

Chemistry - A Quantitative Science

Dennis Wertz

North Carolina State University

Select the bookmark icon in the margin to the left to navigate to a section in the text.

Periodic Table of the Elements

																<div>1 H 1.0079</div>				<div>2 He 4.0026</div>	
<div>3 Li 6.941</div>		<div>4 Be 9.0122</div>										<div>5 B 10.811</div>		<div>6 C 12.011</div>	<div>7 N 14.007</div>	<div>8 O 15.999</div>	<div>9 F 18.998</div>	<div>10 Ne 20.180</div>			
<div>11 Na 22.990</div>		<div>12 Mg 24.305</div>										<div>13 Al 26.982</div>		<div>14 Si 28.086</div>	<div>15 P 30.974</div>	<div>16 S 32.066</div>	<div>17 Cl 35.453</div>	<div>18 Ar 39.948</div>			
<div>19 K 39.098</div>		<div>20 Ca 40.078</div>	<div>21 Sc 44.956</div>	<div>22 Ti 47.88</div>	<div>23 V 50.942</div>	<div>24 Cr 51.996</div>	<div>25 Mn 54.938</div>	<div>26 Fe 55.847</div>	<div>27 Co 58.933</div>	<div>28 Ni 58.693</div>	<div>29 Cu 63.546</div>	<div>30 Zn 65.39</div>	<div>31 Ga 69.723</div>	<div>32 Ge 72.61</div>	<div>33 As 74.922</div>	<div>34 Se 78.96</div>	<div>35 Br 79.904</div>	<div>36 Kr 83.80</div>			
<div>37 Rb 85.478</div>		<div>38 Sr 87.62</div>	<div>39 Y 88.906</div>	<div>40 Zr 91.224</div>	<div>41 Nb 92.906</div>	<div>42 Mo 95.94</div>	<div>43 Tc (98)</div>	<div>44 Ru 101.07</div>	<div>45 Rh 102.91</div>	<div>46 Pd 106.42</div>	<div>47 Ag 107.87</div>	<div>48 Cd 112.41</div>	<div>49 In 114.82</div>	<div>50 Sn 118.71</div>	<div>51 Sb 121.75</div>	<div>52 Te 127.60</div>	<div>53 I 126.90</div>	<div>54 Xe 131.29</div>			
<div>55 Cs 132.91</div>		<div>56 Ba 137.33</div>	<div>57 La 138.91</div>	<div>72 Hf 178.49</div>	<div>73 Ta 180.95</div>	<div>74 W 183.84</div>	<div>75 Re 186.21</div>	<div>76 Os 190.23</div>	<div>77 Ir 192.22</div>	<div>78 Pt 195.08</div>	<div>79 Au 196.97</div>	<div>80 Hg 200.59</div>	<div>81 Tl 204.38</div>	<div>82 Pb 207.2</div>	<div>83 Bi 208.98</div>	<div>84 Po (209)</div>	<div>85 At (210)</div>	<div>86 Rn (222)</div>			
<div>87 Fr (223)</div>		<div>88 Ra 226.03</div>	<div>89 Ac 227.03</div>	<div>104 Rf (261)</div>	<div>105 Db (262)</div>	<div>106 Sg (263)</div>	<div>107 Bh (264)</div>	<div>108 Hs (265)</div>	<div>109 Mt (268)</div>	<div>110 Uun (269)</div>	<div>111 Uuu (272)</div>	<div>112 Uub (277)</div>									
				<div>58 Ce 140.11</div>	<div>59 Pr 140.91</div>	<div>60 Nd 144.24</div>	<div>61 Pm (145)</div>	<div>62 Sm 150.36</div>	<div>63 Eu 151.97</div>	<div>64 Gd 157.25</div>	<div>65 Tb 158.93</div>	<div>66 Dy 162.5</div>	<div>67 Ho 164.93</div>	<div>68 Er 167.26</div>	<div>69 Tm 168.93</div>	<div>70 Yb 173.04</div>	<div>71 Lu 174.97</div>				
				<div>90 Th 232.04</div>	<div>91 Pa 231.04</div>	<div>92 U 238.03</div>	<div>93 Np 237.05</div>	<div>94 Pu (244)</div>	<div>95 Am (243)</div>	<div>96 Cm (247)</div>	<div>97 Bk (247)</div>	<div>98 Cf (251)</div>	<div>99 Es (252)</div>	<div>100 Fm (257)</div>	<div>101 Md (258)</div>	<div>102 No (259)</div>	<div>103 Lr (262)</div>				

CHAPTER 1

Stoichiometry

1.0 Introduction

1.1 The Mole

1.2 Determining Chemical Formulas

1.3 Substance or Composition Stoichiometry

1.4 Balancing Chemical Equations

1.5 Reaction Stoichiometry

1.6 Chapter Summary and Objective

1.7 Exercises

1.0 INTRODUCTION

Chemistry - A Molecular Science (CAMS), the first half of this two-volume sequence, stressed bonding, structure, and reactivity. The material was qualitative and stressed several types of reactions and the factors that affected their relative extents of reaction. However, as the title of this text suggests, chemistry is also a quantitative science. Chemists must not only predict the products of a reaction, they must also predict the amount of product that can be expected, and the amount of waste that must be removed. They also need to know how much energy is required or how much heat is generated by a reaction. They must also understand how the reaction occurs so that they can optimize the reaction conditions. These are the types of problems addressed in this text.

We begin our study of the quantitative aspects of chemistry with **stoichiometry**, the science that deals with the quantitative relationships between the elements in a compound (substance stoichiometry) and between the substances in a chemical reaction (reaction stoichiometry). It is the topic of this first chapter because a thorough knowledge of stoichiometry is vital to an understanding of the material presented in this course. Understanding how quantitative data and results are presented is also important, so you should review *Appendix A, Reporting Quantitative Measurements and Results*, for a treatment of precision, significant figures, and rounding errors.

THE OBJECTIVES OF THIS CHAPTER ARE TO SHOW YOU HOW TO:

- determine the formula of a substance from its composition;
- balance chemical equations by inspection;
- use chemical equations to determine the relative amounts of reactants and products involved in a reaction;
- determine a limiting reactant; and
- determine the composition of a reaction mixture after the reaction is complete.

1.1 THE MOLE

Chemists use chemical equations to design possible routes to desired molecules and to discuss chemical processes. However, the individual molecules represented in the equations are far too small to be seen, so chemists must use a very large number of molecules in their reaction in order that the reactants and products can be observed. Indeed, the number of molecules required to make a visible sample is staggering. Consider that 1 μL^* of water - about $1/50^{\text{th}}$ of a drop - contains about 100,000,000,000,000,000 or 10^{17} molecules and a typical reaction in the laboratory involves thousands of times that number. Such large numbers are cumbersome, so scientists use a more convenient unit when discussing numbers of molecules. This unit is called a **mole** (mol):

$$1 \text{ mol} = 6.0221 \times 10^{23} \text{ items}$$

$6.0221 \times 10^{23} = N_A$ is **Avogadro's number**. A mole is used to indicate a number of atoms just as a dozen is used to indicate a number of eggs. Converting from moles to atoms is done the same as converting dozens to items. $1.5 \text{ doz} = (1.5 \text{ doz})(12 \text{ items} \cdot \text{doz}^{-1}) = 18 \text{ items}$ and $1.5 \text{ mol} = (1.5 \text{ mol})(6.0 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}) = 9.0 \times 10^{23} \text{ atoms}$. The mole is used simply because it is much easier to discuss the number of atoms in moles than it is as individual items - 0.10 mol H_2O is a much more convenient expression than 6.0×10^{22} H_2O molecules.

Chemists need to be able to readily prepare mixtures of reactants that have the correct atom or molecule ratios to react, but they certainly cannot count such large numbers. Instead, they use other more easily determined properties that are related to the numbers of atoms and/or molecules. The first such method we examine is mass. Mass can be used to 'count' atoms and molecules because *a mole is the number of atoms present in one gram atomic weight* of any atom or in one gram molecular weight of any molecule*. Thus, the mass of a mole of any substance, which is known as its **molar mass (M_m)**, equals its atomic or molecular weight expressed in grams. For example, the atomic weight of Mg is 24.3, so its molar mass is $24.3 \text{ g} \cdot \text{mol}^{-1}$, and the molecular weight of CO_2 is 44.0, so its molar mass is $44.0 \text{ g} \cdot \text{mol}^{-1}$. Thus, molar mass allows us to quickly convert a mass into a number of moles or a number of moles into a mass. Chemists use this fact to quickly 'count' the number of moles of substance by simply weighing it.

Mass \leftrightarrow mole conversions are most easily done with the **factor-label method**. It uses the units of the given quantity and those of the conversion factors to assure the proper operations are performed. To use this method, arrange the factors so that the denominator

* A gram atomic weight is a mass of atoms equal to the atomic weight of the atom expressed in grams.

of each factor cancels the numerator of the previous quantity until the units of the answer are obtained. This is shown explicitly in the following examples, where the units that cancel have lines drawn through them.

Example 1.1

Determine the molar masses to the nearest whole number.

N_2F_4

One mole of N_2F_4 contains 2 mol N and 4 mol F. The atomic masses of N and F are 14 and 19, respectively, so the molar mass of N_2F_4 is

$$\frac{2 \cancel{\text{mol N}}}{1 \text{ mol } \text{N}_2\text{F}_4} \times \frac{14 \text{ g } \cancel{\text{N}}}{1 \cancel{\text{mol N}}} + \frac{4 \cancel{\text{mol F}}}{1 \text{ mol } \text{N}_2\text{F}_4} \times \frac{19 \text{ g } \cancel{\text{F}}}{1 \cancel{\text{mol F}}} = \frac{104 \text{ g } \text{N}_2\text{F}_4}{1 \text{ mol } \text{N}_2\text{F}_4} = 104 \text{ g} \cdot \text{mol}^{-1}$$

We included the 'per mol substance' in the above, but it will be implied rather than written explicitly in future molar mass determinations.

$\text{Ca}_3(\text{PO}_4)_2$

One mol $\text{Ca}_3(\text{PO}_4)_2$ contains 3 mol Ca, 2 mol P, and 8 mol O, so the mass of one mole is

$$3 \cancel{\text{mol Ca}} \times \frac{40 \text{ g } \cancel{\text{Ca}}}{1 \cancel{\text{mol Ca}}} + 2 \cancel{\text{mol P}} \times \frac{31 \text{ g } \cancel{\text{P}}}{1 \cancel{\text{mol P}}} + 8 \cancel{\text{mol O}} \times \frac{16 \text{ g } \cancel{\text{O}}}{1 \cancel{\text{mol O}}} = 310 \text{ g} \cdot \text{mol}^{-1}$$

The 'per mol $\text{Ca}_3(\text{PO}_4)_2$ ' is not included, but it is implied in the molar mass.

Example 1.2

a) What is the mass of 3.24 mol N_2O_5 ?

First, use the molar masses of N and O to determine the molar mass of N_2O_5 .

$$2 \cancel{\text{mol N}} \times \frac{14.0 \text{ g } \cancel{\text{N}}}{1 \cancel{\text{mol N}}} + 5 \cancel{\text{mol O}} \times \frac{16.0 \text{ g } \cancel{\text{O}}}{1 \cancel{\text{mol O}}} = 108.0 \text{ g} \cdot \text{mol}^{-1}$$

Next, use the molar mass to convert the given moles into mass.

$$3.24 \cancel{\text{mol N}_2\text{O}_5} \times \frac{108.0 \text{ g } \text{N}_2\text{O}_5}{1 \cancel{\text{mol N}_2\text{O}_5}} = 350. \text{ g } \text{N}_2\text{O}_5$$

b) How many moles of N_2O_5 are present in a 12.7-g sample of N_2O_5 ?

