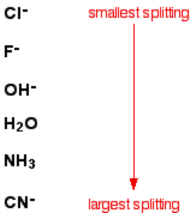
> any d electrons left to move around. This is no different from an ion based on Mg^{2+} or Al^{3+}. Scandium(III) complexes are colorless because no visible light is absorbed. In the zinc case, the 3d level is completely full - there are not any gaps to promote an electron in to. Zinc complexes are also colorless.

Factors Affecting the Color of Transition Metal complexes

In each case we are going to choose a particular metal ion for the center of the complex, and change other factors. color changes in a fairly haphazard way from metal to metal across a transition series.

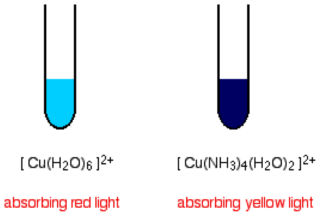
The nature of the ligand

Different ligands have different effects on the energies of the d orbitals of the central ion. Some ligands have strong electrical fields which cause a large energy gap when the d orbitals split into two groups. Others have much weaker fields producing much smaller gaps. Remember that the size of the gap determines what wavelength of light is going to get absorbed. The list shows some common ligands. Those at the top produce the smallest splitting; those at the bottom the largest splitting.



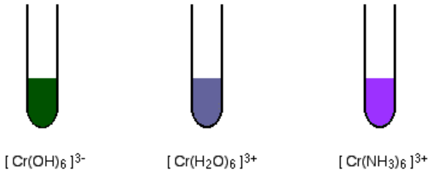
The greater the splitting, the more energy is needed to promote an electron from the lower group of orbitals to the higher ones. In terms of the color of the light absorbed, greater energy corresponds to shorter wavelengths. That means that as the splitting increases, the light absorbed will tend to shift away from the red end of the spectrum towards orange, yellow and so on.

There is a fairly clear-cut case in copper(II) chemistry. If you add an excess of ammonia solution to hexaaquacopper(II) ions in solution, the pale blue (cyan) color is replaced by a dark inky blue as some of the water molecules in the complex ion are replaced by ammonia.



The first complex must be absorbing red light in order to give the complementary color cyan. The second one must be absorbing in the yellow region in order to give the complementary color dark blue. Yellow light has a higher energy than red light. You need that higher energy because ammonia causes more splitting of the d orbitals than water does.

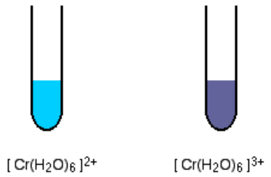
It is not often as simple to see as this, though! Trying to sort out what is being absorbed when you have murky colors not on the simple color wheel further up the page is much more of a problem. The diagrams show some approximate colors of some ions based on chromium(III).



It is obvious that changing the ligand is changing the color, but trying to explain the colors in terms of our simple theory is not easy.

The oxidation state of the metal

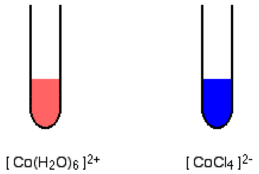
As the oxidation state of the metal increases, so also does the amount of splitting of the d orbitals. Changes of oxidation state therefore change the color of the light absorbed, and so the color of the light you see. Taking another example from chromium chemistry involving only a change of oxidation state (from +2 to +3):



The 2+ ion is almost the same color as the hexaaquacopper(II) ion, and the 3+ ion is the hard-to-describe violet-blue-grey color.

The coordination of the Ion

Splitting is greater if the ion is octahedral than if it is tetrahedral, and therefore the color will change with a change of co-ordination. The problem is that an ion will normally only change co-ordination if you change the ligand - and changing the ligand will change the color as well. Hence, you cannot isolate out the effect of the co-ordination change. For example, a commonly quoted case comes from cobalt(II) chemistry, with the ions $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$.



The difference in the colors is going to be a combination of the effect of the change of ligand, and the change of the number of ligands.

Contributors and Attributions

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CHAPTER OVERVIEW

9: Redox Chemistry and Electrochemistry

Topic hierarchy

9.1: Galvanic Cells

Learning Objectives

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 9.1.1). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \tag{9.1.1}$$

$$\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s) \tag{9.1.2}$$

$$\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq) \tag{9.1.3}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

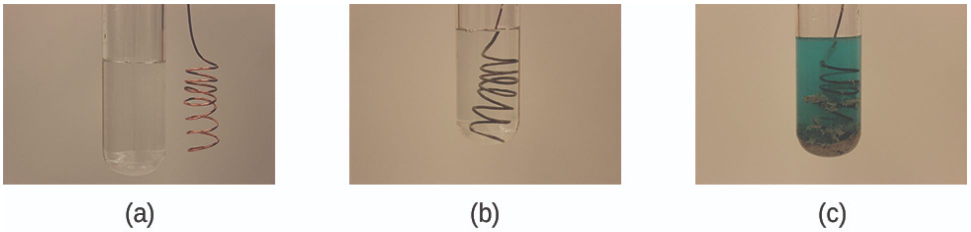

Figure 9.1.1: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 9.1.2) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($AgNO_3$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the cell potential. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\mathrm{J}}{\mathrm{C}} \tag{9.1.4}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

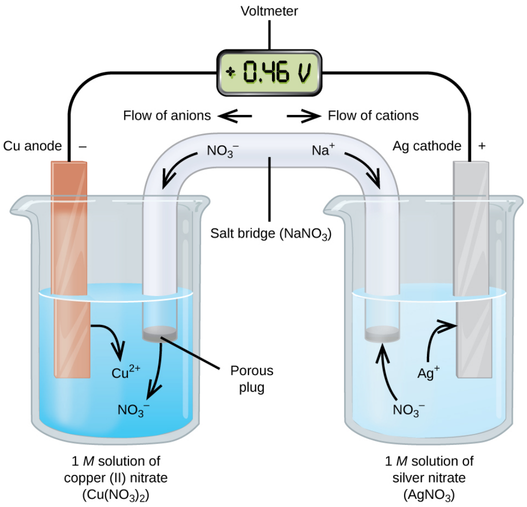

Figure $9.1.2$: In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right. There is a lot going on in Figure $9.1.2$, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The cell notation (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure $9.1.2$ is then

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu}^{2+}(aq,\ 1\ M)\,\|\,\mathrm{Ag}^{+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s) \tag{9.1.5}$$

Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure $9.1.3$. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation: } \mathrm{Mg}(s) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\,\mathrm{e}^- \tag{9.1.6}$$

$$\text{reduction: } 2\,\mathrm{H}^+(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2(g) \tag{9.1.7}$$

$$\text{overall: } \mathrm{Mg}(s) + 2\,\mathrm{H}^+(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + \mathrm{H}_2(g) \tag{9.1.8}$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s) \,|\, \mathrm{Mg}^{2+}(aq) \,\|\, \mathrm{H}^+(aq) \,|\, \mathrm{H}_2(g) \,|\, \mathrm{Pt}(s) \tag{9.1.9}$$

The magnesium electrode is an active electrode because it participates in the oxidation-reduction reaction. Inert electrodes, like the platinum electrode in Figure 9.1.3, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

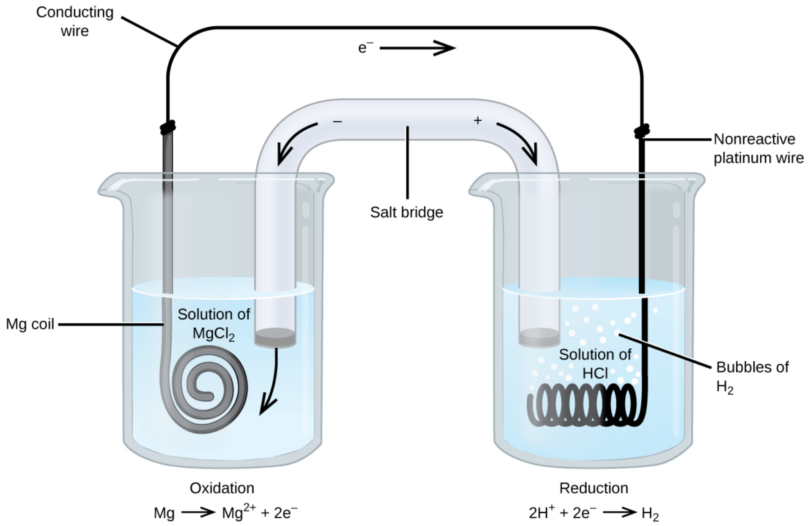

Figure 9.1.2: The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $\mathrm{Mg} + 2\,\mathrm{H}^+ \longrightarrow \mathrm{Mg}^{2+} + \mathrm{H}_2$, *which is represented in cell notation as:* $\mathrm{Mg}(s) \,|\, \mathrm{Mg}^{2+}(aq) \,\|\, \mathrm{H}^+(aq) \,|\, \mathrm{H}_2(g) \,|\, \mathrm{Pt}(s)$

Example 9.1.1: Using Cell Notation

Consider a galvanic cell consisting of

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 3\,\mathrm{Cu}(s) \tag{9.1.10}$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+}, and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\text{oxidation: } 2\,\mathrm{Cr}(s) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 6\,\mathrm{e}^- \tag{9.1.11}$$

$$\text{reduction: } 3\,\mathrm{Cu}^{2+}(aq) + 6\,\mathrm{e}^- \longrightarrow 3\,\mathrm{Cu}(s) \tag{9.1.12}$$

$$\text{overall: } 2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 3\,\mathrm{Cu}(s) \tag{9.1.13}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$$\mathrm{Cr}(s) \,|\, \mathrm{Cr}^{3+}(aq) \,\|\, \mathrm{Cu}^{2+}(aq) \,|\, \mathrm{Cu}(s). \tag{9.1.14}$$

Oxidation occurs at the anode and reduction at the cathode.

Example 9.1.2: Using Cell Notation

Consider a galvanic cell consisting of

$$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l) \tag{9.1.15}$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and MnO_4^- is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

$$\text{oxidation: } 5(Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-) \tag{9.1.16}$$

$$\underline{\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)} \tag{9.1.17}$$

$$\text{overall: } 5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l) \tag{9.1.18}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$$Pt(s) \,|\, Fe^{2+}(aq),\ Fe^{3+}(aq) \,\|\, MnO_4^-(aq),\ H^+(aq),\ Mn^{2+}(aq) \,|\, Pt(s). \tag{9.1.19}$$

Oxidation occurs at the anode and reduction at the cathode.

Exercise 9.1.1

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Answer

From the information given in the problem:

$$\text{anode (oxidation): } Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \tag{9.1.20}$$

$$\underline{\text{cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)} \tag{9.1.21}$$

$$\text{overall: } Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \tag{9.1.22}$$

Using cell notation:

$$Zn(s) \,|\, Zn^{2+}(aq) \,\|\, Cu^{2+}(aq) \,|\, Cu(s).$$

Summary

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, $\|$. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, $|$. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

Glossary

active electrode
electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

anode
electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

cathode
electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cell notation
shorthand way to represent the reactions in an electrochemical cell

cell potential
difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

galvanic cell
electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

inert electrode
electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

voltaic cell
another name for a galvanic cell

Contributors and Attributions

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9.2: Standard Reduction Potentials

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in the Figure below and is called the standard hydrogen electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,\mathrm{H^+}(aq,\ 1\ M)+2\,\mathrm{e^-}\rightleftharpoons \mathrm{H_2}(g,\ 1\ \mathrm{atm})\quad E^\circ=0\ \mathrm{V} \tag{9.2.1}$$

$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

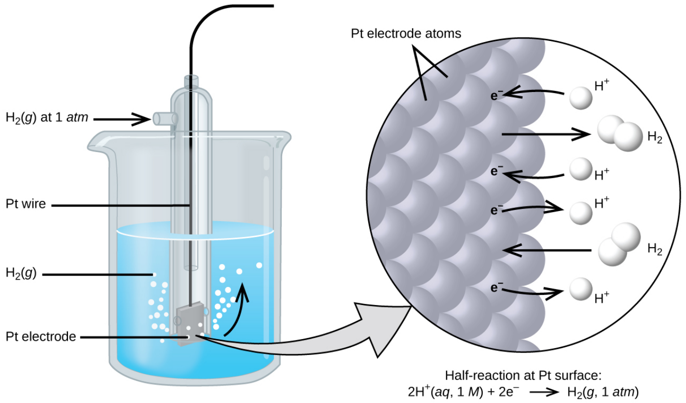

Figure 9.2.1: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 9.2.2). In cell notation, the reaction is

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,|\,\mathrm{Cu}(s) \tag{9.2.2}$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{array}{c}\text{Anode (oxidation): }\mathrm{H_2}(g)\longrightarrow 2\,\mathrm{H^+}(aq)+2\,\mathrm{e^-}\\ \text{Cathode (reduction): }\mathrm{Cu^{2+}}(aq)+2\,\mathrm{e^-}\longrightarrow \mathrm{Cu}(s)\\ \hline \text{Overall: }\mathrm{Cu^{2+}}(aq)+\mathrm{H_2}(g)\longrightarrow 2\,\mathrm{H^+}(aq)+\mathrm{Cu}(s)\end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}}=E^\circ_{\text{cathode}}-E^\circ_{\text{anode}} \tag{9.2.3}$$

$$+0.34\ \mathrm{V}=E^\circ_{\mathrm{Cu^{2+}/Cu}}-E^\circ_{\mathrm{H^+/H_2}}=E^\circ_{\mathrm{Cu^{2+}/Cu}}-0=E^\circ_{\mathrm{Cu^{2+}/Cu}} \tag{9.2.4}$$

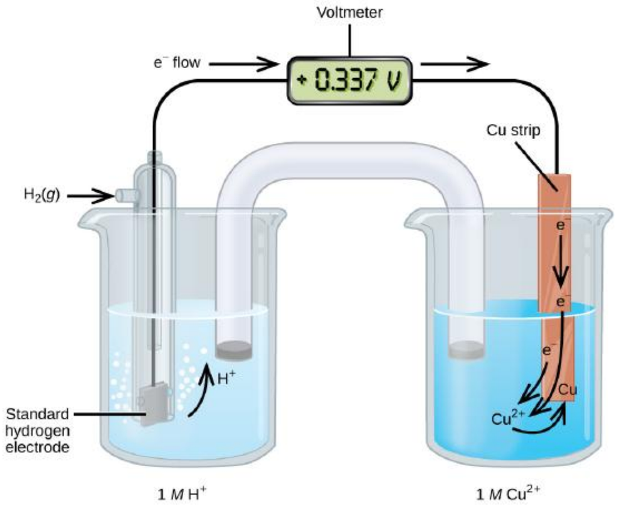

Figure 9.2.2: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure 9.2.2, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s) \tag{9.2.5}$$

Electrons flow from left to right, and the reactions are

$$\begin{array}{l} \text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \\ \hline \text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s) \end{array}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_\text{cell} = E^\circ_\text{cathode} - E^\circ_\text{anode} \tag{9.2.6}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}} \tag{9.2.7}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_cell, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s) \tag{9.2.8}$$

$$\begin{array}{l} \text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \\ \text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s) \\ \hline \text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s) \end{array}$$

$$E^\circ_\text{cell} = E^\circ_\text{cathode} - E^\circ_\text{anode} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V} \tag{9.2.9}$$

Again, note that when calculating E°_cell, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table 9.2.1. A more complete list is provided in Tables P1 or P2.