Use the molar mass determined in Part A to convert from mass to moles.

$$12.7 \text{ g } \text{N}_2\text{O}_5 \times \frac{1 \text{ mol } \text{N}_2\text{O}_5}{108.0 \text{ g } \text{N}_2\text{O}_5} = 0.118 \text{ mol } \text{N}_2\text{O}_5$$

PRACTICE EXAMPLE 1.1

Determine the masses of the following.

a) 2.88 mol PF_3

molar mass:

$$M_m = \underline{\hspace{2cm}} \text{ g} \cdot \text{mol}^{-1}$$

mass

$$\underline{\hspace{2cm}} \text{ g}$$

b) 0.0448 mol $\text{C}_3\text{H}_8\text{O}$

molar mass

$$M_m = \underline{\hspace{2cm}} \text{ g} \cdot \text{mol}^{-1}$$

mass

$$\underline{\hspace{2cm}} \text{ g}$$

Determine the number of moles of compound in the following.

c) 18.6 g K_2SO_4

molar mass

$$M_m = \underline{\hspace{2cm}} \text{ g} \cdot \text{mol}^{-1}$$

moles

$$\underline{\hspace{2cm}} \text{ mol}$$

d) 0.2668 g H_3PO_4

molar mass

$$M_m = \underline{\hspace{2cm}} \text{ g} \cdot \text{mol}^{-1}$$

moles

$$\underline{\hspace{2cm}} \text{ mol}$$

Example 1.3

How many Al atoms are present in a piece of aluminum foil that has a mass 0.065 g?

The number of atoms is given by the number of moles of Al ($M_m = 27 \text{ g}\cdot\text{mol}^{-1}$).

$$0.065 \text{ g Al} \times \frac{1 \text{ mol Al}}{27 \text{ g Al}} = 2.4 \times 10^{-3} \text{ mol Al}$$

which is a perfectly good answer to the question. However, the number of moles of Al can be converted to the number atoms with the use of Avogadro's number.

$$2.4 \times 10^{-3} \text{ mol Al} \times \frac{6.02 \times 10^{23} \text{ Al atoms}}{1 \text{ mol Al}} = 1.4 \times 10^{21} \text{ Al atoms}$$

Both steps can be combined into one operation as follows:

$$0.065 \text{ g Al} \times \frac{1 \text{ mol Al}}{27 \text{ g Al}} \times \frac{6.02 \times 10^{23} \text{ Al atoms}}{1 \text{ mol Al}} = 1.4 \times 10^{21} \text{ Al atoms}$$

The number of moles of molecules in a gas can also be determined with the ideal gas law.

$$PV = nRT$$

Eq. 1.1

P is the pressure of the gas in atmospheres, **V** is its volume in liters, **n** is the number of moles of gas, **R** = $0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the ideal gas law constant, and **T** is the temperature on the Kelvin scale (**K** = $^{\circ}\text{C} + 273.15$).

Example 1.4

How many moles of H_2 are in a 3.06 L container at 22°C if its pressure is 742 torr?

Convert the Celsius temperature to the Kelvin scale: $T = 22 + 273 = 293 \text{ K}$

Use the equality $760 \text{ torr} = 1 \text{ atm}$ to convert the pressure to atmospheres.

$$P = 742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$$

Solve the ideal gas law for **n** and substitute the known quantities.

$$n = \frac{PV}{RT} = \frac{(0.976 \text{ atm})(3.06 \text{ L})}{(0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(293 \text{ K})} = 0.124 \text{ mol}$$

PRACTICE EXAMPLE 1.2

How many molecules are present in each sample?

a) 2.66 mmol CO_2

_____ molecules of CO_2

b) 12.0 μg of N_2O_5

_____ molecules of N_2O_5

PRACTICE EXAMPLE 1.3

What is the mass of CO_2 in a 500.0 mL flask at 75°C if its pressure is 1089 torr?

Pressure in atmospheres

P = _____ atm

Temperature on the Kelvin scale

T = _____ K

Moles of CO_2

n =

= _____ mol

Mass of CO_2

m = _____ g

1.2 DETERMINING CHEMICAL FORMULAS

The *elemental composition* of a substance is typically given as the mass percents of its component elements. The *mass percent* of an element in a compound is the fraction of the total mass of the compound due to the element expressed as a percent (part of a hundred).

Example 1.5

A 3.17-g sample of an oxide of lead was found to contain 2.94 g of lead. What is the elemental composition of the oxide expressed as mass percents?

The mass of sample and the mass of lead in the sample are given, but the mass of oxygen must be determined by difference.

$$\text{Mass of O} = \text{mass of sample} - \text{mass of Pb} = 3.17 - 2.94 = 0.23 \text{ g O}$$

The mass percent of each element is determined as the mass of the element divided by the mass of the sample times 100%.

$$\frac{2.94 \text{ g Pb}}{3.17 \text{ g oxide}} \times 100\% = 92.7\% \text{ Pb} \quad \text{and} \quad \frac{0.23 \text{ g O}}{3.17 \text{ g oxide}} \times 100\% = 7.3\% \text{ O}$$

Alternatively, we could have found the mass percent of Pb with the given data and then used the fact that the sum of the mass percents of all elements in the compound must sum to 100%. Thus, the mass percent of O could be found as follows:

$$\% \text{O} = 100.0\% \text{ total} - 92.7\% \text{ Pb} = 7.3\% \text{ O}$$

In Example 1.5, the elemental composition of a compound was determined from experimental data. However, elemental compositions can also be determined from the chemical formula and molar masses. Consider the case of Fe_2O_3 , the material responsible for the orange color of clay. One mole of Fe_2O_3 has a mass of

$$2 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe}} + 3 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 111.70 \text{ g Fe} + 48.00 \text{ g O} = 159.70 \text{ g Fe}_2\text{O}_3$$

A mole of Fe_2O_3 has a mass of 159.70 g and contains 111.70 g Fe and 48.00 g of O. To determine the elemental composition of a substance as mass fraction, divide each of the elemental masses by the molar mass of the substance,

$$\text{mass fraction Fe} = \frac{111.70 \text{ g Fe}}{159.70 \text{ g Fe}_2\text{O}_3} = 0.6994; \quad \text{mass fraction O} = \frac{48.00 \text{ g O}}{159.70 \text{ g Fe}_2\text{O}_3} = 0.3006$$

Multiplication of the mass fraction by 100 converts it into a **mass percent**. Thus, any pure sample of Fe_2O_3 is 69.94% iron and 30.06% oxygen by mass. Mass percents are also conversion factors that can be used to convert between a mass of a compound and the

PRACTICE EXAMPLE 1.4

A 2.687-g sample of a compound composed of Ba, Co, and O is found to contain 1.856 g Ba and 0.398 g Co. What is the composition of the compound expressed as mass percents of the elements?

$$\text{mass \% Ba} = \quad \times 100\% = \quad \%$$

$$\text{mass \% Co} = \quad \times 100\% = \quad \%$$

$$\text{mass of O} = \quad \text{g}$$

$$\text{mass \% O} = \quad \times 100\% = \quad \%$$

Alternatively,

$$\text{mass \% O} = 100.0\% - \quad \% = \quad \%$$

masses of its elements because the units of the mass percent of an element can be expressed as (g of element/100 g compound).

Example 1.6

- a) Ammonium nitrate is a good source of nitrogen that is used in the fertilizer industry. What percent of the mass of NH_4NO_3 is due to nitrogen?

Determine the molar mass of NH_4NO_3

$$\begin{aligned} M_m &= 2 \text{ mol N} \times \frac{14.0 \text{ g N}}{1 \text{ mol N}} + 4 \text{ mol H} \times \frac{1.01 \text{ g H}}{1 \text{ mol H}} + 3 \text{ mol O} \times \frac{16.0 \text{ g O}}{1 \text{ mol O}} \\ &= 28.0 \text{ g N} + 4.0 \text{ g H} + 48.0 \text{ g O} = 80.0 \text{ g NH}_4\text{NO}_3 \end{aligned}$$

80.0 g of ammonium nitrate contains 28.0 g of nitrogen, so the percent nitrogen is

$$\% \text{ N} = \frac{28.0 \text{ g N}}{80.0 \text{ g NH}_4\text{NO}_3} \times 100\% = 35.0\%$$

- b) How many pounds of N are in 25.0 lb of NH_4NO_3 ?

Mass percent is a ratio of masses, so the choice of mass units in the factor is arbitrary as long as they are the same in the numerator and the denominator. Thus, we can use the above mass percent to convert pounds even though it was determined from grams.

$$25.0 \text{ pounds NH}_4\text{NO}_3 \times \frac{35.0 \text{ pounds N}}{100 \text{ pounds NH}_4\text{NO}_3} = 8.75 \text{ pounds N}$$

Alternatively, we could use the ratio used to get the percents as our conversion factor

$$25.0 \text{ pounds NH}_4\text{NO}_3 \times \frac{28 \text{ pounds N}}{80.0 \text{ pounds NH}_4\text{NO}_3} = 8.75 \text{ pounds N}$$

The formula Fe_2O_3 shows two iron atoms for every three oxygen atoms; it does *not* indicate that a molecule of Fe_2O_3 has two iron atoms and three oxygen atoms. Indeed, Fe_2O_3 , which is the mineral hematite, exists as an extended solid with no discrete Fe_2O_3 units. Formulas that show only the smallest whole number ratio of atoms present in a compound are called **simplest formulas** or **empirical formulas**. The simplest or empirical formula of a substance can be determined from its mass composition in two steps:

1. Determine the number of moles of each element present in a fixed mass of the compound. This information can be given as experimental masses as in Example 1.5, or as percent compositions as in Example 1.6. If percent composition is given, the simplest procedure is to assume a fixed mass of 100 g, so the percents equal the masses of the elements present.

PRACTICE EXAMPLE 1.5

What are the mass percents of the elements in $\text{Ca}(\text{ClO}_3)_2$?

Molar mass of $\text{Ca}(\text{ClO}_3)_2$ = _____ $\text{g} \cdot \text{mol}^{-1}$

mass % Ca = _____ x100% = _____ %

mass % Cl = _____ x100% = _____ %

mass % O = _____ x100% = _____ %

2. Find the simplest whole number ratio of the moles present by dividing each result of Step 1 by the smallest result. If any of the new numbers are not integers, multiply all of the numbers by the number that makes them all integers. The resulting integers are the subscripts of the simplest formula. Table 1.1 gives the multipliers to use for some common decimals.

Example 1.7

A 7.50-g sample of iron is heated in oxygen to form an iron oxide. If 10.36 g of the oxide is formed, what is its simplest formula?

In this example, the elemental masses are given. The fixed mass of the compound is 10.36 g, and it contains 7.50 g Fe. The mass of oxygen that it contains is determined by difference: mass O = 10.36 g Fe_xO_y – 7.50 g Fe = 2.86 g O.

Step 1. Convert the two elemental masses to moles.

$$7.50 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 0.134 \text{ mol Fe} \quad \text{and} \quad 2.86 \text{ g O} \times \frac{1 \text{ mol O}}{16.0 \text{ g O}} = 0.179 \text{ mol O}$$

Step 2. Determine the ratio of the elemental moles obtained in Step 1.

$$\frac{0.179 \text{ mol O}}{0.134 \text{ mol Fe}} = \frac{1.33 \text{ mol O}}{1 \text{ mol Fe}}$$

Multiply the numerator and denominator by 3 to obtain a ratio of integers.

$$\frac{(3)(1.33 \text{ mol O})}{(3)(1 \text{ mol Fe})} = \frac{4 \text{ mol O}}{3 \text{ mol Fe}}$$

There are 4 mol O for every 3 mol Fe, so the simplest formula is Fe₃O₄, which is the mineral known as magnetite.

Table 1.1 Some common decimals and their multipliers

decimal	multiplier	decimal	multiplier
0.125	8	0.5	2
0.167	6	0.625	8
0.200	5	0.667	3
0.250	4	0.75	4
0.333	3	0.833	6
0.375	8	0.875	8

Example 1.8

KClO_x decomposes into KCl and O₂. What is the value of x in a compound that produces 468.5 mg KCl and 230.0 mL of O₂ gas at 756.2 torr and 23 °C?

X is the number of moles of O per mole of KCl, so we find the number of moles of each. Use the ideal gas law to determine moles of O₂.

$$n = \frac{PV}{RT} = \frac{(\frac{756}{760} \text{ atm})(0.230 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(296 \text{ K})} = 9.42 \times 10^{-3} \text{ mol} = 9.42 \text{ mmol}$$

There are 2 mol O/mol O₂, so the sample contains 2(9.42) = 18.84 mmol O. Divide the given mass of KCl by its molar mass (74.6 g·mol⁻¹) to obtain moles of KCl.

$$0.4685 \text{ g KCl} \times \frac{1 \text{ mol KCl}}{74.6 \text{ g KCl}} = 6.28 \times 10^{-3} \text{ mol} = 6.28 \text{ mmol}$$

Obtain x as the ratio of moles O/moles KCl

$$x = \frac{18.84 \text{ mmol}}{6.28 \text{ mmol}} = 3.00$$

The compound is KClO_3 , potassium chlorate.

The empirical formulas of benzene and acetylene are both CH . Indeed, there are hundreds of compounds with that empirical formula. Yet, there are no molecules that are composed of a single carbon atom and a single hydrogen atom. Formulas that represent the actual numbers of atoms in a molecule are called **molecular formulas**. A molecular formula always contains an integral number of simplest or empirical formulas: molecular formula = (simplest formula)_n. The molecular formula of benzene is C_6H_6 , so a benzene molecule contains six empirical units, $(\text{CH})_6$. The molar mass of the compound must also be an integral number of simplest formula molar masses: $M_m(\text{compound}) = nM_m(\text{empirical formula})$, where n is an integer. Thus, the value of n and the molecular formula can be determined from the empirical formula if the molar mass of the compound is known.

$$n = \frac{\text{molar mass of molecular formula}}{\text{molar mass of empirical formula}} \quad \text{Eq. 1.2}$$

For example, the molar mass of the CH unit is $13 \text{ g} \cdot \text{mol}^{-1}$ and the molar mass of C_6H_6 is $78 \text{ g} \cdot \text{mol}^{-1}$, so we would determine n as follows:

$$n = \frac{78 \text{ g} \cdot \text{mol}^{-1}}{13 \text{ g} \cdot \text{mol}^{-1}} = 6$$

Example 1.9

a) The amino acid lysine is 49.296% C, 9.653% H, 19.162% N, and 21.889% O. What is the empirical or simplest formula of lysine?

Step 1. Assume a 100-g sample of lysine, so the mass of each element is equal to its percent then determine the number of moles of each element.

$$\begin{array}{ll} \frac{49.296 \text{ g C}}{12.011 \text{ g/mol}} = 4.104 \text{ mol C} & \frac{9.653 \text{ g H}}{1.008 \text{ g/mol}} = 9.576 \text{ mol H} \\ \frac{19.162 \text{ g N}}{14.007 \text{ g/mol}} = 1.368 \text{ mol N} & \frac{21.889 \text{ g O}}{15.999 \text{ g/mol}} = 1.368 \text{ mol O} \end{array}$$

PRACTICE EXAMPLE 1.6

Heating a 589-mg sample of the red hydrate of cobalt(II) sulfate ($\text{CoSO}_4 \cdot x\text{H}_2\text{O}$) produces 347 mg of the anhydrous blue solid. What is the mass percent of water in this hydrate?

mass of $\text{CoSO}_4 \cdot x\text{H}_2\text{O}$ = _____ mg

mass of CoSO_4 = _____ mg

mass of H_2O : _____ mg

mass % H_2O = _____ x 100 % = _____ %

What is the value of x (mmols H_2O /mmol CoSO_4) in the formula of the hydrate?

M_m of H_2O = _____ mg/mmol

M_m of CoSO_4 = _____ mg/mmol

The hydrate contains

= _____ mmol CoSO_4

= _____ mmol H_2O

x = $\frac{\text{mmol H}_2\text{O}}{\text{mmol CoSO}_4}$ = _____

The formula of the hydrate is _____

Step 2. There are four elements, so we divide each of the above numbers of moles by the smallest (either mol N or mol O) to obtain the mole ratios.

$$\begin{array}{lcl} \frac{4.104 \text{ mol C}}{1.368 \text{ mol N}} = \frac{3.002 \text{ mol C}}{1 \text{ mol N}} & & \frac{9.653 \text{ mol H}}{1.368 \text{ mol N}} = \frac{7.056 \text{ mol H}}{1 \text{ mol N}} \\ \frac{1.368 \text{ mol N}}{1.368 \text{ mol N}} = \frac{1.000 \text{ mol N}}{1 \text{ mol N}} & & \frac{1.368 \text{ mol O}}{1.368 \text{ mol N}} = \frac{1.000 \text{ mol O}}{1 \text{ mol N}} \end{array}$$

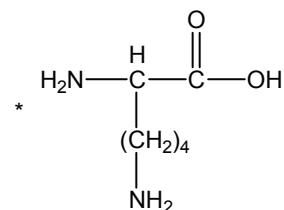
The C:H:N:O ratio is 3:7:1:1, so the simplest formula is $\text{C}_3\text{H}_7\text{NO}$.

b) The molar mass of lysine is $146.18 \text{ g}\cdot\text{mol}^{-1}$, what is its molecular formula?

The molar mass of an empirical unit of lysine is: $3(12.011) \text{ g}\cdot\text{mol}^{-1} \text{ C} + 7(1.008) \text{ g}\cdot\text{mol}^{-1} \text{ H} + 14.007 \text{ g}\cdot\text{mol}^{-1} \text{ N} + 15.999 \text{ g}\cdot\text{mol}^{-1} \text{ O} = 73.090 \text{ g}\cdot\text{mol}^{-1}$, so n is determined to be

$$n = \frac{M_m(\text{lysine})}{M_m(\text{C}_3\text{H}_7\text{NO})} = \frac{146.18 \text{ g}\cdot\text{mol}^{-1}}{73.090 \text{ g}\cdot\text{mol}^{-1}} = 2.000$$

The molecular formula of lysine is $(\text{C}_3\text{H}_7\text{NO})_2$. However, the molecular formula is written as $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$ because $(\text{C}_3\text{H}_7\text{NO})_2$ incorrectly implies that lysine is composed of two identical $\text{C}_3\text{H}_7\text{NO}$ units.*



Lysine is an amino acid with a molecular formula of $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$.

Example 1.10

a) What is the empirical formula of ascorbic acid (vitamin C) if combustion of a 0.579-g sample of ascorbic acid produced 0.868 g CO_2 and 0.237 g H_2O .

Ascorbic acid contains only C, H, and O atoms. Combustion converts all of the carbon into CO_2 and all of the hydrogen into H_2O , so the number of moles of carbon and hydrogen in the sample is determined as follows:

$$0.868 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 0.0197 \text{ mol C}$$

$$0.237 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 0.0263 \text{ mol H}$$

Oxygen is added in the combustion reaction, so the amount in the sample cannot be determined from the amounts of CO_2 and H_2O . Instead, we must determine the mass of oxygen by difference. Thus, we convert the moles of carbon and hydrogen into grams.†

$$0.0197 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.237 \text{ g C}$$

$$0.0263 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.0265 \text{ g H}$$

Then we use the total mass of the sample and the masses of the elements to get the mass of oxygen by difference.

$$\text{mass O} = 0.579 \text{ g ascorbic acid} - 0.237 \text{ g C} - 0.0265 \text{ g H} = 0.316 \text{ g O}$$

† We convert to masses only because we need to know how much oxygen the sample contains. If the sample did not contain oxygen, we would simply determine the mol H/mol C ratio from the moles determined above to get the empirical formula.

Determine the number of moles of oxygen in the sample

$$0.316 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0197 \text{ mol O}$$

The number of moles of C and O are the same, so their subscripts are the same. To find the ratio of C or O to H, divide the number of moles of H by the number of moles of C.

$$\frac{0.0263 \text{ mol H}}{0.0197 \text{ mol C}} = \frac{1.33 \text{ mol H}}{1 \text{ mol C}}$$

Multiplication of the numerator and denominator by 3 to eliminate the decimal yields a 4:3 ratio, and the empirical formula is $\text{C}_3\text{H}_4\text{O}_3$.

b) What is its molecular formula if its molar mass is $176 \text{ g}\cdot\text{mol}^{-1}$?

The molar mass of the empirical unit is $3(12.01) + 4(1.01) + 3(16.00) = 88.1 \text{ g}\cdot\text{mol}^{-1}$. Division of the molar mass of the compound by the molar mass of the empirical unit yields the number of empirical units in the molecular formula. $176/88 = 2$, so the molecular formula is $\text{C}_6\text{H}_8\text{O}_6$. Again, the formula would not be written as $(\text{C}_3\text{H}_4\text{O}_3)_2$ because there are not two identical and identifiable $\text{C}_3\text{H}_4\text{O}_3$ units in the molecule.*

1.3 SUBSTANCE OR COMPOSITION STOICHIOMETRY

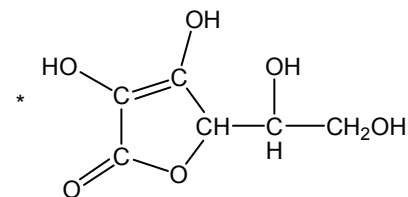
Stoichiometry problems involve the conversion of an amount of one substance (the given substance) into a comparable amount of another substance (the substance that is sought). This is done by converting the given amount to moles and then multiplying by the mole ratio that relates the sought and given substances.

$$\text{moles given} \times \frac{\text{moles sought}}{\text{moles given}} = \text{moles sought} \quad \text{Eq. 1.3}$$

The mole ratio is called the **stoichiometric factor, link, or ratio**. In substance or composition stoichiometry, the ratio is obtained from the subscripts in the chemical formula of the compound. The stoichiometric factors that can be obtained from the formula Fe_2O_3 are

$$\frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} \quad \frac{3 \text{ mol O}}{1 \text{ mol Fe}_2\text{O}_3} \quad \frac{2 \text{ mol Fe}}{3 \text{ mol O}}$$

Note that the reciprocals of the above are also stoichiometric factors. As demonstrated in Example 1.11, the amount of one element that is combined with a known amount of another can be determined by using Equation 1.3 and molar masses.



Ascorbic acid (vitamin C) has a molecular formula of $\text{C}_6\text{H}_8\text{O}_6$.