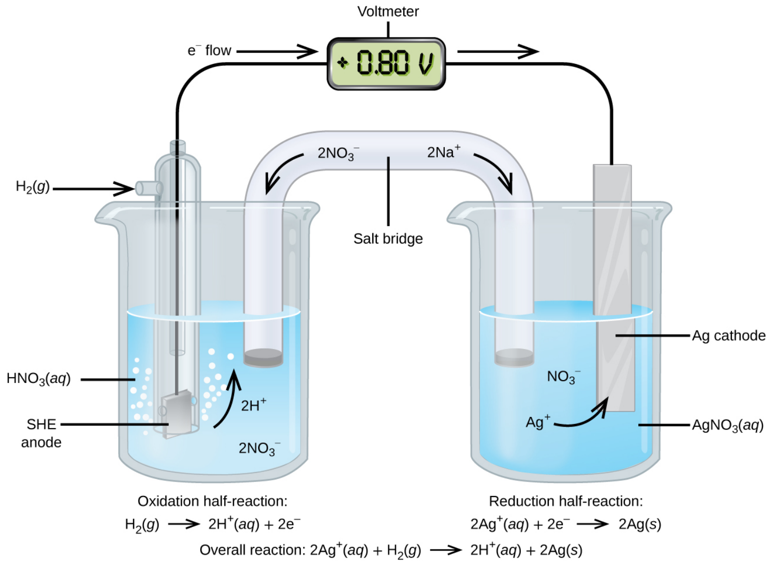

Figure 9.2.3: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table 9.2.1: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.69
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.507
$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.35827
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2\,e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$	+0.558
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.5355
$NiO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Ni(OH)_2(s) + 2\,OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.1375
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2\,e^- \longrightarrow Co(s)$	−0.28

Half-Reaction	E° (V)
$PbSO_4(s) + 2\,e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$	−1.185
$Zn(OH)_2(s) + 2\,e^- \longrightarrow Zn(s) + 2\,OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.662
$Mg^{2}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.372
$Na^{+}(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$	−2.912
$K^{+}(aq) + e^- \longrightarrow K(s)$	−2.931
$Li^{+}(aq) + e^- \longrightarrow Li(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Example 9.2.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 9.2.1, the reactions involved in the galvanic cell, both written as reductions, are

$$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E^\circ_{Au^{3+}/Au} = +1.498\text{ V} \tag{9.2.10}$$

$$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s) \quad E^\circ_{Ni^{2+}/Ni} = -0.257\text{ V} \tag{9.2.11}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \quad E^\circ_{anode} = E^\circ_{Ni^{2+}/Ni} = -0.257\text{ V}$$

$$\text{Cathode (reduction): } Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E^\circ_{cathode} = E^\circ_{Au^{3+}/Au} = +1.498\text{ V}$$

The least common factor is six, so the overall reaction is

$$3\,Ni(s) + 2\,Au^{3+}(aq) \longrightarrow 3\,Ni^{2+}(aq) + 2\,Au(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.498\text{ V} - (-0.257\text{ V}) = 1.755\text{ V} \tag{9.2.12}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 9.2.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$\mathrm{Mg}(s) + 2\,\mathrm{Ag}^{+}(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\,\mathrm{Ag}(s) \qquad E^{\circ}_{\text{cell}} = 0.7996\text{ V} - (-2.372\text{ V}) = 3.172\text{ V}$$

Contributors and Attributions

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, *E*°, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

Key Equations

- $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$

Glossary

standard cell potential $(E^{\circ}_{\text{cell}})$

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (*E*°)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

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9.3: The Nernst Equation

Learning Objectives

- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

We will now extend electrochemistry by determining the relationship between E°_cell and the thermodynamics quantities such as $\Delta G°$ (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = \text{J} \tag{9.3.1}$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23}\ e^-}{mol} \times \frac{1.602 \times 10^{-19}\ C}{e^-} \\ &= 9.648 \times 10^4\ \frac{C}{mol} \\ &= 9.648 \times 10^4\ \frac{J}{V \cdot mol} \end{aligned}$$

Therefore

$$\text{total charge} = (\text{number of moles of e}^-) \times F = nF \tag{9.3.2}$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_ele) by

$$E_\text{cell} = \frac{-w_\text{ele}}{nF} \qquad \text{or} \qquad w_\text{ele} = -nFE_\text{cell} \tag{9.3.3}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele}.

$$\begin{aligned} \Delta G &= w_\text{max} = w_\text{ele} \\ &= -nFE_\text{cell} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{cell} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE^\circ_\text{cell} \tag{9.3.4}$$

This provides a way to relate standard cell potentials to equilibrium constants, since

$$\Delta G^\circ = -RT \ln K \tag{9.3.5}$$

$$-nFE^\circ_\text{cell} = -RT \ln K \tag{9.3.6}$$

or

$$E^\circ_\text{cell} = \frac{RT}{nF} \ln K \tag{9.3.7}$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$\begin{aligned} E^\circ_\text{cell} &= \frac{RT}{nF}\ln K \\ &= \frac{\left(8.314\,\frac{\text{J}}{\text{K·mol}}\right)(298.15\ K)}{n \times 96,485\ \text{C/V·mol}}\ln K \\ &= \frac{0.0257\ \text{V}}{n}\ln K \end{aligned}$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., $\log_{10}$ or just log), which changes the constant by a factor of 2.303:

$$E^\circ_\text{cell} = \frac{0.0592\ \text{V}}{n}\log K \tag{9.3.8}$$

Thus, if $\Delta G°$, K, or E°_cell is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 9.3.1.

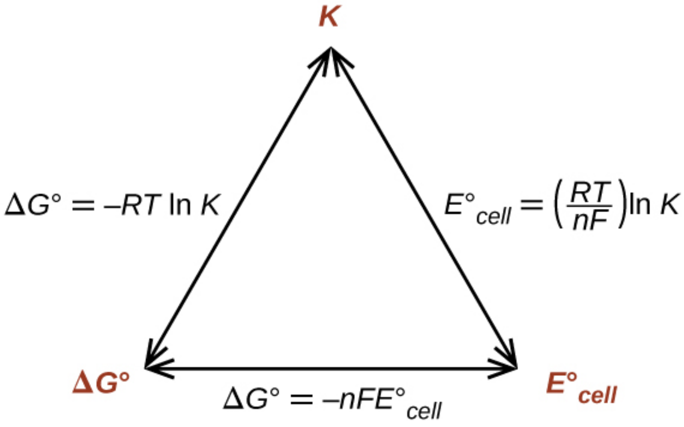

Figure 9.3.1: The relationships between ΔG°, K, and E°_cell. *Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.*

Given any one of the quantities, the other two can be calculated.

Example 9.3.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?

$$2\ \text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\ \text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.

$$\begin{aligned} &\text{anode (oxidation): Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\,\text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447\ \text{V} \\ &\text{cathode (reduction): } 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) \qquad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7996\ \text{V} \\ &E^\circ_\text{cell} = E^\circ_\text{cathode} - E^\circ_\text{anode} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247\ \text{V} \end{aligned}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With $n = 2$, the equilibrium constant is then

$$E^\circ_\text{cell} = \frac{0.0592\ \text{V}}{n}\log K$$

$$
\begin{aligned}
K &= 10^{n \times E^\circ_{\text{cell}}/0.0592\ \text{V}} \\
&= 10^{2 \times 1.247\ \text{V}/0.0592\ \text{V}} \\
&= 10^{42.128} \\
&= 1.3 \times 10^{42}
\end{aligned}
$$

The standard free energy is then

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96,485\ \frac{\text{J}}{\text{V}\cdot\text{mol}} \times 1.247\ \text{V} = -240.6\ \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

Exercise 9.3.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\,\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\,\text{Cu}^{+}(aq)$$

Answer

Spontaneous; *n* = 2; $E^\circ_{\text{cell}} = +0.291\ \text{V}$; $\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{9.3.9}$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q \tag{9.3.10}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{9.3.11}$$

Equation 9.3.11 is the generalized Nernst equation that is applicable at any temperature. However, is can be simplified for reactions occuring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257\ \text{V}}{n} \ln Q \tag{9.3.12}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n} \log_{10} Q \tag{9.3.13}$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation 9.3.11. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

Example 9.3.2: Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

$$\text{Co}(s) + \text{Fe}^{2+}(aq,\ 1.94\ M) \longrightarrow \text{Co}^{2+}(aq,\ 0.15\ M) + \text{Fe}(s)$$

Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,

$$\begin{aligned}
&\text{Anode (oxidation): } \mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2\,\mathrm{e}^- && E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}} = -0.28\ \mathrm{V} \\
&\text{Cathode (reduction): } \mathrm{Fe}^{2+}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Fe}(s) && E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.447\ \mathrm{V} \\
&E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447\ \mathrm{V} - (-0.28\ \mathrm{V}) = -0.17\ \mathrm{V}
\end{aligned}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

$$Q = \frac{[\mathrm{Co}^{2+}]}{[\mathrm{Fe}^{2+}]} = \frac{0.15\ M}{1.94\ M} = 0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 9.3.13)

$$\begin{aligned}
E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592\ \mathrm{V}}{n} \log Q \\
&= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2} \log 0.077 \\
&= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} = -0.14\ \mathrm{V}
\end{aligned}$$

The process is (still) nonspontaneous.

Exercise 9.3.2

What is the cell potential for the following reaction at room temperature?

$$\mathrm{Al}(s) \mid \mathrm{Al}^{3+}(aq,\ 0.15\ M) \parallel \mathrm{Cu}^{2+}(aq,\ 0.025\ M) \mid \mathrm{Cu}(s)$$

What are the values of *n* and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer

$n = 6$; $Q = 1440$; $E_{\text{cell}} = +1.97$ V, spontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

Example 9.3.3: Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(aq,\ 0.10\ M) \parallel \mathrm{Zn}^{2+}(aq,\ 0.50\ M) \mid \mathrm{Zn}(s)$$

Solution

From the information given:

$$\begin{array}{ll}
\text{Anode: } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) + 2\,\mathrm{e}^- & E^\circ_{\text{anode}} = -0.7618\ \mathrm{V} \\
\text{Cathode: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}(s) & E^\circ_{\text{cathode}} = -0.7618\ \mathrm{V} \\
\hline
\text{Overall: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) & E^\circ_{\text{cell}} = 0.000\ \mathrm{V}
\end{array}$$

The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592\text{ V}}{2}\log\frac{0.10}{0.50} = +0.021\text{ V}$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1. $Q < 1$ in this case, so the process is spontaneous.

Exercise 9.3.3

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 *M*, what was the concentration at the anode?

Answer

Q = 0.00042; $[Zn^{2+}]_{cat}$ = 2.1 \times 10^{-4} *M*.

Contributors and Attributions

Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant (F = 96,485 C/mol e^-). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

Key Equations

- $E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K$
- $E^\circ_{\text{cell}} = \frac{0.0257\text{ V}}{n}\ln K = \frac{0.0592\text{ V}}{n}\log K \qquad (\text{at } 298.15\ K)$
- $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q \qquad (\text{Nernst equation})$
- $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257\ V}{n}\ln Q = E^\circ_{\text{cell}} - \frac{0.0592\text{ V}}{n}\log Q \qquad (\text{at } 298.15\ K)$
- $\Delta G = -nFE_{cell}$
- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (F)

charge on 1 mol of electrons; F = 96,485 C/mol e^-

Nernst equation

equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

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9.4: Batteries and Fuel Cells

Learning Objectives

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is “best” and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

> *Visit this site to learn more about batteries.*

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure 9.4.1). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) + 2\,\mathrm{e^-} \qquad E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.7618\ \mathrm{V} \tag{9.4.1}$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl^-} \tag{9.4.2}$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl^-} \tag{9.4.3}$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.

A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface of the cylinder, indicated as a thin red line, is labeled “zinc can (electrode).” Just beneath this is a slightly thicker dark grey surface that covers the lateral surface, top, and bottom of the battery, which is labeled “Porous separator.” Inside is a purple region with many evenly spaced small darker purple dots, labeled “Paste of M n O subscript 2, N H subscript 4 C l, Z n C l subscript 2, water (cathode).” A dark grey rod, labeled “Carbon rod (electrode),” extends from the top of the battery, leaving a gap of less than one-fifth the height of the battery below the rod to the bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled “Metal bottom cover (negative).” The very top of the cylinder has a thin grey surface that curves upward at the center over the top of the carbon electrode at the center of the cylinder. This upper surface is labeled “Metal top cover (positive).” A thin dark grey line just below this surface is labeled “Insulator.” Below this, above the purple region, and outside of the carbon electrode at the center is an orange region that is labeled “Seal.”

Figure 9.4.1: The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell.

Alkaline batteries (Figure 9.4.2) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{array}{ll}
\text{anode: } \mathrm{Zn}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} & E^\circ_{\text{anode}} = -1.28\ \mathrm{V} \\
\text{cathode: } 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{OH^-}(aq) & E^\circ_{\text{cathode}} = +0.15\ \mathrm{V} \\
\hline
\text{overall: } \mathrm{Zn}(s) + 2\,\mathrm{MnO_2}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) & E^\circ_{\text{cell}} = +1.43\ \mathrm{V}
\end{array}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

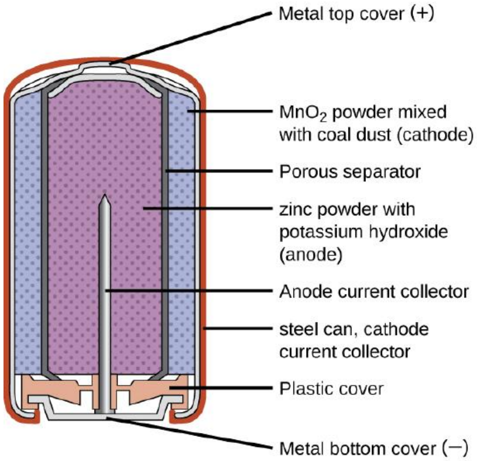

Figure 9.4.2: Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries.

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure 9.4.3) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{l}\text{anode: } \mathrm{Cd}(s)+2\,\mathrm{OH}^-(aq)\longrightarrow \mathrm{Cd(OH)_2}(s)+2\,\mathrm{e}^-\\ \text{cathode: } \mathrm{NiO_2}(s)+2\,\mathrm{H_2O}(l)+2\,\mathrm{e}^-\longrightarrow \mathrm{Ni(OH)_2}(s)+2\,\mathrm{OH}^-(aq)\\ \hline \text{overall: } \mathrm{Cd}(s)+\mathrm{NiO_2}(s)+2\,\mathrm{H_2O}(l)\longrightarrow \mathrm{Cd(OH)_2}(s)+\mathrm{Ni(OH)_2}(s)\end{array}$$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

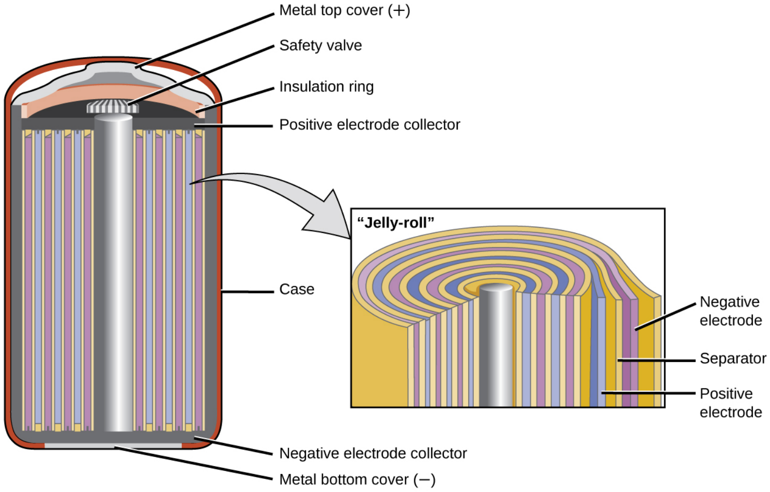

Figure 9.4.3: NiCd batteries use a “jelly-roll” design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 9.4.4) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{l} \text{anode: } \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-} \\ \text{cathode: } x\mathrm{Li^+} + x\mathrm{e^-} + x\mathrm{C_6} \rightleftharpoons x\mathrm{LiC_6} \\ \hline \text{overall: } \mathrm{LiCoO_2} + x\mathrm{C_6} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{LiC_6} \end{array}$$

With the coefficients representing moles, *x* is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

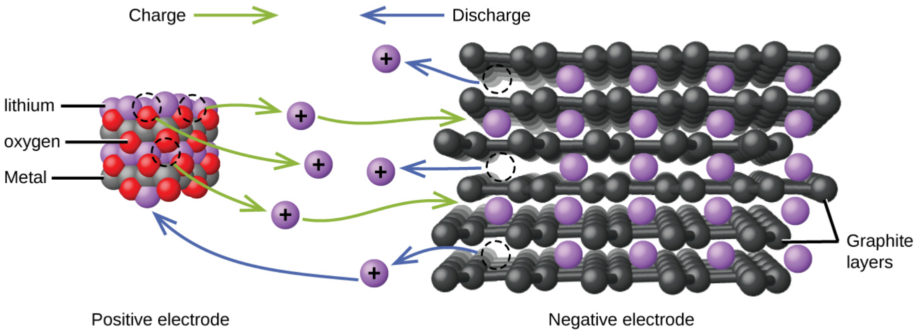

Figure 9.4.4: In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

The lead acid battery (Figure 9.4.5) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{array}{l} \text{anode: } \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\ \text{cathode: } \mathrm{PbO_2}(s) + \mathrm{HSO_4^-}(aq) + 3\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l) \\ \hline \text{overall: } \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \longrightarrow 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l) \end{array}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

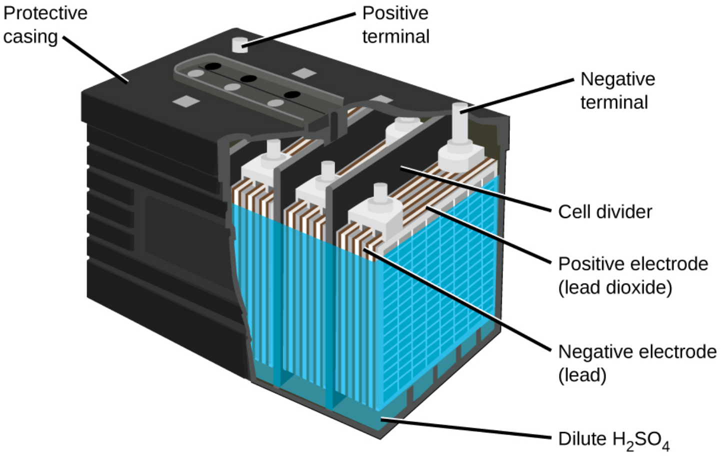

Figure 9.4.5: The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

Fuel Cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 9.4.6).

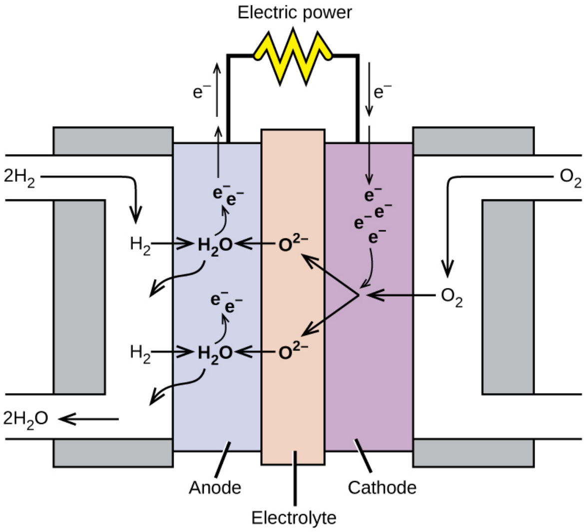

Figure 9.4.6: In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are

$$\begin{array}{l} \text{anode: } 2\,H_2 + 2\,O^{2-} \longrightarrow 2\,H_2O + 4\,e^- \\ \text{cathode: } O_2 + 4\,e^- \longrightarrow 2\,O^{2-} \\ \hline \text{overall: } 2\,H_2 + O_2 \longrightarrow 2\,H_2O \end{array}$$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Contributors and Attributions

Summary

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

Summary

alkaline battery

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

nickel-cadmium battery

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

primary battery

single-use nonrechargeable battery

secondary battery

battery that can be recharged

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9.5: Corrosion

Learning Objectives

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathrm{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu}(s) + \tfrac{1}{2}\mathrm{O_2}(g) \rightarrow \underset{\text{red}}{\mathrm{Cu_2O}(s)}$$

$$\mathrm{Cu_2O}(s) + \tfrac{1}{2}\mathrm{O_2}(g) \rightarrow \underset{\text{black}}{2\,\mathrm{CuO}(s)}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the CuO.

$$2\,\mathrm{CuO}(s) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2}(s)}$$

$$3\,\mathrm{CuO}(s) + 2\,\mathrm{CO_2}(g) + \mathrm{H_2O}(l) \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2}(s)}$$

$$4\,\mathrm{CuO}(s) + \mathrm{SO_3}(g) + 3\,\mathrm{H_2O}(l) \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6}(s)}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.

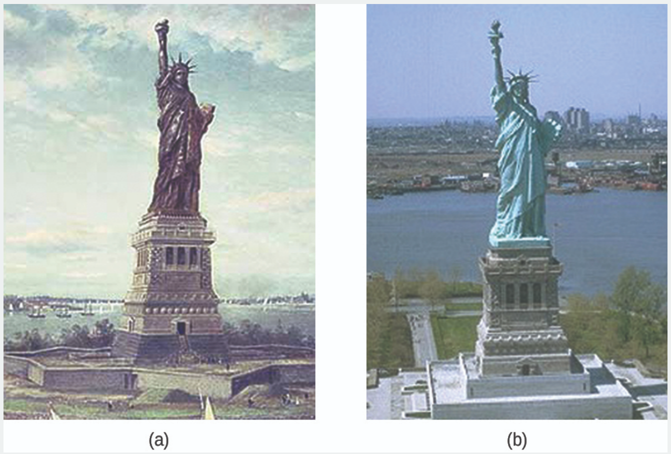

Figure 9.5.1: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: } \mathrm{Fe}_{(s)} \rightarrow \mathrm{Fe}^{2+}_{(aq)} + 2\,\mathrm{e}^{-} \quad E^{\circ}_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.44\ \mathrm{V} \tag{9.5.1}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: } \mathrm{O}_{2(g)} + 4\,\mathrm{H}^{+}_{(aq)} + 4\,\mathrm{e}^{-} \rightarrow 2\,\mathrm{H_2O}_{(l)} \quad E^{\circ}_{\mathrm{O_2/O_2}} = +1.23\ \mathrm{V} \tag{9.5.2}$$

$$\text{overall: } 2\,\mathrm{Fe}_{(s)} + \mathrm{O}_{2(g)} + 4\,\mathrm{H}^{+}_{(aq)} \rightarrow 2\,\mathrm{Fe}^{2+}_{(aq)} + 2\,\mathrm{H_2O}_{(l)} \quad E^{\circ}_{\text{cell}} = +1.67\ \mathrm{V} \tag{9.5.3}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\,\mathrm{Fe}^{2+}_{(aq)} + \mathrm{O}_{2(g)} + (4+2x)\mathrm{H_2O}_{(l)} \rightarrow 2\,\mathrm{Fe_2O_3}\cdot x\mathrm{H_2O}_{(s)} + 8\,\mathrm{H}^{+}_{(aq)} \tag{9.5.4}$$

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

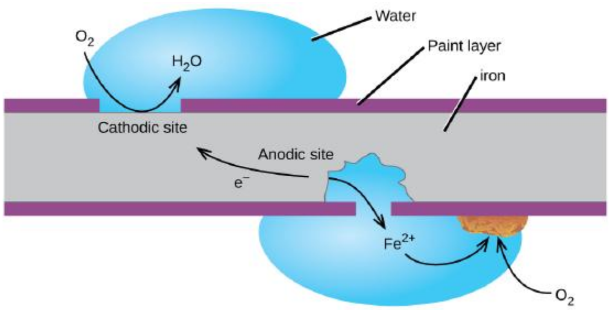

Figure 9.5.2: Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

A diagram is shown of an underground storage tank system. Underground, to the left end of the diagram is a horizontal grey tank which is labeled “Object to be protected.” A black line extends upward from the center of the tank above ground. An arrow points upward at the left side of the line segment. A horizontal black line segment continues right above ground, which is labeled “No power source is needed.” A line segment extends up and to the right, which is labeled “ Lead wire.” A line segment with a downward pointing arrow to its right extends downward below the ground to a second metal tank-like structure, labeled “Sacrificial anode” which is vertically oriented. Five black arrows point left underground toward the first tank. These arrows are collectively labeled “Protective current.”

Figure 9.5.3: One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

Another important way to protect metal is to make it the cathode in a galvanic cell. This is cathodic protection and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium. This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called sacrificial anodes because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

Summary

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The "protected" metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

Glossary

cathodic protection

method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

corrosion

degradation of metal through an electrochemical process

galvanized iron

method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

sacrificial anode

more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Contributors and Attributions

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9.6: Electrolysis

Learning Objectives

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In electrolytic cells, electrical energy causes nonspontaneous reactions to occur in a process known as electrolysis. The charging electric barttery shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile. The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure $9.6.1$. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode: } 2\,\mathrm{Cl^-}(l) \longrightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \qquad E^\circ_{\mathrm{Cl_2/Cl^-}} = +1.3\text{ V} \tag{9.6.1}$$

$$\text{cathode: } \mathrm{Na^+}(l) + \mathrm{e^-} \longrightarrow \mathrm{Na}(l) \qquad E^\circ_{\mathrm{Na^+/Na}} = -2.7\text{ V} \tag{9.6.2}$$

$$\text{overall: } 2\,\mathrm{Na^+}(l) + 2\,\mathrm{Cl^-}(l) \longrightarrow 2\,\mathrm{Na}(l) + \mathrm{Cl_2}(g) \qquad E^\circ_{\mathrm{cell}} = -4.0\text{ V} \tag{9.6.3}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

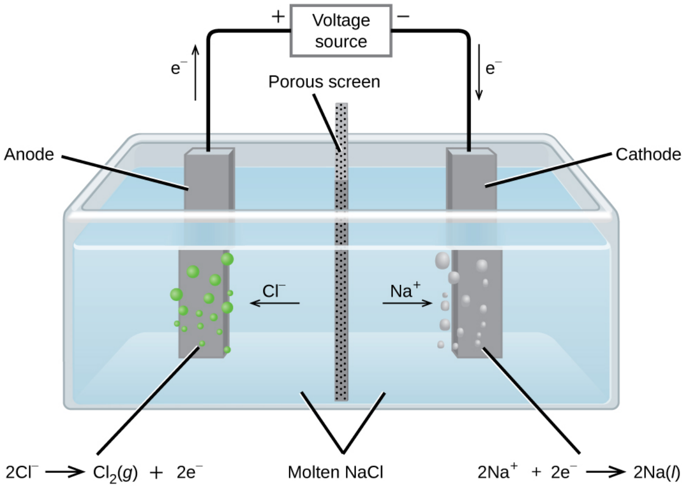

Figure $9.6.1$: Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure $9.6.2$). The reactions are

$$\text{anode: } 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) + 4\,\mathrm{e^-} \qquad E^\circ_{\mathrm{anode}} = +1.229\text{ V} \tag{9.6.4}$$

$$\text{cathode: } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \qquad E^\circ_{\mathrm{cathode}} = 0\text{ V} \tag{9.6.5}$$

$$\text{overall: } 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \qquad E^\circ_{\mathrm{cell}} = -1.229\text{ V} \tag{9.6.6}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

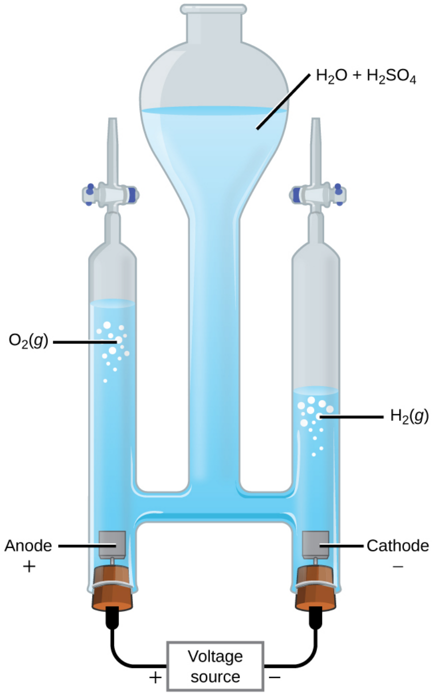

Figure 9.6.2: Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i) } 2\,\mathrm{Cl^-}(aq) \longrightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = +1.35827\text{ V} \tag{9.6.7}$$

$$\text{(ii) } 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) + 4\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = +1.229\text{ V} \tag{9.6.8}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The overpotential is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii) } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \qquad E^\circ_{\text{cathode}} = 0\text{ V} \tag{9.6.9}$$

$$\text{(iv) } 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) + 2\,\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cathode}} = -0.8277\text{ V} \tag{9.6.10}$$

$$\text{(v) } \mathrm{Na^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Na}(s) \qquad E^\circ_{\text{cathode}} = -2.71\text{ V} \tag{9.6.11}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only 1×10^{-7} *M*. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$\text{overall: } 2\,\mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}(aq) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) + 2\,\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cell}} = -2.186\text{ V} \tag{9.6.12}$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure $9.6.3$).