PRACTICE EXAMPLE 1.7

- a) What is the simplest formula of a hydrocarbon if a 0.250-g sample produces 0.784 g of CO_2 and 0.321 g of H_2O upon complete combustion?**

The sample contains

_____ mol H

_____ mol C

The simplest whole number mole ratio is

mol H/mol C =

The empirical formula is _____

- b) What is the molecular formula of the compound if its molar mass is 84.16 g/mol ?**

The number of empirical units in molecular formula

$n =$

The molecular formula is _____

Example 1.11

What is the mass of chlorine in a sample of CCl₄ that contains 4.72 g of carbon?

Convert the given mass of carbon into moles, then use stoichiometric ratio to convert moles of carbon to moles of chlorine. Finally, use the molar mass of chlorine to calculate the mass of Cl. The factor-label method can be used to establish the order of each operation: start with the given quantity and string the factors so that the denominator of each has the same unit as the previous numerator.

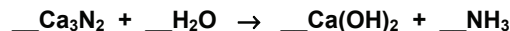
$$4.72 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \frac{4 \text{ mol Cl}}{1 \text{ mol C}} \times \frac{35.5 \text{ g Cl}}{1 \text{ mol Cl}} = 55.9 \text{ g Cl}$$

Example 1.11 is a typical stoichiometry problem. First, the mass of the given substance is converted into moles by dividing by its molar mass. Next, the moles of the given substance are multiplied by the stoichiometric factor to obtain the moles of the desired substance. In a composition stoichiometry problem, the stoichiometric factor is the ratio of the subscripts in the formula. Finally, the number of moles of the desired substance is converted to mass by multiplying by its molar mass. The process for determining the mass of reactant or product in a reaction is identical except that the stoichiometric ratio is obtained from a balanced equation, the topic of Section 1.4.

1.4 BALANCING CHEMICAL EQUATIONS

A chemical equation reads like a sentence, where the formulas of the reactants and the products are the words that are read from left to right. Thus, the *reactants* (substances present before reaction) are on the left while the *products* (substances present after reaction) appear on the right. A chemical equation expresses the *relative* amounts and the identities of the substances involved in chemical and physical changes.

Neither the number nor the identity of the atoms involved in a chemical reaction changes. Consequently, chemical equations are balanced to assure that the number of atoms of each kind is the same on both sides. A procedure that can be used to balance many chemical equations is demonstrated by balancing the following chemical equation:



Step 1. Identify a starting substance.

Start with the substance on either side of the equation that has the greatest number of atoms or the largest subscripts. In this case, both Ca₃N₂ and Ca(OH)₂ contain five atoms, but we start with Ca₃N₂ because its subscripts are larger.

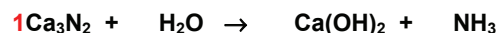
PRACTICE EXAMPLE 1.8

What mass of barium is in a sample of Ba₃(PO₄)₂ that contains 4.00 g of phosphorus?

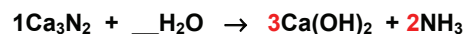
mass = _____ g Ba

Step 2. Identify a coefficient for the starting substance.

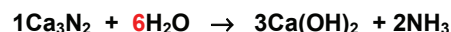
A coefficient of 1 (one) is used as the starting coefficient unless there is an obvious reason to choose a different number.

**Step 3. Determine which atoms have been fixed in Step 2. Then balance those atoms by placing coefficients on the other side of the equation.**

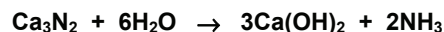
A coefficient of 1 for Ca_3N_2 sets the number of calcium and nitrogen atoms on the reactant (left) side at three and two, respectively, so the coefficients of $\text{Ca}(\text{OH})_2$ and NH_3 must be three and two, respectively.

**Step 4. Balance those atoms that have been fixed in Step 3, by placing coefficients on the side of the equation opposite to the side worked on in Step 3.**

The number of hydrogen atoms and oxygen atoms were both fixed on the product side in Step 3. The 12 hydrogen atoms and 6 oxygen atoms are balanced by fixing the coefficient of water at 6.



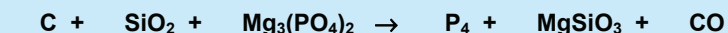
The equation is now balanced because there are 3Ca, 2N, 12H, and 6O on each side. Coefficients of one are not usually included, so the reaction would be written as



In a more complicated reaction, the above process, moving back and forth between the left and right sides of the reaction, is continued until all of the atoms are balanced.

Example 1.12

Balance the following chemical equation, which is the reaction for the commercial production of phosphorus:



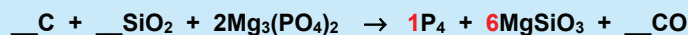
Step 1. We choose $\text{Mg}_3(\text{PO}_4)_2$ as the starting substance because it contains the greatest number of atoms.

Step 2. Note that a coefficient of one for $\text{Mg}_3(\text{PO}_4)_2$ produces only two P atoms, while a minimum of four are needed to balance the right side. Consequently, we use two as our starting coefficient.



Step 3. Our starting coefficient has fixed the number of magnesium atoms at six and the number of phosphorus atoms at four. However, it did not fix the number of oxygen atoms

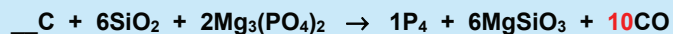
because we do not yet know the coefficient of SiO_2 . Balancing the magnesium and phosphorus atoms on the product side of the reaction, we obtain



Step 4. The coefficient of MgSiO_3 fixes the number of silicon atoms at six. The oxygen atoms are not fixed because we do not yet know the coefficient of CO . Balancing the silicon atoms on the reactant side, we obtain



Step 5. The number of oxygen atoms has now been fixed at 28 on the reactant side (16 in $2\text{Mg}_3(\text{PO}_4)_2$ and 12 in 6SiO_2). There are already 18 oxygen atoms on the product side (6MgSiO_3), so only ten must be balanced with CO .



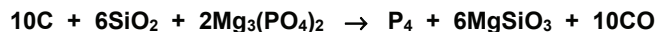
Step 6. Balance the carbon atoms to obtain the final balanced equation.



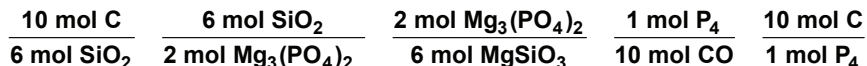
The procedure presented above can be used to balance most chemical reactions. However, there are some redox reactions that cannot be balanced by inspection. The methods used to balance redox equations are presented in Appendix F.

1.5 REACTION STOICHIOMETRY

In reaction stoichiometry, the amount of one substance that reacts with, is produced by, or is required to produce a given amount of another substance is determined. The problems are done in a manner that is identical to the method shown for composition stoichiometry problems (Example 1.11) except for the nature of the stoichiometric ratio. In reaction stoichiometry, the stoichiometric ratios are derived from the coefficients in the balanced equation. For example, consider the reaction that was balanced in Example 1.12.



Some of the stoichiometric ratios that can be derived from this reaction are

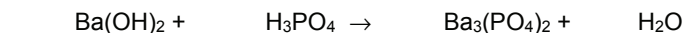


The stoichiometric ratio converts the number of moles of a given substance (denominator) into the equivalent number of moles of a desired substance (numerator).

The number of moles of substance can be given directly, but it is more often given by its mass if it is a solid, its pressure, volume and temperature if it is a gas, or by its volume and molarity if it is a solute. We consider only the first two types of calculations in this chapter and postpone examples using molarity until Chapter 2. However, once the moles

PRACTICE EXAMPLE 1.9

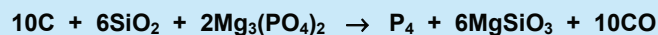
Balance the following chemical equation for the precipitation of barium phosphate.



of the given substance have been determined, they are multiplied by the appropriate stoichiometric ratio regardless of how they were determined. Example 1.13 illustrates the procedure.

Example 1.13

All of the following problems are based on the reaction balanced in Example 1.12:



- a) What minimum mass of SiO_2 ($M_m = 60.1 \text{ g}\cdot\text{mol}^{-1}$) would be required to react with 5.00 g of carbon?

Carbon is the *given* substance and silicon dioxide is the *desired* substance.

$$5.00 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} \times \frac{6 \text{ mol SiO}_2}{10 \text{ mol C}} \times \frac{60.1 \text{ g SiO}_2}{1 \text{ mol SiO}_2} = 15.0 \text{ g SiO}_2$$

- b) What minimum mass of magnesium phosphate ($M_m = 263 \text{ g}\cdot\text{mol}^{-1}$) would be required to produce 12.0 g of phosphorus ($M_m = 124 \text{ g}\cdot\text{mol}^{-1}$)?

Phosphorus is the *given* substance and magnesium phosphate is the *desired* substance.

$$12.0 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{124 \text{ g P}_4} \times \frac{2 \text{ mol Mg}_3(\text{PO}_4)_2}{1 \text{ mol P}_4} \times \frac{263 \text{ g Mg}_3(\text{PO}_4)_2}{\text{mol Mg}_3(\text{PO}_4)_2} = 50.9 \text{ g Mg}_3(\text{PO}_4)_2$$

- c) What volume (in L) of carbon monoxide measured at 1.00 atm and 20. °C* would result if 15.0 g of carbon reacted?

Carbon is the *given* substance and carbon monoxide is the *desired* substance. In this example, we will have to use the ideal gas law ($PV = nRT$) to convert from moles of CO into liters of CO. We begin by calculating the number of moles of CO that should form.

$$15.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \frac{10 \text{ mol CO}}{10 \text{ mol C}} = 1.25 \text{ mol CO}$$

We can now solve the ideal gas law (Eq. 1.1) for the volume. Remember that the temperature must be expressed on the Kelvin scale.

$$T = 20. \text{ }^\circ\text{C} + 273 = 293 \text{ K}$$

$$V = \frac{nRT}{P} = \frac{(1.25 \text{ mol CO})(0.0821 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(293 \text{ K})}{1.00 \text{ atm}} = 30.1 \text{ L}$$

* The decimal after the 20 is used to indicate that the zero is significant. See Appendix A for more on significant figures.

LIMITING REACTANTS

In the calculations done to this point, the mass of only one substance has been given but normally several reactants are added, and it is seldom that they are all added in the exact mass ratios required for complete reaction. In this case, one reactant limits the amount of reaction because when any *one reactant* is completely consumed, the reaction stops. The reactant that is completely consumed is called the **limiting reactant**. Any reactants that are not completely consumed are excess reactants. For example, your automobile engine is powered by the combustion of gasoline, so it requires both gasoline and oxygen to run. There is an excess of oxygen in the air, so the gasoline is the limiting reactant. When the limiting reactant is consumed the reaction stops; *i.e.*, you run out of gas even though there is plenty of oxygen still available.

All calculations pertaining to a reaction are based on its limiting reactant, so if the amount of more than one reactant is given, we must determine which is the limiting amount before we can do anything else. To determine the limiting reactant, we must determine which reactant (A) produces the least amount of product (B), which would be done as follows:

$$\text{mol A} \times \frac{\text{coefficient of B}}{\text{coefficient of A}} = \text{mol B}$$

The reactant that can produce the smallest number of moles of B is the limiting reactant. Thus, one way to determine the limiting reactant is to determine how much of one product each of the reactants can produce. However, we can shorten the step a little by rearranging the above to the form given in Equation 1.4

$$\left(\frac{\text{mol A}}{\text{coefficient of A}} \right) \times \text{coefficient of B} = \text{mol B} \quad \text{Eq. 1.4}$$

The amount of any product B that can be produced by a given number of moles of any reactant can be obtained by multiplying the (mole/coefficient) ratio of that reactant by the coefficient of the product in the balanced chemical equation. We conclude that the smallest number of moles of product is obtained from the reactant that has the smallest (mole/coefficient) ratio. Thus, the limiting reactant can be found by doing the following:

Divide the number of moles of each reactant present by its coefficient in the balanced equation. The reactant with the smallest ratio is the limiting reactant.