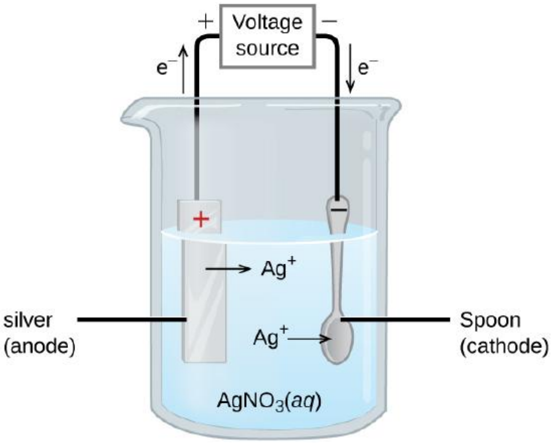

Figure $9.6.3$: The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\text{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^{+}(aq) + \mathrm{e}^{-} \tag{9.6.13}$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\text{cathode: } \mathrm{Ag}^{+}(aq) + \mathrm{e}^{-} \longrightarrow \mathrm{Ag}(s) \tag{9.6.14}$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (*I*) is the ampere (A), which is the equivalent of 1 coulomb per second (1 A = 1 $\frac{\mathrm{C}}{\mathrm{s}}$). The total charge (*Q*, in coulombs) is given by

$$Q = I \times t = n \times F \tag{9.6.15}$$

where

- *t* is the time in seconds,
- *n* the number of moles of electrons, and
- *F* is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 9.6.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday’s constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n=\frac{Q}{F}=\frac{\frac{10.23\ \mathrm{C}}{\mathrm{s}}\times 1\ \mathrm{hr}\times\frac{60\ \mathrm{min}}{\mathrm{hr}}\times\frac{60\ \mathrm{s}}{\mathrm{min}}}{96,485\ \mathrm{C/mol\ e^-}}=\frac{36,830\ \mathrm{C}}{96,485\ \mathrm{C/mol\ e^-}}=0.3817\ \mathrm{mol\ e^-} \tag{9.6.16}$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } \mathrm{Ag^+}(aq)+\mathrm{e^-}\longrightarrow \mathrm{Ag}(s) \tag{9.6.17}$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag}=0.3817\ \mathrm{mol\ e^-}\times\frac{1\ \mathrm{mol\ Ag}}{1\ \mathrm{mol\ e^-}}\times\frac{107.9\ \mathrm{g\ Ag}}{1\ \mathrm{mol\ Ag}}=41.19\ \mathrm{g\ Ag} \tag{9.6.18}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Exercise 9.6.1

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer

$\mathrm{Al^{3+}}(aq)+3\,\mathrm{e^-}\longrightarrow \mathrm{Al}(s)$; 7.77 mol Al = 210.0 g Al.

Example 9.6.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume}=\left(0.010\ \mathrm{mm}\times\frac{1\ \mathrm{cm}}{10\ \mathrm{mm}}\right)\times\left(3.3\ \mathrm{m^2}\times\left(\frac{10,000\ \mathrm{cm^2}}{1\ \mathrm{m^2}}\right)\right)=33\ \mathrm{cm^3} \tag{9.6.19}$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass}=\text{volume}\times\text{density}=33\ \cancel{\mathrm{cm^3}}\times\frac{7.19\ \mathrm{g}}{\cancel{\mathrm{cm^3}}}=237\ \mathrm{g\ Cr} \tag{9.6.20}$$

$$\text{mol Cr} = 237\text{ g Cr} \times \frac{1\text{ mol Cr}}{52.00\text{ g Cr}} = 4.56\text{ mol Cr} \tag{9.6.21}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\text{ mol Cr} \times \frac{3\text{ mol e}^-}{1\text{ mol Cr}} \times \frac{96485\text{ C}}{\text{mol e}^-} = 1.32 \times 10^6\text{ C} \tag{9.6.22}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\text{ C}}{33.46\text{ C/s}} = 3.95 \times 10^4\text{ s} = 11.0\text{ hr} \tag{9.6.23}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

Exercise 9.6.2

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

231 g Zn required 23,000 minutes.

Contributors and Attributions

Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Summary

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating

depositing a thin layer of one metal on top of a conducting surface

overpotential

difference between the theoretical potential and actual potential in an electrolytic cell; the “extra” voltage required to make some nonspontaneous electrochemical reaction to occur

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9.7: Redox Principles and Balancing Redox Reactions

Learning Objectives

- Describe the concepts of oxidation and reduction
- Compute the oxidation states for elements in compounds
- Identify species in a reaction that are being oxidized and those that are being reduced
- Balance redox reactions

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term oxidation was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\,\mathrm{Na}(s) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(s) \tag{9.7.1}$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a half-reaction:

$$\begin{aligned} 2\,\mathrm{Na}(s) &\rightarrow 2\,\mathrm{Na^+}(s) + 2\,\mathrm{e^-} \\ \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} &\rightarrow 2\,\mathrm{Cl^-}(s) \end{aligned}$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\textbf{oxidation} = \text{loss of electrons} \tag{9.7.2}$$

$$\textbf{reduction} = \text{gain of electrons} \tag{9.7.3}$$

In this reaction, then, sodium is *oxidized* and chlorine undergoes reduction. Viewed from a more active perspective, sodium functions as a reducing agent (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an oxidizing agent (oxidant), as it effectively removes electrons from (oxidizes) sodium.

$$\textbf{reducing agent} = \text{species that is oxidized} \tag{9.7.4}$$

$$\textbf{oxidizing agent} = \text{species that is reduced} \tag{9.7.5}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g) \tag{9.7.6}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess *if the compound was ionic*.

Assigning Oxidation Numbers (Oxidation States)

The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
    - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals

- Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, O_2^{2-}), very rarely $-\frac{1}{2}$ (so-called superoxides, O_2^-), positive values when combined with F (values vary)
- Halogens: generally −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in those cases, varying values), −1 for F always,

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Example 9.7.3: Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. H_2S
b. SO_3^{2-}
c. Na_2SO_4

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$

$$x = 0 - (2 \times +1) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } SO_3^{2-} = -2 = (3 \times -2) + (1 \times x)$$
$$x = -2 - (3 \times -2) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on } SO_4^{2-} = -2 = (4 \times -2) + (1 \times x)$$

$$x = -2 - (4 \times -2) = +6$$

Exercise 9.7.3

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

a. $K\underline{N}O_3$
b. $\underline{Al}H_3$
c. $\underline{N}H_4^+$
d. $H_2\underline{P}O_4^-$

Answer a

N, +5

Answer b

Al, +3

Answer c

N, −3

Answer d

P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as shown below\). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\textbf{oxidation} = \text{increase in oxidation number} \tag{9.7.7}$$

$$\textbf{reduction} = \text{decrease in oxidation number} \tag{9.7.8}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted below are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10\,\mathrm{Al}(s) + 6\,\mathrm{NH_4ClO_4}(s) \rightarrow 4\,\mathrm{Al_2O_3}(s) + 2\,\mathrm{AlCl_3}(s) + 12\,\mathrm{H_2O}(g) + 3\,\mathrm{N_2}(g) \tag{9.7.9}$$

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\mathrm{Zn}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g) \tag{9.7.10}$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\mathrm{Cu}(s) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{Ag}(s) \tag{9.7.11}$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 9.7.4).

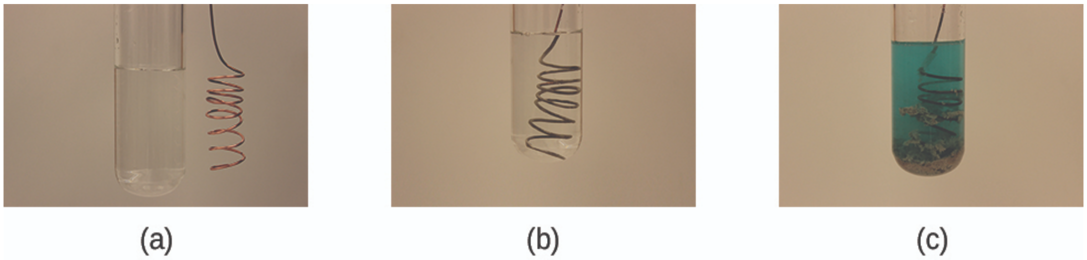

Figure 9.7.4: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 9.7.4: Describing Redox Reactions

Identify which equations represent redox reactions. For those reactions identified as redox, name the oxidizing agent and the reducing agent.

a. $\mathrm{ZnCO_3}(s) \rightarrow \mathrm{ZnO}(s) + \mathrm{CO_2}(g)$
b. $2\,\mathrm{Ga}(l) + 3\,\mathrm{Br_2}(l) \rightarrow 2\,\mathrm{GaBr_3}(s)$
c. $2\,\mathrm{H_2O_2}(aq) \rightarrow 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g)$
d. $\mathrm{BaCl_2}(aq) + \mathrm{K_2SO_4}(aq) \rightarrow \mathrm{BaSO_4}(s) + 2\,\mathrm{KCl}(aq)$
e. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(*l*) to +3 in $GaBr_3$(*s*). The reducing agent is Ga(*l*). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(*l*) to −1 in $GaBr_3$(*s*). The oxidizing agent is Br_2(*l*).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in H_2O_2(*aq*) to 0 in O_2(*g*). Oxygen is also reduced, its oxidation number decreasing from −1 in H_2O_2(*aq*) to −2 in H_2O(*l*). For disproportionation reactions, the same substance functions as an oxidant and a reductant.
d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C_2H_4(*g*) to +4 in CO_2(*g*). The reducing agent (fuel) is C_2H_4(*g*). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(*g*) to −2 in H_2O(*l*). The oxidizing agent is O_2(*g*).

Exercise 9.7.4

This equation describes the production of tin(II) chloride:

$$\mathrm{Sn}(s) + 2\,\mathrm{HCl}(g) \rightarrow \mathrm{SnCl_2}(s) + \mathrm{H_2}(g)$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. Sn(*s*) is the reductant, HCl(*g*) is the oxidant.

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions (or protons), and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge[1] by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.
7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
   - Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
   - On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
   - Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges[2] are balanced.

Example 9.7.5: Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$$\mathrm{Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}}$$

Solution

Write the two half-reactions.

Each half-reaction will contain one reactant and one product with one element in common.

$$\begin{gathered}\mathrm{Fe^{2+} \rightarrow Fe^{3+}} \\ \mathrm{Cr_2O_7^{2-} \rightarrow Cr^{3+}}\end{gathered}$$

Balance all elements except oxygen and hydrogen. The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$\begin{gathered}\mathrm{Fe^{2+} \rightarrow Fe^{3+}} \\ \mathrm{Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}}\end{gathered}$$

Balance oxygen atoms by adding H_2O *molecules*. The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$$\begin{gathered}\mathrm{Fe^{2+} \rightarrow Fe^{3+}} \\ \mathrm{Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O}\end{gathered}$$

Balance hydrogen atoms by adding H^+*ions*. The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$$\begin{gathered}\mathrm{Fe^{2+} \rightarrow Fe^{3+}} \\ \mathrm{Cr_2O_7^{2-} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O}\end{gathered}$$

Balance charge by adding electrons. The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion). Adding one electron to the right side bring that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved.

The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 $Cr_2O_7^{2-}$ ion and 14 H^+ ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr^{3+} ions). Adding six electrons to the left side will bring that side's total charge to (12+ + 6−) = 6+, and charge balance is achieved.

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-}$$

$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O}$$

Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$\mathrm{6\,Fe^{2+} \rightarrow 6\,Fe^{3+} + 6\,e^-}$
$\mathrm{Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O}$

Add the balanced half-reactions and cancel species that appear on both sides of the equation.

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightarrow 6\,Fe^{3+} + 6\,e^- + 2\,Cr^{3+} + 7\,H_2O} \tag{9.7.12}$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$\mathrm{6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O} \tag{9.7.13}$$

A final check of atom and charge balance confirms the equation is balanced.

	Reactants	**Products**
Fe	6	6
Cr	2	2
O	7	7
H	14	14
charge	24+	24+

Exercise 9.7.5

In acidic solution, hydrogen peroxide reacts with $\mathrm{Fe^{2+}}$ to produce $\mathrm{Fe^{3+}}$ and $\mathrm{H_2O}$. Write a balanced equation for this reaction.

Answer

$$\mathrm{H_2O_2}(aq) + 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Fe^{2+}} \rightarrow 2\,\mathrm{H_2O}(l) + 2\,\mathrm{Fe^{3+}}$$

Summary

Chemical reactions are classified according to similar patterns of behavior. Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

Footnotes

1. 1 The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.
2. 2 The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

Glossary

combustion reaction

vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

half-reaction

an equation that shows whether each reactant loses or gains electrons in a reaction.

oxidation

process in which an element’s oxidation number is increased by loss of electrons

oxidation-reduction reaction

(also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

oxidation number

(also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

oxidizing agent

(also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

reduction

process in which an element’s oxidation number is decreased by gain of electrons

reducing agent

(also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

single-displacement reaction

(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

Contributors and Attributions

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CHAPTER OVERVIEW

10: Atmospheric Chemistry and Air Pollution

10.1: Atmospheric Composition

The major gases that comprise today's atmosphere are in Table 10.1.1. The mixing ratio of a gas X is defined as the fraction of total moles that are the moles of gas X. For instance, 78 moles of every 100 total moles of air is nitrogen, so nitrogen's mixing ratio is 0.78. Note that in atmospheric composition, the mixing ratio is the *moles* of the gas divided by the *total moles of air*. In contrast, the water vapor mixing ratio is the *mass* of water vapor divided by the *mass of dry air*.

Table 10.1.1: Major Constituents in Earth’s Present Atmosphere

Constituent	Molecular Mass (g/mol)	Mixing Ratio (mol mol^{-1})	Role in the Atmosphere
nitrogen (N_2)	28.013	0.7808	transparent; provides heat capacity and momentum; exchanged with biomass; decomposed in combustion
oxygen (O_2)	31.998	0.2095	transparent except for in extreme ultraviolet; provides some heat capacity and momentum; exchanged with life; source of important reactive gases like ozone
argon (Ar)	39.948	0.0093	no role
carbon dioxide (CO_2)	44.010	0.000415 (415 ppmv)	transparent in visible; absorbs infrared light (i.e., contributes to radiative forcing); exchanged with life; product of combustion
neon (Ne)	20.183	0.0000182	no role, but makes colorful glowing signs
water vapor (H_2O)	18.015	2x10^{-6} to 0.05	gas transparent in visible; absorbs infrared light (i.e., contributes to global warming); exists as vapor, liquid, and solid; exchanged with life; product of combustion
aerosol particles	varies	0-500 ug m^{-3} (note different units)	essential for cloud formation; interact with visible and infrared light; exchanged with surfaces and life
methane (CH_4)	16.04	0.00000187 (1872 ppbv)	transparent in visible; absorbs in infrared (i.e. contributes to global warming); exchanged with life; source of CO_2 and H_2O
ozone (O_3)	48.00	0.01 – 10 ppm	transparent in visible; absorbs in UV and infrared; reactive and source of more reactive gases
particles	varies	0 to ~100 μg m^{-3} of air	absorbs and scatters light; acts as CCN and IN (see below)

Key features of the gases include their compressibility (i.e., ability to expand or shrink in volume), their transparency in the visible, their momentum, and their heat capacity. Water vapor has the additional important feature of existing in the vapor, liquid, and solid phases in the atmosphere and on Earth’s surface. The most important properties of small particles include their ability to dissolve in water in order to be **Cloud Condensation Nuclei (CCN)** or to maintain a lattice structure similar to ice in order to be Ice Nuclei (IN), as well as their ability to absorb and scatter sunlight. These properties depend completely on the particle size and composition. Most atmospheric gases participate in the atmosphere's chemistry, which is initiated by sunlight, as you will soon see.

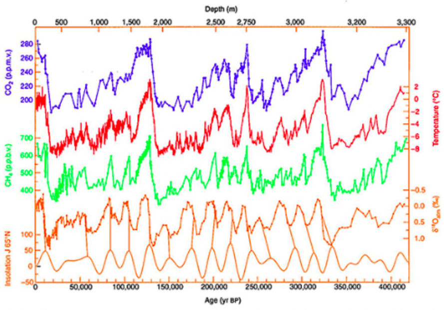
Units used when quantifying atmospheric composition

Several different units are typically used when specifying the amounts of gases. One is the mass mixing ratio, which is the mass of a chemical species divided by the total mass of air. A second is the volume mixing ratio, which is just the number of molecules of a chemical species in a unit volume divided by the total number of all molecules in a unit volume. For gases with relatively large fractions like nitrogen, oxygen, and argon, we use percent to indicate this fraction. For minor gases like carbon dioxide and ozone, we use parts per million (10^{-6}) ppmv or parts per billion (10^{-9}) ppbv by volume (with the lowercase 'v' meaning by volume not mass). Lastly we often also use the concentration, in mass per unit volume, to calculate reaction rates and lifetimes.

10.2: Changes in Atmospheric Composition

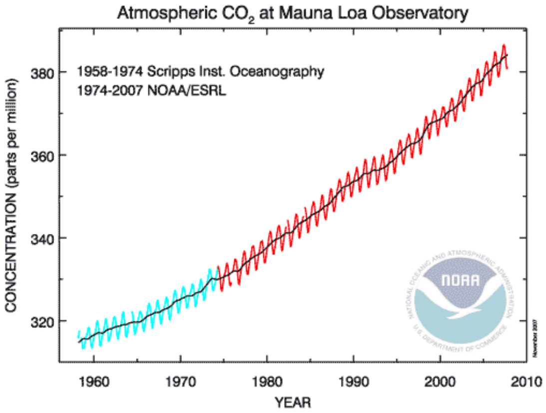
Since the rise of oxygen, 2 billion years ago, the nitrogen and oxygen fractions in the atmosphere have been stable. Water vapor is highly variable but, on average, appears to also have been fairly stable. Recent data from satellites and sondes indicate that perceptible water (the total amount of water that is in a column from the surface to space) has increased 1.3 ± 0.3% per decade over the oceans in the past 25 years (Trenberth et al., Climate Dynamics, 2005).

Historical (up to 500 years before the present) changes in CO_2 and CH_4 show large, rapid variations. Note that the historical range for CO_2 is 200-300 parts per million (10^{-6}), and for methane is 350-400 parts per billion (ppbv)**.** These changes in gas amounts have been driven by changes in Earth's temperature, which come from changes in Earth's orbit, the axis of Earth's rotation, and volcanoes. Until recently, changes in Earth's temperature caused changes in these gas amounts, which then reinforced the warming. In the past century, changes in the gas amounts have been driving the observed change in Earth's temperature.



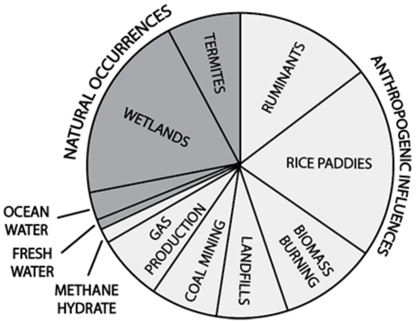
Changes in carbon dioxide, methane, and temperature over the past half million years. As measured from gases trapped in an ice core at Vostok, Antarctica. Credit: "Vostok 420ky curves insolation". Licensed under Public Domain via Wikimedia Commons

The recent changes in carbon dioxide show a fairly constant increase over the past 50 years. There is a smaller seasonal cycle imposed on this trend. This seasonal behavior occurs because CO_2 is taken up by plants in the northern hemisphere in summer, since most of the plants are in the northern hemisphere. Note that the current increase to above 400 ppm now extends well above any other time in the past half million years. Much of this CO_2increase can be linked to fossil fuel combustion. We will examine the scientific consequences of these CO_2 levels in the lesson on applications of radiation.

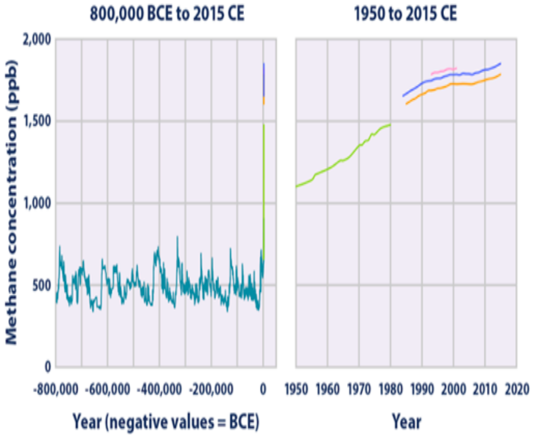


Atmospheric CO_2 mixing ratios measured at Mauna Loa, Hawaii for more than 50 years. Credit: NOAA

Another important trace gas is methane (CH_4), which is often called natural gas when it is used to produce power and heat. Methane has many sources, some of them natural and some of them anthropogenic (meaning human-made). Its atmospheric mixing ratio is now greater than 1800 parts per billion (ppb, or a fraction of 10^{-9} of air). We see from the figures below that almost 2/3 of atmospheric methane sources are anthropogenic and that methane measured at Hawaii, like all other locations, has been increasing except for the early to mid 2000s. This slowdown is not understood, but since the late 2000s, methane has been increasing again.



Sources of atmospheric methane: Freshwater, ocean water, wetlands, termites, ruminants, rice paddies, biomass burning, landfills, coal mining, gas production, methane hydrate. Ruminants are cattle, sheep, goats, etc. 2/3 of the total is due to human activities.



Changes in methane. Left, since 800,000 years ago. Right, since 1950. Note the tripling in the past 100 years, well above any levels since 800,000 years ago. The decade-long slow-down in the methane increase from 2000 to 2010 is not well understood. Credit: EPA

There are trends and variations in many of the other trace gases as well. Some others, like nitrous oxide (N_2O), are increasing, while others, like human-made chlorofluorocarbons (CCl_2F_2, CCl_3F) are decreasing. There are other trace gases that increase as the sun rises and decrease as it sets and are heavily involved in atmospheric chemistry. We will talk about these gases next.

10.3: Other Trace Gases

Hundreds of different trace gases have been measured in the atmosphere and perhaps thousands more have yet to be measured. Many of these are **volatile organic compounds (VOCs)**. *Volatile* means that, while the compound may exist in the liquid or solid phase, it easily evaporates or partitions from aqueous phase into the gas phase. *Organic* means that the compound contains carbon but is not carbon dioxide, carbon monoxide, or carbides and carbonates found in rocks. There are also other chemicals like the nitrogen oxides (e.g., nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3)), sulfur compounds (e.g., sulfur dioxide (SO_2), sulfuric acid (H_2SO_4)) and halogen compounds (e.g., methylene chloride (CH_2Cl_2), chlorofluorocarbons (CCl_2F_2)).

In addition to these thousands of chemicals that are emitted into the atmosphere every day, there are also some very reactive compounds that are created by atmospheric chemistry and play the important role of cleaning the atmosphere of many gases. The most important reactive gases are ozone (O_3) and hydroxyl radical (·OH). We will focus the discussion of atmospheric chemistry on these two.

The Atmosphere’s Oxidizing Capacity

Earth’s atmosphere is an *oxidizing environment*: gases that are emitted into the atmosphere react in a way that increases their oxygen content. Gases that contain oxygen tend to adsorb more readily onto surfaces and more water soluble, which means that they adsorb when they hit a surface, or they can be readily taken up in clouds and rain drops and be deposited on Earth’s surface. We call gases adsorbing onto surfaces “dry deposition,” and gases being taken up in precipitation and rained out “wet deposition.”

Let’s consider methane, the primary gaseous constituent in natural gas and biogas. Methane is increasingly being extracted from below Earth’s surface and used to electrical power generation, residential heating, other stationary uses, and increasingly to fuel vehicles. In complete combustion, each methane molecule is converted into CO_2 and two H_2O. In the process, four oxygen atoms or two oxygen molecules are consumed.

This same process occurs in the atmosphere, but at much lower temperatures and at a much slower rate. In both cases, the first step in the methane oxidation sequence is the reaction with the hydroxyl radical (·OH). A chemical radical is a molecule with an unpaired valence electron, often represented with the dot shown on the molecular formula. Such molecules are significantly reactive because the unpaired electron is less stable than if it were to gain or lose an electron.

Where does ·OH come from?

Before we tackle this question, let’s first look at where ozone (O_3) comes from. We will start with the stratosphere (a.k.a, good ozone because it blocks solar UV that harms humans, other animals, agriculture, and ecosystems) and then eventually we will consider tropospheric ozone (a.k.a., bad ozone, which is the ozone that hurts our health when we breathe it and that damages plants and their fruit).

10.4: Stratospheric Ozone Formation

Ozone is ozone no matter where it is in the atmosphere. Good ozone is good only because it is in the stratosphere where we cannot breathe it (Figure 10.4.1). Bad ozone also absorbs solar ultraviolet light, but it is down near Earth's surface where we can breathe it. For UV protection, we are interested in the total number of ozone molecules between us and the Sun. 90% of ozone molecules are in the stratosphere and 10% are in the troposphere - some down near Earth's surface where we can breathe them. There are important issues affecting human and ecological health for both good ozone and bad ozone. For good ozone, the most important issues are the reduction of ozone globally, the **Antarctic Ozone Hole**, and Arctic ozone loss that is caused by chlorofluorocarbons. Reduced ozone means more solar UV gets to the ground causing more skin cancer. For bad ozone, the most important issues include the production of too much ozone in cities and nearby regions that is caused by too many pollutants from traffic, industrial processes, power generation, and other human activities. Increased ozone means more people have respiratory and heart problems. Let's look at both the good and the bad, starting with the stratospheric ozone.

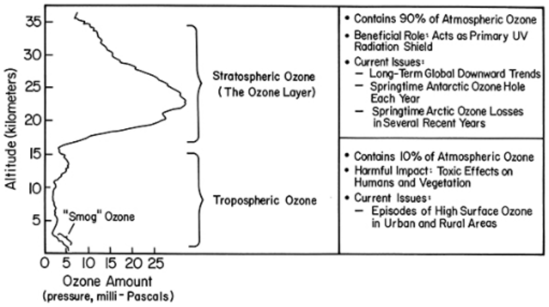


Figure 10.4.1: A cross-section of the typical vertical ozone profile for the tropics. Credit: World Meteorological Organization

Click for a text description of the Cross Section image.

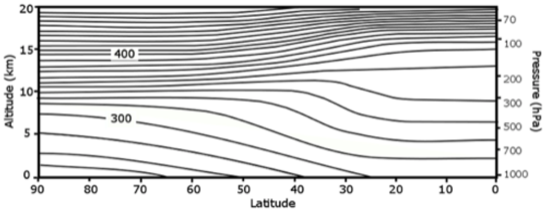
Explanation diagram of the typical vertical ozone profile for the tropics

Stratospheric Ozone (the ozone layer, ~15-35 km) contains 90% of atmospheric ozone beneficial role: acts as primary UV radiation shield Current issues

- long-term global downward trends
- springtime Antarctic ozone hole each year
- springtime arctic ozone losses in several recent years
- episodes of high surface ozone in urban and rural areas

Tropospheric Ozone (0-15 km) contains 10% of atmospheric ozone harmful impact: toxic effects on humans and vegetation current issues

To get the total amount of ozone between us and the Sun, we simply add up the ozone amount starting at the surface and going up to the top of the ozone layer. Note how much more ozone there is in the stratosphere. At higher latitudes, the bottom of the stratospheric ozone layer is at approximately 10-12 km. Recall the following image from Lesson 2:



Potential temperature (solid lines, K) as a function of latitude and altitude. Note that the decrease in potential temperature with height is small in the troposphere and large in the stratosphere. Credit: W. Brune, after Andews, Holton, and Leovy

The process of stratospheric ozone formation starts with ozone (O_3), which is made by ultraviolet sunlight in the stratosphere (but not the troposphere, as we shall see). The two reactions are:

$$O_2 + \text{hard}\,UV \rightarrow O + O \tag{10.4.1}$$

$$O + O_2 + N_2 \rightarrow O_3 + N_2 \tag{10.4.2}$$

Note that N_2 doesn't really react in this last chemical equation, but instead, simply bumps into the O_3 molecule as it is being formed and stabilizes it by removing some of the energy from O_3. We call O_3 an oxidant because it can react with some compounds and oxidize them.

This O_3 can be broken apart by ultraviolet light to make O_2 and O. Usually O combines with O_2 to form O_3 in this way: $O+O_2+N_2 \rightarrow O_3+N_2$, so nothing really happens, except that the solar energy that breaks apart the O_2 ends up as extra energy for the O_3 and for the colliding N_2 and, as a result, ends up warming the air. Sometimes O collides with O_3 and reacts: $O+O_3 \rightarrow O_2+O_2$. Putting all of the reactions together, we can see the chemical lifecycle of ozone in the stratosphere. This set of reactions was proposed in the 1930s by Chapman:

Stratospheric Ozone and Atomic Oxygen Production, Cycling, and Loss

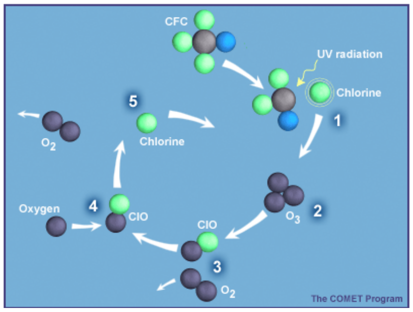
O_2 + hard UV → O + O	production
$2(O + O_2 + N_2 \rightarrow O_3 + N_2)$	cycling
O_3 + UV → O_2 + O	cycling
$O + O_3 \rightarrow O_2 + O_2$	loss
Net: UV → higher T	

These four reactions could produce the basic characteristics of the ozone layer as it was in the 1940s through the 1970s. However, this theory produced peak ozone levels that were 50 milli-Pascals, not the 25-30 milli-Pascals seen in the first figure above. Thus, the measured levels of stratospheric ozone were about half of those predicted by Chapman's theory - it was a real puzzle. However, in the 1970s, scientists proposed new sets of reactions by other gases that accomplished the same results as the loss reaction shown above. A famous example involved chlorine, which comes mostly from human-made chlorofluorocarbons (CFCs):

The Stratospheric Chlorine Catalytic Cycles That Destroy Ozone

CFCs + UV → product + Cl	production
$Cl + O_3 \rightarrow ClO + O_2$	cycling
$ClO + O \rightarrow Cl + O_2$	cycling
$Cl + CH_4 \rightarrow HCl + CH_3$	loss
Net O_3+O: $O_3 + O \rightarrow O_2 + O_2$	

During the cycle, chlorine (Cl) and chlorine monoxide (ClO) aren't destroyed but instead are just recycled into each other. With each cycle, two ozone molecules are lost (one directly and a second because O almost always reacts with O_2 to form O_3). This cycle can run for hundreds of thousands of times before Cl gets tied up in HCl. So ClO and Cl levels of tens of parts per trillion of air (10^{-12}) are able to destroy several percent of the few parts per million of O_3. Sherry Rowland and Mario Molina figured this cycle out and wrote a paper about it in 1974. They received a Nobel Prize in Chemistry in 1995 for this work. When catalytic cycles involving chlorine, nitrogen oxides, and OH are included with the theory, the agreement between the theory and the measurements gets much better.



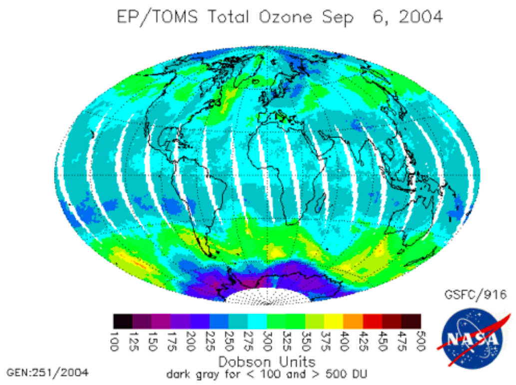
The chlorine catalytic cycle that destroys ozone. Credit: UCAR

Exercise

Note that the total ozone amount at midlatitudes is greater than the amount in the tropics. This should seem strange to you because the solar UV that is part of the Chapman mechanism is strongest in the tropics. Why do you think that total ozone is distributed this way?