PRACTICE EXAMPLE 1.10

- a) What mass of $\text{Ba}_3(\text{PO}_4)_2$ can be produced from 16.8 g of $\text{Ba}(\text{OH})_2$? See Practice Example 1.9 for the chemical equation.

$$\text{molar mass of Ba}_3(\text{PO}_4)_2 = \text{_____ g.mol}^{-1}$$

$$\text{molar mass of Ba(OH)}_2 = \text{_____ g.mol}^{-1}$$

$$\text{moles of Ba(OH)}_2 \text{ reacting} = \text{_____ mol}$$

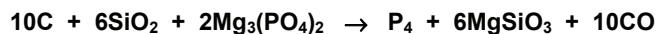
$$\text{moles of Ba}_3(\text{PO}_4)_2 \text{ produced} = \text{_____ mol}$$

$$\text{mass of Ba}_3(\text{PO}_4)_2 \text{ produced} = \text{_____ g}$$

- b) What mass of H_3PO_4 is required to react with 16.8 g of $\text{Ba}(\text{OH})_2$?

$$\text{mass} = \text{_____ g H}_3\text{PO}_4$$

As an example, let us determine the limiting reactant when 10.0 g of C, 20.0 g of SiO₂, and 40.0 g of Mg₃(PO₄)₂ are used in the following reaction:



First, determine the number of moles of each reactant.

$$10.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} = 0.833 \text{ mol C}$$

$$20.0 \text{ g SiO}_2 \times \frac{1 \text{ mol SiO}_2}{60.1 \text{ g SiO}_2} = 0.333 \text{ mol SiO}_2$$

$$40.0 \text{ g Mg}_3(\text{PO}_4)_2 \times \frac{1 \text{ mol Mg}_3(\text{PO}_4)_2}{263 \text{ g Mg}_3(\text{PO}_4)_2} = 0.152 \text{ mol Mg}_3(\text{PO}_4)_2$$

Next, use the moles determined above and the coefficients in the chemical equation to determine the mole/coefficient ratios of the reactants.

$$\frac{0.833 \text{ mol C}}{10 \text{ mol C}} = 0.0833 \quad \frac{0.333 \text{ mol SiO}_2}{6 \text{ mol SiO}_2} = 0.0555 \quad \frac{0.152 \text{ mol Mg}_3(\text{PO}_4)_2}{2 \text{ mol Mg}_3(\text{PO}_4)_2} = 0.0760$$

SiO₂ has the smallest ratio, so it is the limiting reactant. There are two important points to make here.

1. The reactant with the smallest mass is not necessarily the limiting reactant. In this example, carbon had the smallest mass yet it has the largest mole/coefficient ratio.
2. The reactant present in the smallest number of moles is not necessarily the limiting reactant. The number of moles of magnesium phosphate present was less than half the number of moles of silicon dioxide, but SiO₂ has the smaller mole/coefficient ratio because the reaction requires three moles of SiO₂ for every one of Mg₃(PO₄)₂.

The limiting reactant in this problem is SiO₂, so all further calculations are based on the fact that all 0.333 mol SiO₂ reacts. For example, the amount of MgSiO₃ (M_m = 100. g·mol⁻¹) that forms is determined to be

$$0.333 \text{ mol SiO}_2 \times \frac{6 \text{ mol MgSiO}_3}{6 \text{ mol SiO}_2} \times \frac{100 \text{ g MgSiO}_3}{1 \text{ mol MgSiO}_3} = 33.3 \text{ g MgSiO}_3$$

To determine how much excess carbon there is, determine how much carbon reacts and subtract that from the amount in the original mixture.

$$0.333 \text{ mol SiO}_2 \times \frac{10 \text{ mol C}}{6 \text{ mol SiO}_2} \times \frac{12.0 \text{ g C}}{1 \text{ mol C}} = 6.7 \text{ g C react}$$

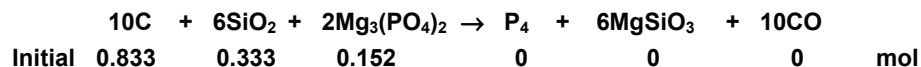
$$10.0 \text{ g C initially} - 6.7 \text{ g C reacts} = 3.3 \text{ g C in excess}$$

Therefore, 3.3 g C would remain unreacted in the reaction vessel because all of the SiO₂ had been consumed.

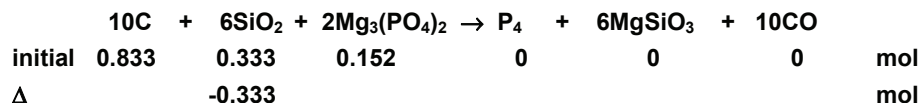
The amount of product formed depends not only on the amounts of reactants but also on the equilibrium constant for the reaction. Indeed, the problem we have just completed can be considered to be an equilibrium problem in which the equilibrium constant is very large, *i.e.*, one in which essentially all of the limiting reactant is consumed.

We now set up the same problem in a way that leads directly to the amounts of both reactants and products present at the end of the reaction. We begin by writing the reaction and labeling three lines under it. The number of moles of each substance present before the reaction begins is placed into the first line, which is referred to as the **initial** line. The number of moles of each substance that reacts or forms during the reaction is placed on the following line. This line represents the changes in the amounts that result from the reaction, so it is designated as the Δ (delta) line. The Δ line is the only line to which stoichiometry is applied, and the numbers in it are based on the limiting reactant. The sum of the initial line and Δ line is placed on the **final** line, which represents the composition of the mixture after the reaction is complete. Together, the three lines constitute the **reaction table** for the reaction.

The reaction table is started by placing the initial number of moles of each substance directly under the substance in the chemical equation.



The Δ line represents the amounts that react or form during the reaction, so all values on it depend upon the limiting reactant. SiO_2 is the limiting reactant, so the entire amount of SiO_2 is entered on the Δ line. Materials that react disappear during reaction, so the amount on the Δ line under reacting substances is negative.



The Δ line is completed by applying the various stoichiometric ratios to the amount of the limiting reactant that is consumed. The reactants are all disappearing and the products are all forming. Consequently, all entries on the reactant side are negative and all entries on the product side are positive. For example, consider the entry under $\text{Mg}_3(\text{PO}_4)_2$.

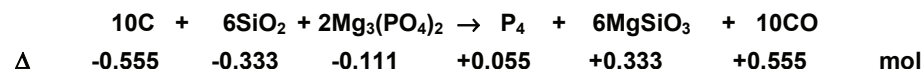
$$0.333 \text{ mol SiO}_2 \times \frac{2 \text{ mol Mg}_3(\text{PO}_4)_2}{6 \text{ mol SiO}_2} = 0.111 \text{ mol Mg}_3(\text{PO}_4)_2 \text{ reacts}$$

$\text{Mg}_3(\text{PO}_4)_2$ reacts, so its entry on the Δ line is -0.111 mol. MgSiO_3 forms as the SiO_2

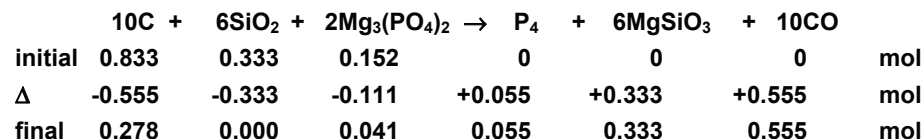
disappears, so its entry would be determined as

$$0.333 \text{ mol SiO}_2 \times \frac{6 \text{ mol MgSiO}_3}{6 \text{ mol SiO}_2} = 0.333 \text{ mol MgSiO}_3 \text{ forms}$$

MgSiO₃ is produced, so its entry on the Δ line is +0.333 mol. Thus, the Δ line is



To determine the final composition, the initial and Δ lines are added as shown below.



Once the reaction table is complete, we know the amounts of all of the substances present at the end of the reaction. If all of the SiO₂ reacts (zero on the final line), then there would be 0.278 mol C and 0.041 mol of Mg₃(PO₄)₂ remaining while 0.055 mol P₄, 0.333 mol MgSiO₃ and 0.555 mol CO would form.

The calculated amount of product is called the **theoretical yield** because it is the amount that should be produced. However, the **actual yield** of most reactions is less than the theoretical yield for several reasons:

- Many reactions reach an equilibrium in which a measurable amount of the limiting reactant remains.
- Purification results in some loss of product.
- Reactants are often involved in more than one type of reaction, and these *side* reactions can result in several different products, which reduces the quantity of the desired product.

In order to represent the efficiency of a procedure, chemists normally report the percent yield for the product. The **percent yield** is defined as the fraction of the theoretical yield that is actually obtained expressed as a percent.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Eq. 1.5

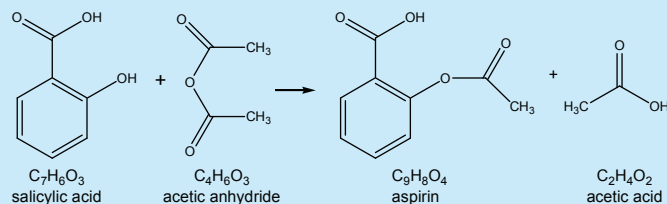
PRACTICE EXAMPLE 1.11

What is the percent yield in the precipitation described in Practice Example 1.10a if 18.3 g of Ba₃(PO₄)₂ is isolated?

$$\% \text{ yield} = \quad \quad \quad \times 100\% = \quad \quad \quad \%$$

Example 1.14

- a) Aspirin (acetylsalicylic acid, $C_9H_8O_4$) is prepared from the following reaction of salicylic acid ($C_7H_6O_3$) and acetic anhydride ($C_4H_6O_3$). The other product is acetic acid ($C_2H_4O_2$).



If 20.00 g of salicylic acid and 17.00 g of acetic anhydride react, what would be the composition of the reaction mixture at completion if the reaction occurs with a 100% yield?

First, convert the initial masses into moles by dividing by the molar masses.

$$\frac{20.00 \text{ g } C_7H_6O_3}{138.12 \text{ g} \cdot \text{mol}^{-1}} = 0.1448 \text{ mol } C_7H_6O_3 \text{ \& } \frac{17.00 \text{ g } C_4H_6O_3}{102.09 \text{ g} \cdot \text{mol}^{-1}} = 0.1665 \text{ mol } C_4H_6O_3$$

There are no products initially, so the initial line of the reaction table is

	$C_7H_6O_3$	+	$C_4H_6O_3$	\rightarrow	$C_9H_8O_4$	+	$C_2H_4O_2$	
initial	0.1448		0.1665		0		0	mol

Both coefficients are one, so $C_7H_6O_3$ has the smallest mole/coefficient ratio and is the limiting reactant. All entries on the Δ line are based on the assumption that 0.1448 mol $C_7H_6O_3$ react. The remainder of the reaction table is

	$C_7H_6O_3$	+	$C_4H_6O_3$	\rightarrow	$C_9H_8O_4$	+	$C_2H_4O_2$	
initial	0.1448		0.1665		0		0	mol
Δ	-0.1448		-0.1448		+0.1448		+0.1448	mol
final	0		0.0217		0.1448		0.1448	mol

Multiplying each of the moles by the molar mass, we obtain the following masses,

$$(0.0217 \text{ mol } C_4H_6O_3)(102.09 \text{ g} \cdot \text{mol}^{-1}) = 2.22 \text{ g } C_4H_6O_3 \text{ do not react}$$

$$(0.1448 \text{ mol } C_9H_8O_4)(180.16 \text{ g} \cdot \text{mol}^{-1}) = 26.09 \text{ g } C_9H_8O_4 \text{ form}$$

$$(0.1448 \text{ mol } C_2H_4O_2)(60.05 \text{ g} \cdot \text{mol}^{-1}) = 8.70 \text{ g } C_2H_4O_2 \text{ form.}$$

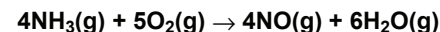
As a check, we note that the total mass at the completion of the reaction is the same as the total starting mass.