Click for answer.

ANSWER: The ozone distribution is due to the motion of air through the stratosphere. Air comes from the troposphere into the stratosphere mostly in the tropics and, as it rapidly moves from west to east, it slowly moves from the tropics to near the poles, where it re-enters the troposphere. So most of the ozone is made in the tropics at higher altitudes and then some of this ozone is destroyed by chemical reactions as the ozone is transported poleward and downward. So, while the ozone mixing ratio decreases slightly from tropics to high latitudes, the ozone concentration (moles per volume) increases as it is transported to lower altitudes where the pressure and number of moles is greater, more than twice as large (see the Lesson 2 image above).



Satellite map of total ozone from September 6, 2004. Note that the total ozone amount is greater at midlatitudes than it is in the tropics, even though the solar UV is most intense in the tropics. The extremely low ozone over Antarctica is the Antarctic Ozone Hole. Credit: NASA GSFC

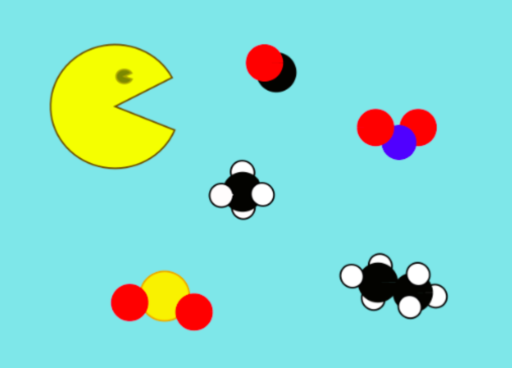
The low ozone over Antarctica above is the Antarctic Ozone Hole; the video below (:31) entitled "Ozone Minimums With Graph" (from NASA) shows changes in ozone concentration between 1979 and 2013. VIdeo is not narrated:

The Antarctic ozone hole is an extreme example of the destructive power of chlorine catalytic cycles. Different catalytic cycles dominate the ozone destruction over Antarctica and, to a lesser extent, the Arctic. But, when aided by chemistry on the surfaces of naturally occurring polar stratospheric clouds, all the Cl in the form of HCl is liberated so that the polar catalytic cycles are able to destroy a few percent of the ozone per day in a plug the size of Antarctica from an altitude of 12 km all the way up to 20 km.

Fortunately, the amount of chlorine being injected into the stratosphere is decreasing due to the Montreal Protocol, the world’s first international global environmental treaty.

10.5: The Story of the Atmosphere's PAC-MAN

The atmosphere's oxidation capacity is its ability to clean itself of all of the gases that are emitted into it. What does stratospheric ozone have to do with the atmosphere's oxidation capacity, which mostly occurs in the troposphere and mostly by the atmosphere's PAC-MAN, hydroxyl (OH)? It turns out that natural dynamic processes actually pull air down from the stratosphere and mix it into the troposphere, eventually mixing some of this ozone to Earth's surface. This naturally occurring surface ozone provides a baseline value for near-surface ozone, but ozone pollution is more than ten times greater than this baseline in cities. Ozone is both sticky on surfaces and fairly reactive in the atmosphere. It is lost both by depositing on surfaces and through being chemically destroyed by reactions in the atmosphere.



Hydroxyl (OH) is the PAC-MAN™ of the atmosphere. It reacts with thousands of different molecules, including carbon monoxide (CO), nitrogen dioxide (NO_2), methane (CH_4), sulfur dioxide (SO_2), and ethane (C_2H_6). Credit: W. Brune

The following chemical sequences are the humble beginnings of the atmosphere's PAC-MAN. OH is generated throughout the stratosphere and troposphere by a two-step reaction sequence. The first step is:

$$O_3 + UV \rightarrow O_2 + O^* \tag{10.5.1}$$

where O* is an excited-state oxygen atom that has extra chemical energy. O* can lose this extra energy by colliding with N_2 and O_2, but it can also collide with a water molecule to make two OH molecules:

$$O^* + H_2O \rightarrow OH + OH \tag{10.5.2}$$

OH is very reactive. You can think of OH as being water that has had a hydrogen taken away and wants it back. There are other sources for OH, but this one is the most important globally. OH reacts with many other atmospheric constituents. In fact, it is so reactive, that its lifetime in the atmosphere is less than a second.

Another important oxidant is nitric oxide (NO). It comes from combustion (power plants, internal combustion engines, fires) or lightning. In cities, the NO mixing ratio is tens of ppb (10^{-9}, by moles) during morning rush hour and a bit smaller during evening rush hour, but there is typically about a ppb around during the day. In very remote areas, the levels of NO are a hundred times less. NO can react with many other chemicals, but it reacts with O_3:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{10.5.3}$$

which forms nitrogen dioxide, NO_2. NO_2 is not very stable:

$$NO_2 + \text{nearUV} \rightarrow NO + O \tag{10.5.4}$$

ut the O reacts immediately with O_2 to form ozone:

$$O + O_2 + N_2 \rightarrow O_3 + N_2 \tag{10.5.5}$$

If a NO_2 molecule is produced, then an O_3 molecule will be produced during the day when the sun is out. *Note that if we think of these three reactions as a cycle, no ozone was either created or destroyed because it is destroyed in [4.5] and created in [4.2].*

What happens to all of the methane emitted into the atmosphere?

Methane is a volatile organic compound (VOC). Methane oxidation is a good model for what happens to all of the volatile organic compounds that you smell every day and all the ones that you can't smell. I am not going to show you the entire reaction sequence.

Instead, here are just a few steps.

The first step is the reaction between methane and hydroxyl:

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{10.5.6}$$

Note that water vapor is made and CH_3 is a radical because it has 12+3 = 15 protons and, therefore, electrons. Just as for most other VOCs, and some other trace emissions, the reaction with OH is the main way methane is removed from the atmosphere. Otherwise, it would build up to high abundance.

CH_3 is very reactive. It adds an O_2:

$$\mathrm{CH_3 + O_2 + N_2 \rightarrow CH_3O_2 + N_2} \tag{10.5.7}$$

If there is any NO around, the following reaction happens:

$$\mathrm{CH_3O_2 + NO \rightarrow CH_3O + NO_2} \tag{10.5.8}$$

followed by:

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{10.5.9}$$

and:

$$HO_2 + NO \rightarrow OH + NO_2 \tag{10.5.10}$$

The chemical CH_2O is formaldehyde. Some of you may have encountered it in high school chemistry or biology and so may be familiar with the smell. You also see that we got the OH molecule back.

Ultimately, formaldehyde gets broken down to CO and the net reaction of methane oxidation is:

$$CH_4 + 2NO + 3O_2 \rightarrow\rightarrow\rightarrow\rightarrow CO_2 + 2H_2O + 2NO_2 \tag{10.5.11}$$

Remember that NO_2 is easily broken apart by the UV sunlight that reaches Earth’s surface, so we can take this reaction sequence a step further and show that in the presence of sunlight, reactions [4.6] and [4.2] give:

$$NO_2 + \text{nearUV} + O_2 \rightarrow NO + O_3 \tag{10.5.12}$$

or

$$CH_4 + 5O_2 \rightarrow\rightarrow\rightarrow\rightarrow CO_2 + 2H_2O + 2O_3 \tag{10.5.13}$$

In this final chemical equation, we do not see OH, HO_2, NO, or NO_2, yet they are essential to the formation of ozone. They are catalytic, which means that they are neither created nor destroyed in the reaction sequence, but instead are simply recycled between OH and HO_2 and between NO and NO_2. There are other reactions that destroy these reactive chemicals by producing other chemicals that are much less reactive and sticky, a main one being:

$$OH + NO_2 + N_2 \rightarrow HNO_3 + N_2 \tag{10.5.14}$$

where HNO_3 is nitric acid, a very sticky and water soluble chemical. However, each OH that is produced can typically oxidize more than ten methane molecules before it reacts with NO_2 to form nitric acid. And as reaction [4.13] shows, each time methane is completely oxidized, two O_3 molecules are produced. That's a lot of chemical steps to remember, but I don't want you to necessarily remember them. *I want you to see that the process started with a reaction of OH with a volatile organic compound (in this case methane) and that in the subsequent reactions, the product molecules had more and more oxygens attached to them. This process is why we say that the atmosphere is an oxidizing environment.*

Where does ozone pollution come from?

Ozone is a different sort of pollutant from others because it is not directly emitted by a factory or power plant or vehicle but instead is produced by atmospheric chemistry.

Three ingredients are needed to make ozone pollution: *volatile organic compounds (VOCs)* (like methane); *nitric oxide (NO from combustion)*; and *sunlight*. When we say this, we assume that we already have some ozone and water to provide the OH to get the reactions started. Every VOC goes through an oxidation process that is similar to the methane oxidation reaction sequence. In the methane oxidation sequence, steps [4.9] and [4.11] make NO_2, which in the presence of sunlight makes ozone through step [4.6] followed by step [4.2]. Voila! Ozone is formed from methane oxidation in the presence of nitrogen oxides and sunlight. Now imagine the thousands of volatile organic compounds in the atmosphere and realize that all of them - both anthropogenic and natural - can participate in the production of ozone pollution. Now you have seen the sequence of chemical reactions that produce tropospheric ozone.

Let's look at a video (3:14) entitled "Ground Level Ozone: What Is It?" that explains ozone production without getting into the gory details of the chemistry.

Ground Level Ozone: What is it? Credit: UCARConnect

Click here for transcript of the Ground Level Ozone video.

> We're all pretty familiar with what O2 is. I hope so. You need to breathe it to live. Yes, O2 is oxygen, that life-giving gas, but what is O3? O3 is another gas essential to our survival but it's definitely not for breathing. O3 is ozone high up in the stratosphere. It's made naturally and absorbs harmful ultraviolet rays from the Sun. Without it life as we know it wouldn't, couldn't exist. We need the ozone layer in the stratosphere. We want it, we rely on it. But don't get too used to singing ozone's praises. High ozone levels at lower altitudes, what we call the troposphere, where we live and breathe or anything but natural and beneficial. In fact, down here it turns out to be a toxic atmospheric pollutants. Yep, you heard me right. ground-level ozone primarily exists due to human activities that burn fossil fuels. Transportation, our power and industrial plants, and other activities expel nitrogen oxides and hydrocarbons. When those compounds interact with sunlight, voila, ozone is created a contributor to smog. that's why I ozone levels increase during the summer months when sunlight is abundant. Yes, smog love summer just like many of us. We run, bike, hike, fish, play, stroll, oh yeah, and breathe. Yes, the fact that more people are outside when it's warmer makes us particularly vulnerable to Ozone's harmful impacts. Ozone is a harmful oxidant when we inhale it it's like getting a sunburn inside your lungs and it can be particularly serious for the young, old, active, and those with respiratory conditions at any age. And it's not just humans that are vulnerable ozone harms plants, crops, and agricultural yield interfering with pretty important processes like well, photosynthesis and even our economy. To make matters worse ozone production increases with higher temperatures which are occurring more frequently with climate change. The EPA sets national ambient air quality standards for several pollutants in the United States including ground level ozone. When a county is out of compliance they need to know what can be done to improve air quality. and let's not forget that air pollution is a global comments. air pollution is shared from surrounding cities states and also country's halfway around the world. What can we do, what are we willing to do to improve current levels? Drive less, carpool, avoid car idling, set your home's thermostat higher in the summer and lower in the winter, avoid gas powered lawn & garden tools on severe ozone days. There's a lot to do and lots to know about air quality knowing more about the sources and contributors to ozone and other atmospheric pollutants will help us chart our course.

Ozone pollution is bad for the health of people, crops, and forests. Ozone can react with some types of VOCs, including types that make up our lungs, and breathing it can cause serious health problems and even death. Ozone reacts with the VOCs that make up plants and stunts their growth and damages their fruit. The Clean Air Act from the 1970s has dramatically decreased the levels of air pollution in the United States, including ozone. The EPA can take the credit for much of the progress against air pollution in the United States. But there is still a ways to go and the progress may be reversed due to effects of climate change. Since ozone pollution increases at higher temperatures, the increases in global temperatures could actually reverse the steady progress in ozone reduction and ozone pollution could once again increase, unless volatile organic compounds and nitrogen oxides are reduced even more.

Now you can see why OH is called the PAC-MAN of the atmosphere. But how can we tell how long it will take for OH to remove from the atmosphere some trace gas like methane? Let’s look at an equation for the budget of methane. It is produced in the atmosphere by all the emissions from cows and wetlands. It is removed from the atmosphere by reactions with OH [4.7]. The rate of removal, that is the change in the methane concentration, is always proportional to the amount of the two reactants, in this case, CH_4 and OH. So, the change in methane is given by the balance between the production and the loss by reaction with OH:

$$\frac{d[CH_4]}{dt} = \backslash) production \backslash(- k_{OH+CH4}[OH][CH_4] \tag{10.5.15}$$

where k_{OH+CH4} is the reaction rate coefficient (units: cm^3 $molecule^{-1}$ s^{-1}) and *[OH]* and *[CH_4]* are the concentrations of OH and CH_4 (units: molecules cm^{-3}). Note that the production is positive and increases CH_4 with time while the loss is negative and decreases CH_4 with time.

We use [OH] to indicate the concentration of OH (molecules cm^{-3}), which is quite different from the OH mixing ratio (ppt = 10^{-12}, or ppb = 10^{-9}). 1 ppt ~ 2.4×10^7 molecules cm^{-3} and 1 ppb ~ 2.4×10^{10} molecules cm^{-3} for typical surface conditions. See the video below (1:47) entitled "Rate Equation" for further explanation:

Rate Equation

Click here for transcript of the Rate Equation video

> Let me explain equation 4.15, which is a rate equation for methane. A rate equation is just a differential equation. The change of something with respect to time equals the production rate of something, minus the fraction of something that is lost each unit of time, multiplied by the amount of something. Note that the loss rate of something is always proportional to something. That something can be anything. It does not have to be a chemical concentration. It could be the amount of milk in your refrigerator, or the number of socks in your drawer, both of which tend to disappear over time. And equation 4.15 is the methane concentration, which has units of molecules per centimeter cubed. The production rate is in units of molecules per centimeter cubed per second. Remember, each term of the equation must have the same units. The last term is the loss rate. The reaction rate coefficient has units of centimeter cubed per molecule per second, but when we multiply it by the OH concentration, we get a product that has units of per second, which is a frequency. Now, OH varies from almost 0 at night, to a peak value at midday. However, we can take an average OH to find the average loss rate of methane. Note that if we assume that the production rate suddenly goes to 0, then we find a very simple equation, which has an exponential solution. We designate the time that it takes the exponential factor to go to minus 1 as a lifetime, which is just the inverse of a loss frequency.

How can we find out what the lifetime of methane is? We assume that the production suddenly stops and equals 0. Then [4.15] becomes:

$$\frac{d[CH_4]}{dt} = -k_{OH+CH4}[OH][CH_4] \tag{10.5.16}$$

$$\frac{d\left[CH_4\right]}{\left[CH_A\right]} = -k_{OH+CH4}[OH]dt \tag{10.5.17}$$

k$_{OH+CH4}$ is the reaction rate coefficient for this reaction. Assume that OH is constant. Because OH is generated mostly from sunlight, it follows the sunshine and is greatest near midday and is very small at night. However, we assume that the OH concentration is the average over the day and night in order to assign it a constant value. Now integrate both sides of the equation:

$$\int_{[CH_4]_0}^{[CH_4]} \frac{d\left[CH_4\right]}{\left[CH_4\right]} = \int_0^t -k_{OH+CH_4}[OH]dt \tag{10.5.18}$$

$$\ln([CH_4]) - \ln([CH_4]_0) = -k_{OH+CH_4}\overline{[OH]}t \tag{10.5.19}$$

$$\ln\left(\frac{[CH_4]}{[CH_4]_0}\right) = -k_{OH+CH_4}\overline{[OH]}t \tag{10.5.20}$$

take exponential of both sides

$$\frac{[CH_4]}{[CH_4]_0} = e^{-k_{OH+CH_4}\overline{[OH]}t} \tag{10.5.21}$$

$$[CH_4] = [CH_4]_0 e^{-k_{OH+CH_4}\overline{[OH]}t} \tag{10.5.22}$$

So we see that *methane decreases exponentially with time*.

The atmospheric lifetime is defined as the time it takes something to decrease to e^{-1} = 0.37 of its initial value. So to find the lifetime of methane in the atmosphere, we see when k$_{OH+CH4}$[OH] t = 1, or:

$$\tau = \frac{1}{k_{OH+\text{CH4}}[OH]} \tag{10.5.23}$$

where τ indicates the lifetime. k$_{OH+CH4}$ =3x10^{-15} cm^3 molecule^{-1} s^{-1} and [OH] ~ 10^6 molecules cm^{-3}, so:

$$\tau = \frac{1}{3x10^{-15}10^6} = 3\times10^8 \text{seconds} \sim 10 \tag{10.5.24}$$

years

This reaction rate coefficient is fairly slow. Other VOCs have reaction rate coefficients that are typically hundreds to hundreds of thousands of times faster, so the lifetimes of most VOCs is hours to days.

The atmospheric lifetime of a gas is very important for determining how far a gas can travel from its source. Some trace gases have lifetimes of hours, so unless they are made by atmospheric chemistry, they can't travel more than a few tens of kilometers from their sources. Other gases have much longer lifetimes - methane is a good example with its 10-year lifetime. In 10 years, it can travel from its sources to most anywhere around the globe, even to the stratosphere. NASA measures the amounts of several gases from space. An excellent NASA website for accessing these satellite data and having it plotted as global maps is the Center for Trace Gas Data & Information Website at the NASA Goddard Space Flight Center's Earth Sciences Distributed Active Archive Center (GES DISC).

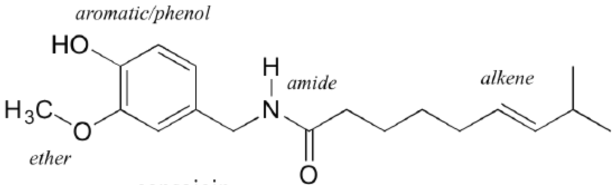
This concept of atmospheric lifetime is pretty important. For instance, what if an industry is spewing a chemical into the atmosphere that is toxic at a certain concentration in the atmosphere? Then it is important to know if that chemical is removed in less time than it takes to become toxic or if it is going to continue to build up at toxic levels and not leave the atmosphere for a long, long time. If its atmospheric lifetime is hundreds to thousands of years, then maybe we shouldn’t let that industry dump that chemical into the air.

CHAPTER OVERVIEW

11: Organic Chemistry Primer

11.1: Functional groups and organic nomenclature

Functional groups are structural units within organic compounds that are defined by specific bonding arrangements between specific atoms. The structure of capsaicin, the compound discussed in the beginning of this chapter, incorporates several functional groups, labeled in the figure below and explained throughout this section.

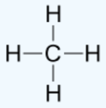


capsaicin

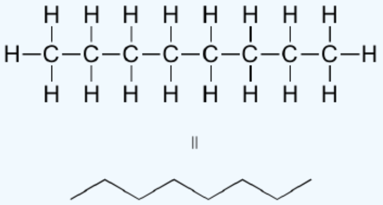
As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because *they are the key structural elements that define how organic molecules react*. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups behave in organic reactions.

The 'default' in organic chemistry (essentially, the *lack* of any functional groups) is given the term **alkane**, characterized by single bonds between carbon and carbon, or between carbon and hydrogen. Methane, CH_4, is the natural gas you may burn in your furnace. Octane, C_8H_{18}, is a component of gasoline.

✓ Alkanes



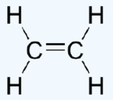
methane



octane

Alkenes (sometimes called **olefins**) have carbon-carbon double bonds, and **alkynes** have carbon-carbon triple bonds. Ethene, the simplest alkene example, is a gas that serves as a cellular signal in fruits to stimulate ripening. (If you want bananas to ripen quickly, put them in a paper bag along with an apple - the apple emits ethene gas, setting off the ripening process in the bananas). Ethyne, commonly called acetylene, is used as a fuel in welding blow torches.

✓ Alkenes and alkynes

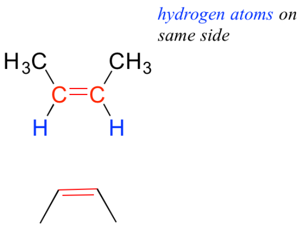


ethene
(an alkene)

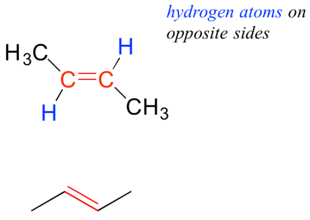
$H-C\equiv C-H$

ethyne
(an alkyne)

In chapter 2, we will study the nature of the bonding on alkenes and alkynes, and learn that that the bonding in alkenes is trigonal planar in in alkynes is linear. Furthermore, many alkenes can take two geometric forms: ***cis*** or ***trans***. The *cis* and *trans* forms of a given alkene are different molecules with different physical properties because, as we will learn in chapter 2, there is a very high energy barrier to rotation about a double bond. In the example below, the difference between *cis* and *trans* alkenes is readily apparent.



cis-alkene



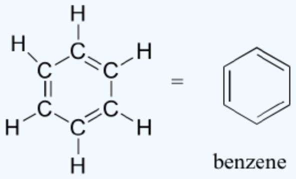
trans-alkene

We will have more to say about the subject of *cis* and *trans* alkenes in chapter 3, and we will learn much more about the reactivity of alkenes in chapter 14.

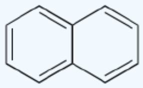
Alkanes, alkenes, and alkynes are all classified as **hydrocarbons**, because they are composed solely of carbon and hydrogen atoms. Alkanes are said to be **saturated hydrocarbons**, because the carbons are bonded to the maximum possible number of hydrogens - in other words, they are *saturated* with hydrogen atoms. The double and triple-bonded carbons in alkenes and alkynes have fewer hydrogen atoms bonded to them - they are thus referred to as **unsaturated hydrocarbons**. As we will see in chapter 15, hydrogen can be added to double and triple bonds, in a type of reaction called 'hydrogenation'.

The **aromatic** group is exemplified by benzene (which used to be a commonly used solvent on the organic lab, but which was shown to be carcinogenic), and naphthalene, a compound with a distinctive 'mothball' smell. Aromatic groups are planar (flat) ring structures, and are widespread in nature. We will learn more about the structure and reactions of aromatic groups in chapters 2 and 14.

✓ Aromatics



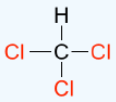
benzene



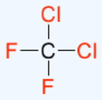
napthalene

When the carbon of an alkane is bonded to one or more halogens, the group is referred to as a **alkyl halide** or **haloalkane**. Chloroform is a useful solvent in the laboratory, and was one of the earlier anesthetic drugs used in surgery. Chlorodifluoromethane was used as a refrigerant and in aerosol sprays until the late twentieth century, but its use was discontinued after it was found to have harmful effects on the ozone layer. Bromoethane is a simple alkyl halide often used in organic synthesis. Alkyl halides groups are quite rare in biomolecules.

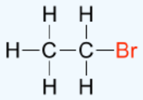
✓ Haloalkanes



trichloromethane
(chloroform)



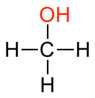
dichlorodifluoromethane
(Freon-12)

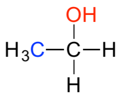


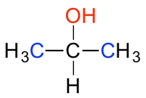
bromoethane

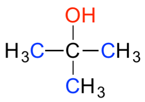
In the **alcohol** functional group, a carbon is single-bonded to an OH group (the OH group, by itself, is referred to as a **hydroxyl**). Except for methanol, all alcohols can be classified as primary, secondary, or tertiary. In a **primary alcohol**, the carbon bonded to the OH group is also bonded to only one other carbon. In a **secondary alcohol** and **tertiary alcohol,** the carbon is bonded to two or three other carbons, respectively. When the hydroxyl group is *directly* attached to an aromatic ring, the resulting group is called a **phenol**. The sulfur analog of an alcohol is called a **thiol** (from the Greek *thio*, for sulfur).

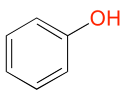
✓ Alcohols, phenols, and thiols

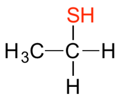

methanol


primary alcohol


secondary alcohol

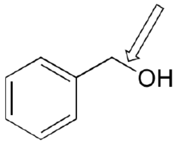

tertiary alcohol


phenol


thiol

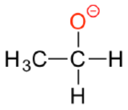
Note that the definition of a phenol states that the hydroxyl oxygen must be *directly* attached to one of the carbons of the aromatic ring. The compound below, therefore, is *not* a phenol - it is a primary alcohol.

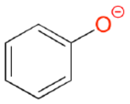
hydroxyl is not attached to carbon in aromatic ring

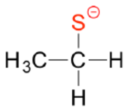

primary alcohol
(*not* a phenol)

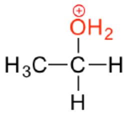
The distinction is important, because as we will see later, there is a significant difference in the reactivity of alcohols and phenols.

The deprotonated forms of alcohols, phenols, and thiols are called **alkoxides**, **phenolates**, and **thiolates**, respectively. A protonated alcohol is an **oxonium** ion.


alkoxide

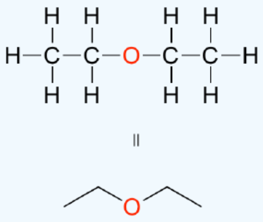

phenolate

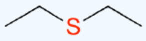

thiolate


oxonium

In an **ether** functional group, a central oxygen is bonded to two carbons. Below is the structure of diethyl ether, a common laboratory solvent and also one of the first compounds to be used as an anesthetic during operations. The sulfur analog of an ether is called a **thioether** or **sulfide**.

✓ Ethers and sulfides

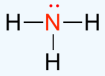

an ether

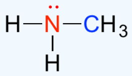

a sulfide

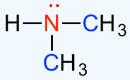
Amines are characterized by nitrogen atoms with single bonds to hydrogen and carbon. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines. Ammonia is a special case with no carbon atoms.

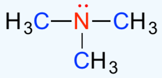
One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations. In the case where a nitrogen has four bonds to carbon (which is somewhat unusual in biomolecules), it is called a quaternary ammonium ion.

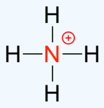
✓ Amines

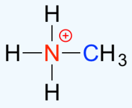

ammonia

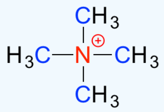

a primary amine


a secondary amine


a tertiary amine

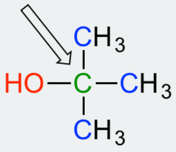

ammonium ion


a primary ammonium ion

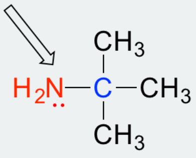

a quaternary ammonium ion

Note

Do not be confused by how the terms 'primary', 'secondary', and 'tertiary' are applied to alcohols versus amines - the definitions are different. In alcohols, what matters is how many other carbons the alcohol *carbon* is bonded to, while in amines, what matters is how many carbons the *nitrogen* is bonded to.


carbon *is bonded*
to ***three*** *carbons*

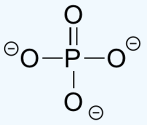
a *tertiary* alcohol

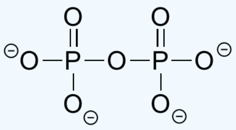

nitrogen *is bonded*
to ***one*** *carbon*

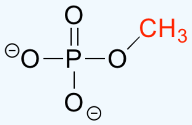
a *primary* amine

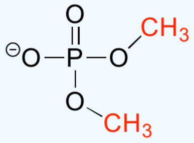
Phosphate and its derivative functional groups are ubiquitous in biomolecules. Phosphate linked to a single organic group is called a **phosphate ester**; when it has two links to organic groups it is called a **phosphate diester**. A linkage between two phosphates creates a **phosphate anhydride**.

Organic phosphates


phosphate


a phosphate anhydride


a phosphate ester

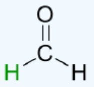

a phosphate diester

Chapter 9 of this book is devoted to the structure and reactivity of the phosphate group.

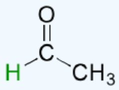
There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.

A group with a carbon-nitrogen double bond is called an **imine**, or sometimes a **Schiff base** (in this book we will use the term 'imine'). The chemistry of aldehydes, ketones, and imines will be covered in chapter 10.

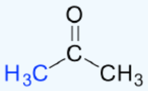
✓ Aldehydes, ketones, and imines



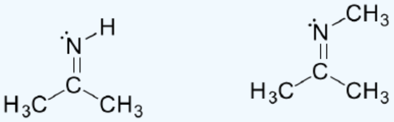
formaldehyde



an aldehyde



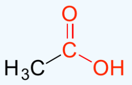
a ketone



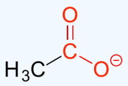
imines

When a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to an oxygen, nitrogen, or sulfur, the functional group is considered to be one of the '**carboxylic acid derivatives**', a designation that describes a set of related functional groups. The eponymous member of this family is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl group. The conjugate base of a carboxylic acid is a **carboxylate**. Other derivatives are carboxylic esters (usually just called **'esters'**), **thioesters**, **amides**, **acyl phosphates**, **acid chlorides**, and **acid anhydrides**. With the exception of acid chlorides and acid anhydrides, the carboxylic acid derivatives are very common in biological molecules and/or metabolic pathways, and their structure and reactivity will be discussed in detail in chapter 11.

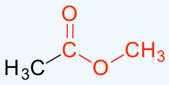
✓ Carboxylic acid derivatives



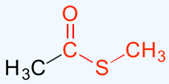
a carboxylic acid



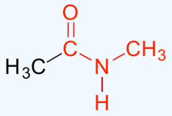
a carboxylate ion



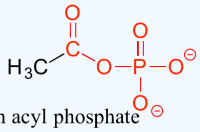
a carboxylic ester



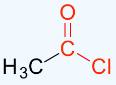
a thioester



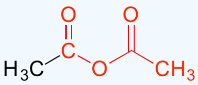
an amide



an acyl phosphate



an acid chloride



an acid anhydride

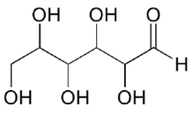
Finally, a **nitrile** group is characterized by a carbon triple-bonded to a nitrogen.