- b) If the reaction produces an 85.3% yield, what mass of aspirin would be isolated?

The theoretical yield of aspirin is 26.09 g, but only 85.3% of this mass was isolated. Therefore, the actual yield is $(0.853)(26.09) = 22.3 \text{ g}$.

PRACTICE EXAMPLE 1.12

The following is the first step of Ostwald process, a three-step reaction sequence that converts NH_3 into HNO_3 :



10.00 g each of NH_3 and O_2 are allowed to react. Assume complete reaction and determine the contents of the flask after the reaction is complete.

$$\text{moles of } NH_3 = \text{_____ mol}$$

$$\text{moles of } O_2 = \text{_____ mol}$$

Determine how much NO could be produced by each

$$\text{from } NH_3 = \text{_____ mol NO}$$

$$\text{from } O_2 = \text{_____ mol NO}$$

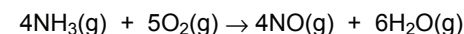
limiting reactant is _____

$$= \text{_____ mol } H_2O \text{ form}$$

$$= \text{_____ mol } O_2 \text{ react}$$

$$= \text{_____ mol } NH_3 \text{ react}$$

Reaction table



initial

Δ

final

Final contents of flask

$$\text{_____ g } NH_3$$

$$\text{_____ g } O_2$$

$$\text{_____ g NO}$$

$$\text{_____ g } H_2O$$

1.6 CHAPTER SUMMARY AND OBJECTIVES

The *elemental composition* of a compound is usually defined in terms of the mass ratios of its elements, while the *chemical formula* expresses the mole ratios of its elements. It is important to be able to convert between these two methods of describing composition. The elemental composition of a substance can be determined from its chemical formula by dividing the mass contribution of each atom in the formula by the molar mass of the substance. The resulting fraction is usually expressed as a percent. The formula of a compound can be determined by performing the reverse procedure - the mass or percent of each element present is converted to moles. The moles of the elements are then expressed as simple whole number ratios to obtain the formula. The resulting formula is the *simplest* or *empirical formula* because it expresses only the simplest ratios of the atoms present. The *molecular formula* can be determined from the empirical formula and the molar mass.

The number of moles of a given species can be converted to the chemically equivalent amount of a sought species with the *stoichiometric ratio*. Stoichiometric ratios are derived from the subscripts in a formula or the coefficients in a balanced equation. Many chemical equations can be balanced by inspection by fixing the coefficient of the substance with the greatest number of atoms and then balancing each atom. The stoichiometric amount of any desired substance can then be determined from an amount of any given substance as follows:

$$\text{moles given} \times \frac{\text{moles sought}}{\text{moles given}} = \text{moles sought}$$

The amount of the *limiting reactant* in a chemical reaction dictates the amount of product that can form. Other reactants in the reaction are said to be in *excess*. The limiting reactant is that reactant with the smallest mole/coefficient ratio. All further calculations are based on the limiting reactant. The amounts of all products and excess reactants that remain after the complete reaction of the limiting reactant are most easily calculated by using a reaction table. The initial line consists of the number of moles of each substance present at the start of the reaction, the Δ line is composed of the number of moles of each substance that is produced or consumed, and the final line is the sum of the initial and Δ lines. The *percent yield* of a reaction is defined as the ratio of the *actual yield* to the *theoretical yield* expressed as a percent.

ANSWERS TO PRACTICE EXAMPLES

- 1.1 a) $88.0 \text{ g}\cdot\text{mol}^{-1}$; 253 g
 b) $60.0 \text{ g}\cdot\text{mol}^{-1}$; 2.69 g
 c) $174 \text{ g}\cdot\text{mol}^{-1}$; 0.107 mol
 d) $98.0 \text{ g}\cdot\text{mol}^{-1}$; 2.72 mmol
- 1.2 a) 1.60×10^{21} molecules of CO_2
 b) 6.69×10^{16} molecules of N_2O_5
- 1.3 1.433 atm; 348 K; 0.0251 mol; 1.10 g
- 1.4 69.07% Ba, 14.8% Co, 16.1% O
- 1.5 206.98 g/mol, 19.36% Ca, 34.26% Cl, 46.38% O
- 1.6 41.1% H_2O , 2.24 mmol CoSO_4 , 13.4 mmol H_2O ,
 $x = 6$, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$
- 1.7 0.0178 mol C; 0.0356 mol H; 2 mol H/1 mol C;
 empirical: CH_2 ; molecular: C_6H_{12}
- 1.8 26.6 g Ba
- 1.9 $3\text{Ba}(\text{OH})_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{Ba}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}$
- 1.10 $\text{Ba}(\text{OH})_2$: 171.31 g/mol; 0.0981 mol react
 $\text{Ba}_3(\text{PO}_4)_2$: 601.93 g/mol; 19.7 g produced
 H_3PO_4 : 97.99 g/mol; 6.4 g required
- 1.11 92.9%
- 1.12 limiting reactant: O_2
 Final contents: 5.74 g NH_3 ; no O_2 ; 7.50 g NO ;
 6.76 g H_2O

After studying the material presented in this chapter and the relevant appendices, you should be able to:

1. convert between mass and moles (Section 1.1);
2. convert between mass or moles and numbers of atoms or molecules (Section 1.1);
3. determine moles of gas from P, V, and T (Section 1.1);
4. determine percent composition of a compound (Section 1.2);
5. determine the simplest formula of a compound from the relative amounts of each of the elements present in a sample (Section 1.2);
6. determine a molecular formula from the simplest formula and molar mass (Section 1.2);
7. use the chemical formula of a compound to determine the mass of one element that is combined with a given mass of another element in the compound (Section 1.3);
8. balance a chemical equation by inspection (Section 1.4);
9. write the stoichiometric ratio relating two substances involved in a chemical reaction (Section 1.5);
10. convert the mass of any substance in a reaction into the stoichiometrically equivalent mass of any other substance involved in the reaction (Section 1.5);
11. determine the limiting reactant of a reaction (Section 1.5);
12. combine the ideal gas law and stoichiometry to determine the amount of gas formed or consumed in a reaction (Section 1.5);
13. determine the complete composition of a reaction mixture after the reaction is complete (Section 1.5); and
14. determine the percent yield given the actual yield of a reaction or use the percent yield to determine the actual yield (Section 1.5).

1.7 EXERCISES

MASS AND MOLES

- Determine molar masses for the following:
a) $C_{22}H_{10}O_2$ b) $Ca(NO_3)_2$ c) P_2O_5 d) $Al_2(CO_3)_3$
- Determine molar masses for the following:
a) $Mg(C_2H_3O_2)_2$ b) $PtCl_2(NH_3)_2$ c) $(NH_4)_2SO_4$ d) $C_{18}H_{27}NO_3$
- Determine mass of each of the following:
a) 0.694 mol $C_{22}H_{10}O_2$ b) 2.84 mol $Ca(NO_3)_2$
c) 0.00652 mol P_2O_5 d) 8.44 mol $Al_2(CO_3)_3$
- Determine mass of each of the following:
a) 1.86 mol $Mg(C_2H_3O_2)_2$ b) 0.0356 mol $PtCl_2(NH_3)_2$
c) 18.4 mol $(NH_4)_2SO_4$ d) 0.488 mol $C_{18}H_{27}NO_3$
- Determine mass of each of the following:
a) 2.24×10^{20} molecules of CO_2 b) 2.24×10^{24} molecules of H_2
c) 12 C atoms d) 8.66×10^{18} Pt atoms
- Determine mass of each of the following:
a) 2.00 million ammonia molecules b) 1 water molecule
c) 6.02×10^{23} PF_3 molecules d) 4.02×10^{28} C atoms
- How many moles of people were on the earth when the population was 6.3 billion (6.3×10^9) people?
- It is estimated that there are over 400 billion (4×10^{11}) stars in the Milky Way galaxy. How many moles of stars is that?
- A bottle contains 12.6 g of $(NH_4)_3PO_4$.
a) How many moles of $(NH_4)_3PO_4$ does it contain?
b) How many oxygen atoms does it contain?
c) What mass of nitrogen atoms does it contain?
d) How many moles of H does it contain?
- A heaping teaspoon of sugar ($C_{12}H_{22}O_{11}$) has a mass of 8.0 g.
a) How many moles of sugar does it contain?
b) How many oxygen atoms does it contain?
c) What mass of carbon atoms does it contain?
d) How many moles of H does it contain?

SUBSTANCE STOICHIOMETRY

- What is the simplest formula of each of the following compounds?
a) $C_{22}H_{10}O_2$ b) C_3H_6O c) C_6H_6 d) $C_3H_6O_3$
- What is the simplest formula of each of the following compounds?
a) $Na_2S_2O_8$ b) B_2H_6 c) $N_3S_3Cl_3$ d) $Na_2Re_2Cl_8$
- What is the elemental composition of each of the molecules in Exercise 11? Express your answer as mass percents?
- What is the elemental composition of each of the compounds in Exercise 12, Express your answer as mass percents?
- How many moles of magnesium are present in a sample of each of the following that contains 3.0 moles of oxygen atoms?
a) $MgSO_4$ b) $MgSO_3$ c) $Mg_3(PO_4)_2$ d) $Mg(ClO_3)_2$
- How many grams of nitrogen atoms are present in a sample of each of the following that contains 1.25 moles of oxygen atoms?
a) NO b) N_2O_3 c) N_2O_5 d) NH_4NO_3
- What mass of Al is in a sample of $Al_2(SO_4)_3$ that contains 3.2 grams of S?
- What mass of potassium is in a sample of potassium carbonate (K_2CO_3) that contains 12.0 g of oxygen?
- Caffeine has the molecular formula $C_8H_{10}N_4O_2$. What mass of caffeine contains 5.0 mg of nitrogen?
- Nicotine is $C_{10}H_{14}N_2$. What mass of nicotine contains 1.5 moles of nitrogen?
- What mass of Na_2CO_3 contains 2.1×10^{22} oxygen atoms?
- What mass of oxygen is in a sample of Na_3PO_4 that contains 3.5×10^{21} sodium atoms?
- What mass of KCl was in a solution if all of the chloride in the solution was precipitated as 1.68 g of $PbCl_2$?
- What mass of Ag_2SO_4 was in a solution if all of the silver was precipitated as 375 mg of Ag_3PO_4 ?

DETERMINING CHEMICAL FORMULAS

- What is the simplest formula of a compound in which 0.362 mol X is combined with 1.267 mol Y? How many moles of X are present in 6.336 mol of the compound?