✓ Nitriles

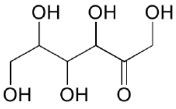
$:N\equiv C-CH_3$

acetonitrile

A single compound often contains several functional groups, particularly in biological organic chemistry. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

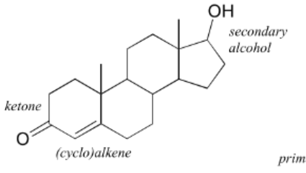


glucose

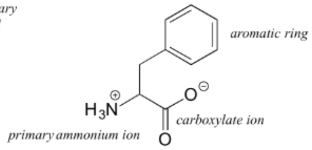


fructose

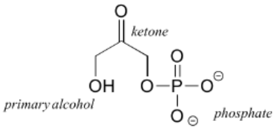
The hormone testosterone, the amino acid phenylalanine, and the glycolysis metabolite dihydroxyacetone phosphate all contain multiple functional groups, as labeled below.



testosterone



phenylalanine



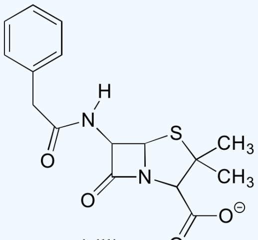
dihydroxyacetone phosphate
(DHAP)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological organic chemistry. Table 9 in the tables section at the back of this book provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

Exercise 1.12

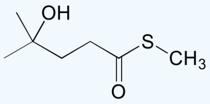
Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.

a)

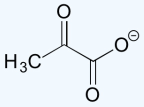


penicillin

b)

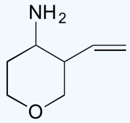


c)



pyruvate

d)



Solutions to exercises

Exercise 1.13

Draw one example each of compounds fitting the descriptions below, using line structures. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus may exceed the octet rule). There are many possible correct answers for these, so be sure to check your structures with your instructor or tutor.

a) a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups

b) an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.

c) A compound with molecular formula C_6H_9NO that has an amide functional group, and does *not* have an alkene group.

Naming organic compounds

A system has been devised by the International Union of Pure and Applied Chemistry (IUPAC, usually pronounced ***eye**-you-pack*) for naming organic compounds. While the IUPAC system is convenient for naming relatively small, simple organic compounds, it is not generally used in the naming of biomolecules, which tend to be quite large and complex. It is, however, a good idea (even for biologists) to become familiar with the basic structure of the IUPAC system, and be able to draw simple structures based on IUPAC names.

Naming an organic compound usually begins with identify what is referred to as the **'parent chain'**, which is the longest straight chain of carbon atoms. We'll start with the simplest straight chain alkane structures. CH_4 is called **methane**, and C_2H_6**ethane**. The table below continues with the names of longer straight-chain alkanes: be sure to commit these to memory, as they are the basis for the rest of the IUPAC nomenclature system (and are widely used in naming biomolecules as well).

✓ Names for straight-chain alkanes:

1 carbon: methane

2 carbons: ethane

3 carbons: propane

4 carbons: butane

5 carbons: pentane

6 carbons: hexane

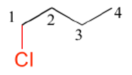
7 carbons: heptane

8 carbons: octane

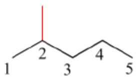
9 carbons: nonane

10 carbons: decane

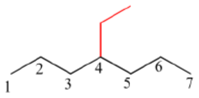
Substituents branching from the main parent chain are located by a carbon number, with *the lowest possible numbers* being used (for example, notice in the example below that the compound on the left is named 1-chlorobutane, *not* 4-chlorobutane). When the substituents are small alkyl groups, the terms **methyl**, **ethyl**, and **propyl** are used.



1-chlorobutane

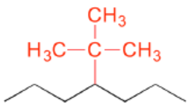


2-methylpentane

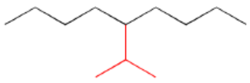


4-ethylheptane

Other common names for hydrocarbon substituent groups are **isopropyl, *tert*-butyl** and **phenyl**.

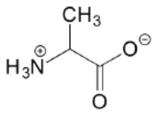


4-*tert*-butylheptane

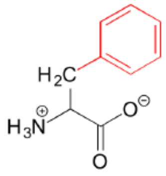


5-isopropylnonane

(non-IUPAC example):

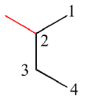


alanine
(an amino acid)

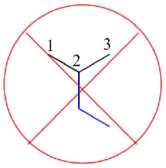


phenylalanine
(an amino acid)

Notice in the example below, an 'ethyl group' (in blue) is not treated as a substituent, rather it is included as part of the parent chain, and the methyl group is treated as a substituent. The IUPAC name for straight-chain hydrocarbons is always based on the *longest possible parent chain*, which in this case is four carbons, not three.



2-methylbutane



not 2-ethylpropane

Cyclic alkanes are called cyclopropane, cyclobutane, cyclopentane, cyclohexane, and so on:

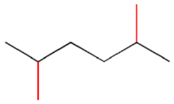
cyclopropane

cyclobutane

cyclopentane

cyclohexane

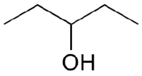
In the case of multiple substituents, the prefixes *di*, *tri*, and *tetra* are used.



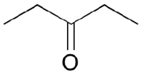
2,5-dimethylhexane

1,2,2,-trifluoropentane

Functional groups have characteristic suffixes. Alcohols, for example, have ‘**ol**’ appended to the parent chain name, along with a number designating the location of the hydroxyl group. Ketones are designated by ‘**one**’.



3-pentanol

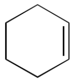


3-pentanone

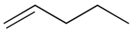
Alkenes are designated with an 'ene' ending, and when necessary the location and geometry of the double bond are indicated. Compounds with multiple double bonds are called dienes, trienes, etc.

$H_2C{=}CH_2$

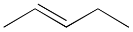
ethene



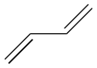
cyclohexene



1-pentene

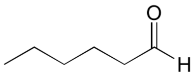


trans-2-pentene

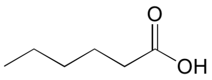


1,3-butadiene

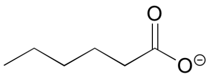
Some groups can only be present on a terminal carbon, and thus a locating number is not necessary: aldehydes end in ‘al’, carboxylic acids in ‘oic acid’, and carboxylates in ‘oate’.



hexanal

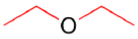


hexanoic acid

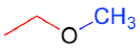


hexanoate

Ethers and sulfides are designated by naming the two groups on either side of the oxygen or sulfur.



diethyl ether

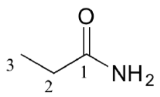


ethyl methyl ether

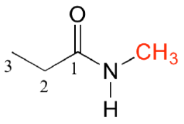
$H_3C-S-CH_3$

dimethyl sulfide

If an amide has an unsubstituted –NH_2 group, the suffix is simply ‘amide’. In the case of a substituted amide, the group attached to the amide nitrogen is named first, along with the letter ‘*N*’ to clarify where this group is located. Note that the structures below are both based on a three-carbon (propan) parent chain.

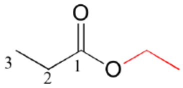


propanamide

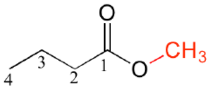


N-methylpropanamide

For esters, the suffix is 'oate'. The group attached to the oxygen is named first.

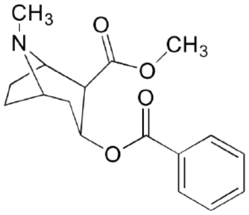


ethyl propanoate



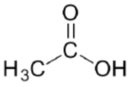
methyl butanoate

All of the examples we have seen so far have been simple in the sense that only one functional group was present on each molecule. There are of course many more rules in the IUPAC system, and as you can imagine, the IUPAC naming of larger molecules with multiple functional groups, ring structures, and substituents can get very unwieldy very quickly. The illicit drug cocaine, for example, has the IUPAC name 'methyl (1*R*,2*R*,3*S*,5*S*)-3-(benzoyloxy)-8-methyl-8-azabicyclo[3.2.1] octane-2-carboxylate' (this name includes designations for stereochemistry, which is a structural issue that we will not tackle until chapter 3).

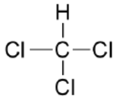


cocaine
(methyl (1*R*,2*R*,3*S*,5*S*)-3-(benzoyloxy)-8-methyl-8-azabicyclo[3.2.1] octane-2-carboxylate)

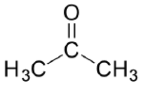
You can see why the IUPAC system is not used very much in biological organic chemistry - the molecules are just too big and complex. A further complication is that, even outside of a biological context, many simple organic molecules are known almost universally by their ‘common’, rather than IUPAC names. The compounds acetic acid, chloroform, and acetone are only a few examples.



acetic acid



chloroform



acetone

In biochemistry, nonsystematic names (like 'cocaine', 'capsaicin', 'pyruvate' or 'ascorbic acid') are usually used, and when systematic nomenclature is employed it is often specific to the class of molecule in question: different systems have evolved, for example, for fats and for carbohydrates. We will not focus very intensively in this text on IUPAC nomenclature or any other nomenclature system, but if you undertake a more advanced study in organic or biological chemistry you may be expected to learn one or more naming systems in some detail.

Exercise 1.14

Give IUPAC names for acetic acid, chloroform, and acetone.

Exercise 1.15

Draw line structures of the following compounds, based on what you have learned about the IUPAC nomenclature system:

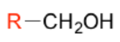
a. methylcyclohexane
b. 5-methyl-1-hexanol
c. 2-methyl-2-butene
d. 5-chloropentanal
e. 2,2-dimethylcyclohexanone

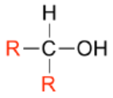
f. 4-penteneoic acid
g. *N*-ethyl-*N*-cyclopentylbutanamide

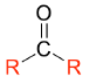
Solutions to exercises

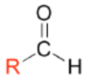
Drawing abbreviated organic structures

Often when drawing organic structures, chemists find it convenient to use the letter 'R' to designate part of a molecule outside of the region of interest. If we just want to refer in general to a functional group without drawing a specific molecule, for example, we can use 'R groups' to focus attention on the group of interest:

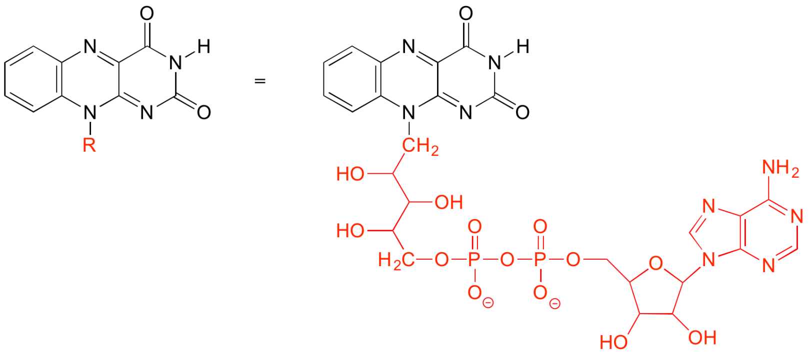

a primary alcohol


a secondary alcohol

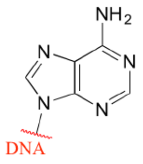

a ketone

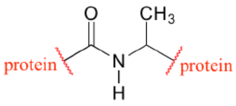

an aldehyde

The 'R' group is a convenient way to abbreviate the structures of large biological molecules, especially when we are interested in something that is occurring specifically at one location on the molecule. For example, in chapter 15 when we look at biochemical oxidation-reduction reactions involving the flavin molecule, we will abbreviate a large part of the flavin structure which does not change at all in the reaction of interest:

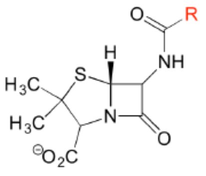

flavin adenine dinucleotide (FAD)

As an alternative, we can use a 'break' symbol to indicate that we are looking at a small piece or section of a larger molecule. This is used commonly in the context of drawing groups on large polymers such as proteins or DNA.

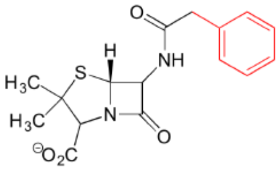

an adenine base in DNA


a small section of a protein

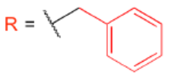
Finally, 'R' groups can be used to concisely illustrate a series of related compounds, such as the family of penicillin-based antibiotics.



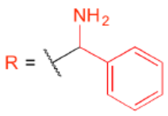
penicillin framework



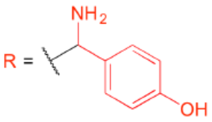
benzyl penicillin



benzyl penicillin



ampicillin

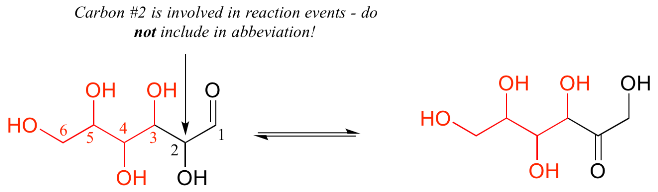


amoxicillin

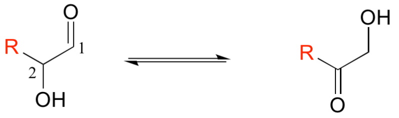
Using abbreviations appropriately is a very important skill to develop when studying organic chemistry in a biological context, because although many biomolecules are very large and complex (and take forever to draw!), usually we are focusing on just one small part of the molecule where a change is taking place.

> As a rule, *you should never abbreviate any atom involved in a bond-breaking or bond-forming event that is being illustrated:* only abbreviate that part of the molecule which is not involved in the reaction of interest.

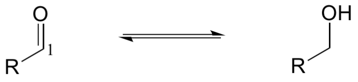
For example, carbon #2 in the reactant/product below most definitely is involved in bonding changes, and therefore should not be included in the 'R' group.


*Carbon #2 is involved in reaction events - do **not** include in abbeviation!*

appropriate abbreviation:



inappropriate abbreviation:



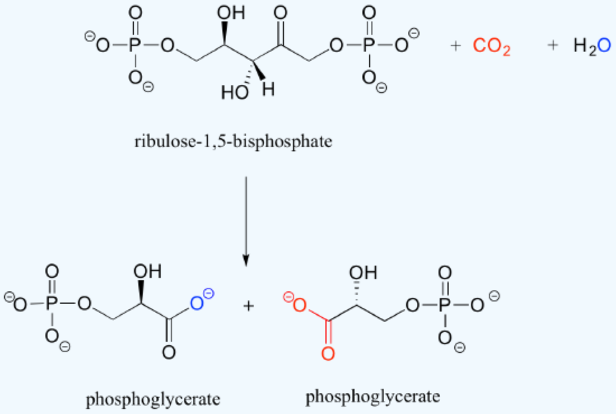
bonding transformation at carbon #2 is not shown

If you are unsure whether to draw out part of a structure or abbreviate it, the safest thing to do is to draw it out.

? :

a) If you intend to draw out the chemical details of a reaction in which the methyl ester functional group of cocaine (see earlier figure) was converted to a carboxylate plus methanol, what would be an appropriate abbreviation to use for the cocaine structure (assuming that you *only* wanted to discuss the chemistry specifically occurring at the ester group)?

b) Below is the (somewhat complicated) reaction catalyzed by an enzyme known as 'Rubisco', by which plants 'fix' carbon dioxide. Carbon dioxide and the oxygen of water are colored red and blue respectively to help you see where those atoms are incorporated into the products. Propose an appropriate abbreviation for the starting compound (ribulose 1,5-bisphosphate), using two different 'R' groups, R_1 and R_2.



Solutions to exercises

Khan Academy video tutorial on functional groups

Contributors and Attributions

- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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