26. What is the simplest formula of a compound if a sample of the compound contains 0.236 mol X, 0.354 mol Y, and 0.590 mol Z? How many moles of Z would be in a sample that contained 0.668 mol X?
27. What is the simplest formula of a hydrocarbon that is 81.71 % C?
28. What is the empirical formula of a rhenium oxide that is 76.88% Re?
29. Ibuprofen (*Advil*[®] or *Motrin*[®]) is an anti-inflammatory agent that is 75.69% C, 8.80% H and 15.51% O. What is the simplest formula of ibuprofen?
30. Acetaminophen (*Tylenol*[®]) is an analgesic (pain killer) and an antipyretic (fever reducer) that is 63.56% C, 6.00% H, 9.27% N and 21.17% O. What is the empirical formula of acetaminophen?
31. The sugar arabinose, found in ripe fruits, is 40.00% C, 6.71% H and 53.29% O and has a molar mass of 150. g·mol⁻¹. What is the molecular formula for this compound?
32. What is the simplest formula of a compound that is 39.81% Cu, 20.09% S, and 40.10% O?
33. Burning 1.346 g of chromium in air results in 1.967 g of an oxide. What is the simplest formula of the oxide of chromium?
34. A 3.228-g sample of platinum oxide is found to contain 2.773 g of platinum. What is the empirical formula of the oxide?
35. A 2.500-g sample of an oxide of lead produces 0.376 g of water when reduced with hydrogen. What is the simplest formula of this lead oxide? Assume all of the oxygen in the oxide is converted to water.
36. What is the empirical formula of a hydrocarbon if combustion of 1.00 mg produces 3.14 mg of CO₂ and 1.29 mg of H₂O? If its molar mass is around 40 g·mol⁻¹, what is its molecular formula?
37. A 0.540-g sample of Anavenol, a compound containing C, H, and O that is used as an anesthetic in veterinary surgeries is analyzed by combustion. What is its empirical formula if the combustion produces 0.310 g of H₂O and 1.515 g of CO₂? If its molar mass is 188.22 g·mol⁻¹, what is the molecular formula for Anavenol?
38. Antifreeze (ethylene glycol) contains carbon, hydrogen and oxygen. Combustion of 50.00 mg of ethylene glycol yields 43.55 mg of H₂O and 70.97 mg of CO₂. What is the empirical formula of ethylene glycol? The molar mass of ethylene glycol is 62.0 g·mol⁻¹, what is its molecular formula?
39. KClO_x produces KCl and O₂ upon heating. What is the value of x if a 22.6-g sample produces 7.07 L of O₂ at 0.956 atm and 25 °C?
40. A 0.525-g sample of an iron carbonyl, Fe(CO)_x, is heated to remove all of the CO. The CO gas is collected in a 0.500-L flask at 26 °C. What is the empirical formula of the carbonyl if the pressure of the CO is 499 torr?
41. Heating a 27.7-mg sample of MnSO₄·xH₂O results in 15.1 mg of anhydrous MnSO₄. What is value of x?
42. What mass of MgCO₃ contains the same mass of oxygen as does 376 mg of MgCr₂O₇?

BALANCING EQUATIONS

43. Balance the equations by inspection:
- $\text{Al}_2\text{S}_3 + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{H}_2\text{S}$
 - $\text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$
 - $\text{Al} + \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2$
 - $\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 - $\text{KOH} + \text{H}_3\text{PO}_4 \rightarrow \text{K}_3\text{PO}_4 + \text{H}_2\text{O}$
 - $\text{Ag} + \text{H}_2\text{S} + \text{O}_2 \rightarrow \text{Ag}_2\text{S} + \text{H}_2\text{O}$
44. Balance the equations by inspection:
- $\text{P}_4\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3$
 - $\text{NaOH} + \text{NCl}_3 \rightarrow \text{HOCl} + \text{N}_2 + \text{NaCl}$
 - $\text{H}_3\text{PO}_4 + \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{HPO}_4$
 - $\text{Bi}_2\text{O}_3 + \text{C} \rightarrow \text{Bi} + \text{CO}$
 - $\text{HCl} + \text{MnO}_2 \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2$
 - $\text{Ca}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{NH}_3$
45. Balance the equations by inspection:
- $\text{FeS}_2 + \text{O}_2 \rightarrow \text{FeSO}_4 + \text{SO}_3$
 - $\text{S}_2\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2 + \text{HCl} + \text{S}$
 - $\text{V}_2\text{O}_5 + \text{C} + \text{Cl}_2 \rightarrow \text{VOCl}_3 + \text{COCl}_2$
 - $\text{NH}_3 + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
 - $\text{BF}_3 + \text{NaBH}_4 \rightarrow \text{NaBF}_4 + \text{B}_2\text{H}_6$
 - $\text{Al}_4\text{C}_3 + \text{HCl} \rightarrow \text{CH}_4 + \text{AlCl}_3$
46. Balance the equations by inspection:
- $\text{Cr}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Cr}(\text{OH})_3$
 - $\text{PCl}_5 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + \text{HCl}$
 - $\text{Mg}_2\text{C} + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{CH}_4$

- d) $\text{BF}_3 + \text{NaH} \rightarrow \text{NaBF}_4 + \text{B}_2\text{H}_6$
 e) $\text{SiO}_2 + \text{Ca}_3(\text{PO}_4)_2 \rightarrow \text{P}_2\text{O}_5 + \text{CaSiO}_3$
 f) $\text{Ba}_3\text{P}_2 + \text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_2 + \text{PH}_3$

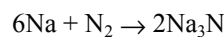
REACTION STOICHIOMETRY

47. A mixture of 3.0 mol of CS_2 and 2.0 mol of O_2 reacts according to the equation: $\text{CS}_2 + 3\text{O}_2 \rightarrow \text{CO}_2 + 2\text{SO}_2$
- What is the limiting reactant?
 - How many moles of SO_2 are produced?
 - How many moles of which reactant are unreacted?
 - If 72 g of SO_2 are actually isolated, what is the percent yield?
48. An excess of O_2 is added to 4.86 g of Fe and allowed to react. What is the percent yield if 6.76 g of Fe_2O_3 are isolated?
49. Consider the reaction $\text{N}_2\text{O}_4 + 2\text{N}_2\text{H}_4 \rightarrow 3\text{N}_2 + 4\text{H}_2\text{O}$
- How many moles of N_2 are formed by reaction of 5.0 g of N_2H_4 ?
 - What mass of N_2O_4 would be required for Part a?
 - What is the percent yield if 4.8 g of water is produced?
50. What mass of oxygen is required for the complete combustion of 7.65 g of propane (C_3H_8) to produce CO_2 and H_2O ?
51. What mass of HCl is produced by the reaction of 23.6 g of PCl_3 and water? The other product is H_3PO_3 .
52. How many liters of O_2 gas measured at 835 torr and 250. °C are formed by the decomposition of 236 g of KClO_3 ? The other product is KCl.
53. Consider the following reaction that occurs at 1000. °C:
- $$4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g}).$$
- A mixture of 2.65 atm of NH_3 and 3.80 atm of O_2 reacts to completion (no limiting reactant remains). Determine the pressures of all gases remaining when the reaction is complete. (Hint: because the reaction is carried out at constant temperature and volume, the pressures are proportional to the number of moles.) What is the total pressure inside the vessel at the beginning and end of the reaction? Why are the total pressures different?
54. Construct the reaction table for the reaction of 2.0 mol Fe_3O_4 and 6.0 mol H_2 to produce elemental iron and water. How many moles of iron form and how many moles of the excess reactant are unused?
55. Construct the reaction table for the reaction of 7.0 g of N_2 and 6.0 g of H_2 to form ammonia. What mass of ammonia forms and what mass of the excess reactant remains after reaction?
56. Consider the reaction between H_3PO_4 and NH_3 to produce $(\text{NH}_4)_2\text{HPO}_4$.
- What mass of ammonia would have to be added to 20.0 g of phosphoric acid if a 10% excess of ammonia is required?
 - What is the theoretical yield of ammonium hydrogenphosphate under the conditions given in Part a?
57. Construct a reaction table for the reaction of 0.200 mol of iron(III) oxide and 0.270 mol of carbon to produce elemental iron and carbon monoxide. What is the percent yield if 19.4 g of iron are produced?
58. Construct the reaction table for the reaction of 1.46 mol Al and 3.61 mol HCl to produce AlCl_3 and H_2 .
59. The most common acid in acid rain is sulfuric acid (H_2SO_4). When sulfuric acid reacts with sodium hydroxide (NaOH), sodium sulfate is formed along with water. The reaction is
- $$\text{H}_2\text{SO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
- A 10.0-L sample of rain water was treated with a 0.200-g tablet of NaOH. When the reaction was complete, 0.0018 moles of NaOH remained unreacted.
- What was the limiting reagent in this reaction?
 - How many grams of H_2SO_4 were in the 10.0-L sample of rain water?
 - How many moles of H_2SO_4 were present in each liter of rain water?
60. One step in the production of margarine from vegetable oils is the hydrogenation of the double bonds. In an experiment to test a new hydrogenation catalyst, a 2.36-g sample of linolenic acid, $\text{C}_{18}\text{H}_{30}\text{O}_2$, was placed in a sealed flask along with a catalyst. Then 1.50 L of H_2 gas (measured at 1.0 atm pressure and 25 °C) was bubbled into the mixture. The completely hydrogenated product of the reaction is stearic acid, $\text{C}_{18}\text{H}_{36}\text{O}_2$.
- Write the balanced reaction for the complete hydrogenation of linolenic acid to stearic acid.
 - What was the limiting reagent in this reaction mixture?
 - After the reaction, 2.06 g of stearic acid was recovered. What was the percent yield of the reaction?

61. It is desired to remove the lead from a solution containing 6.41 g of $\text{Pb}(\text{NO}_3)_2$ by adding KCl and precipitating PbCl_2 . What mass of KCl should be added if a 15.0% excess is required? What mass of PbCl_2 would form? The other product is KNO_3
62. Consider the reaction $5\text{P}_4\text{O}_6 + 8\text{I}_2 \rightarrow 4\text{P}_2\text{I}_4 + 3\text{P}_4\text{O}_{10}$.
- How many grams of I_2 should be added to 4.50 g of P_4O_6 in order to have a 10.0% excess?
 - What is the theoretical yield of P_4O_{10} ?
 - How many grams of P_2I_4 would be isolated if actual yield is 83.7%?
63. Consider the reaction of 27.8 g of FeS_2 with O_2 to produce Fe_2O_3 and SO_2 .
- What mass of oxygen would be required for a 20% excess?
 - What is the theoretical yield of Fe_2O_3 ?
 - What mass of SO_2 would form if the actual yield is 94.2%?
64. Construct the reaction table for the reaction of 19.25 g V_2O_5 , 12.80 g C, and 30.66 g of Cl_2 to produce COCl_2 and VOCl_3 .
- MISCELLANEOUS PROBLEMS**
65. What element forms an oxide X_2O_3 that is 88.39% X by mass?
66. The compound X_2Y_3 is found to be 75.0% X. What is the ratio of the molar masses?
67. Aspartame, $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_5$, is the active ingredient in *Nutrasweet*[®].
- What is the elemental composition of aspartame expressed as percents?
 - What is the mass of a sample of aspartame that contains 2.6 mg of carbon?
 - A tablet of *Equal*[®] has a mass of 0.088 g and the “sweetness of one teaspoon of sugar.” A teaspoon of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) has a mass of 4.8 g. Assume the *Equal*[®] tablet is 30% aspartame and estimate the relative “sweetness” of a molecule of aspartame and a molecule of sugar.
68. Methyl alcohol, CH_3OH , is a clean-burning fuel. It can be synthesized from $\text{CO}(\text{g})$ and $\text{H}_2(\text{g})$, obtained from coal and water, respectively. If you start with 12.0 g of H_2 and 74.5 g of CO , what mass of methyl alcohol can be obtained theoretically?
69. Cisplatin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, a compound used in chemotherapy for cancer patients, is synthesized by reacting ammonia with tetrachloroplatinate, K_2PtCl_4 , to form the product and potassium chloride.
- What is the maximum mass of cisplatin that can be formed by the reaction of 60.0 g of K_2PtCl_4 and 40.0 g of ammonia?
 - What is the percent yield if 35.0 g are obtained experimentally?
70. Excess hydrochloric acid reacts with 0.750 g of aluminum to form aluminum chloride and hydrogen gas.
- How many liters of gas would be collected at 0 °C and 1.00 atm?
 - How many grams of aluminum chloride would be formed?
71. A 5.00-g mixture of NaCl and BaCl_2 is dissolved in water, then a solution of Na_2SO_4 is added to precipitate BaSO_4 . What percent of the mass of the original mixture is due to BaCl_2 if the mass of BaSO_4 is 2.78 g?
72. What is the molar mass of hemoglobin if its four iron atoms are 0.33% of its mass?
73. Chlorophyll contains 2.72% magnesium. If there is one magnesium per chlorophyll molecule, what is the molar mass of chlorophyll?
74. Vitamin B_1 is 16.6% N by mass and contains 4 nitrogen atoms. What is its molar mass?
75. A mixture of NH_4Cl and NH_4Br is 27.4% NH_4Cl by mass. What mass of the mixture contains 0.200 mol NH_4^{1+} ions?
76. A mixture is 18.6% NaCl , 22.1% CaCl_2 , and 59.3% NaBr .
- What mass of the mixture contains 0.500 mole of chloride ions?
 - How many moles of sodium ions are present in 23.8 g of the mixture?
77. A metal (M) reacts with acid according to the following equation:
- $$2\text{M} + 6\text{HCl} \rightarrow 2\text{MCl}_3 + 3\text{H}_2.$$
- What is the metal if reaction of 0.305 g of M produces 161 mL of H_2 measured at 23 °C and 753 torr?
78. What is the identity of a metal (M) if 4.26 g of MCl_2 produces 11.00 g of AgCl upon reaction with excess AgNO_3 ? The balanced equation is
- $$\text{MCl}_2 + 2\text{AgNO}_3 \rightarrow 2\text{AgCl} + \text{M}(\text{NO}_3)_2.$$
79. Epsom salts have the formula $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$. What is the value of x if drying a 3.268-g sample results in 1.596 g of anhydrous MgSO_4 ?

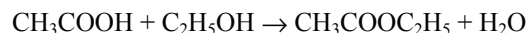
80. The inflation in automotive air bags is the result of the rapid decomposition of sodium azide (a compound that contains only Na and N) to metallic sodium and nitrogen gas. What is the simplest formula of sodium azide if the decomposition 8.462 g of sodium azide produces 4.8052 L of N_2 measured at 23.6 °C and 752 torr?

81. Sodium nitride is prepared by reacting nitrogen gas with sodium.



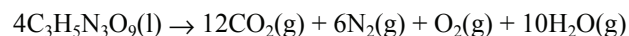
How many liters of nitrogen measured at 765 torr and 27.5 °C are required for the complete reaction of 7.22 g of Na? How many grams of sodium nitride would be produced?

82. Ethyl acetate, the active ingredient in nail polish remover, is an ester prepared by the reaction of acetic acid (vinegar) and ethanol (grain alcohol):



The amount of ester is increases by removing water (LeChatelier's principle). In a given reaction, 7.65 g CH_3COOH and 9.88 g CH_3OH are mixed and allowed to react. What is the percent yield if 8.96 g of the ester is isolated?

83. How many carbon atoms are present in a 2.0 carat diamond? 1 carat = 0.200 g.
84. The explosion of nitroglycerin is due to the following exothermic reaction:



What volume of gas is produced at 1.00 atm and 200 °C by the reaction of 2.35 g of nitroglycerin?

85. A mixture of KBr and MgBr_2 , which has a mass of 6.81 g, is dissolved in water. An excess of AgNO_3 is then added to the solution to precipitate all of the bromide as AgBr. What are the mass percents of K and Mg in the mixture if 13.24 g of AgBr precipitate?
86. 3.62 g of a Group 1A metal reacts with an excess of oxygen to produce 4.36 g of its oxide. What is the metal?

87. Vanillin, which is the primary ingredient in vanilla flavoring, contains C, H, and O. What is its empirical formula if the combustion of 0.6427 g of vanillin produces 0.3043 g of H_2O and 1.487 g of CO_2 ? If the molar mass of vanillin is found to be near 150 $\text{g}\cdot\text{mol}^{-1}$, what is its molecular formula?
88. 6.824 g of an iron chloride is dissolved in acid. Lead nitrate is then added to the solution to precipitate all of the chloride as PbCl_2 . What is the empirical formula of an iron chloride if 17.568 g of PbCl_2 is produced?
89. Analysis of a compound shows that it is 17.71% N, 40.55% S, and 40.46% O by mass. It is also known to contain H. What is its empirical formula? If its molar mass is close to 240 $\text{g}\cdot\text{mol}^{-1}$, what is its molecular formula?
90. It is desired to prepare exactly 5.0 g of PbCl_2 by the reaction of KCl and $\text{Pb}(\text{NO}_3)_2$. How many grams of each starting material should be used if a 10% excess of KCl is recommended and a 78% yield can be expected?
91. Construct a reaction table for the reaction of 12.0 g N_2 with 21.0 g O_2 to produce N_2O_5 . How many g of N_2O_5 are produced, and what is the mass of the excess reactant if the reaction goes 100% to completion?

CHAPTER 2

Solutions

2.0 Introduction

2.1 Concentration Units

2.2 Changing Concentration Units

2.3 Dilutions

2.4 Determining Concentrations

2.5 Colligative Properties

2.6 Colloids

2.7 Chapter Summary and Objectives

2.8 Exercises

2.0 INTRODUCTION

A **solution** is a homogeneous mixture of at least two chemical substances: a single **solvent** in which at least one **solute** has been dissolved. The maximum concentration that a solute can attain in a given solvent at some temperature is known as the **solubility** of the solute in that solvent at that temperature. A solution is said to be **saturated** if the concentration of the solute equals its solubility.

There are no restrictions on the nature of the solvent, but the solute particles are considered to be dispersed in the solvent, so if there is a liquid present, it is considered the solvent. If more than one liquid is present, the liquid present in the greater amount is considered to be the solvent, but water is such a common solvent that it is usually considered to be the solvent if it is present in a substantial amount even if it is not present in the greatest amount.

Solutions in which water is the solvent are called **aqueous** solutions. Solutes in aqueous solutions can be classified as either electrolytes or nonelectrolytes. **Electrolytes** are species that produce ions in solution. They can be further classified as weak or strong. Substances that exist in water exclusively as ions are called *strong electrolytes*. Ionic substances and strong acids and bases are strong electrolytes. *Weak electrolytes* exist *predominantly* in the molecular form in water, but a small fraction also exists as ions. Weak acids and weak bases are weak electrolytes. **Nonelectrolytes** produce no ions when they dissolve in water. Sugars and alcohols are examples of nonelectrolytes.

While liquid solutions are most common, solutions of solids and gases are also abundant. For example, our atmosphere is a solution of gases (N_2 , O_2 , Ar, and others). Stainless steel is a solid solution of iron with small amounts of manganese and carbon dissolved in it. The resulting solid solution is stronger and more corrosion resistant than the iron (solvent) alone. Solder is a solid solution of tin and lead with a melting point that is much lower than that of either metal.

THE OBJECTIVES OF THIS CHAPTER ARE TO SHOW YOU HOW TO:

- determine and express the concentration of a solution in common concentration units;
- calculate the amount of solute present in a given volume of sample of known concentration;
- prepare solutions of known concentrations;
- convert from one unit of concentration into another;
- calculate a solution's vapor pressure, boiling and freezing points, and osmotic pressure; and
- apply volume and concentration data to solution stoichiometry.

2.1 CONCENTRATION UNITS

The **concentration** of a solute, which is the ratio of amount of solute to the amount of solvent or solution, dictates many of the properties of a solution because it is a measure of the relative number of solvent-solvent and solvent-solute interactions. If the ratio is small, the solution is said to be *dilute*, and its properties are similar to those of the solvent because the solution is dominated by solvent-solvent interactions. However, if the ratio is high, the solution is *concentrated*, and the properties can deviate substantially from those of the solvent as the number of solute-solvent interactions becomes important. Dilute solutions may have properties similar to those of the solvent, but the solutes can still have profound effects. Consider that drinking water can provide protection from tooth decay with fluoride ion concentrations of only a few ions for every million water molecules, and it can retard the mental development of children with lead ion concentrations of only a few lead ions in a billion water molecules.

There are many ways of expressing concentration because there are many ways in which it can be determined and used. In this section, we define some of the most common concentration units and give examples of their use.

MOLARITY (M)

As shown in Equation 2.1, **molarity** is the number of moles of solute per liter of solution.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{n}{V} = \frac{\text{mmoles of solute}}{\text{mL of solution}} \quad \text{Eq. 2.1}$$

The concentration unit is pronounced ‘molar’ and abbreviated as M. The molar concentration of a substance is normally abbreviated by writing the formula of the substance in square brackets. Thus, $[\text{Cl}^{1-}] = 1 \text{ M}$ is read “the chloride ion concentration is one molar.” *Molarity is the best unit for concentration for solutions that will be used to deliver a required number of moles of solute.*

It is often more convenient to express the volume in milliliters rather than liters. If the volume in Equation 2.1 is expressed in milliliters, then n in Equation 2.1 must be in millimoles (mmol).^{*} This is equivalent to multiplying the numerator and the denominator by 1000, an operation that does not change the value of the ratio. Thus, *the molarity of a solution is also the number of millimoles of solute per milliliter of solution.*

^{*} The same logic applies to μL and nL , in which the numerator would be in μmol and nmol , respectively.

Example 2.1

a) How would 500.* mL of 0.0865 M K_2HPO_4 solution be prepared?

Solve Equation 2.1 for n , the number of moles of K_2HPO_4 .

$$n = M \times V = (0.0865 \text{ mol} \cdot \text{L}^{-1})(0.500 \text{ L}) = 0.04325 \text{ mol } \text{K}_2\text{HPO}_4$$

An extra significant digit is carried in the above. 500. mL of solution must contain 0.04325 mol K_2HPO_4 . The mass of K_2HPO_4 is determined from the number of moles and its molar mass, $174.17 \text{ g} \cdot \text{mol}^{-1}$.

$$0.04325 \text{ mol } \text{K}_2\text{HPO}_4 \times \frac{174.17 \text{ g } \text{K}_2\text{HPO}_4}{1 \text{ mol } \text{K}_2\text{HPO}_4} = 7.53 \text{ g } \text{K}_2\text{HPO}_4$$

The solution would be made by dissolving 7.53 g K_2HPO_4 in about 300 mL of water in a 500 mL volumetric flask such as is represented in Figure 2.1. Water would then be added to bring the solution to the fill line. Finally, the stopper would be placed in the flask and the flask inverted several times to thoroughly mix the solution.

b) What volume of 0.0865 M K_2HPO_4 contains 3.50 mmol of K^{1+} ions?

Equation 2.1 is rearranged to solve for the volume in terms of the number of moles of

solute and the molarity: $V = \frac{n}{M}$

where n and M are the number of moles (mmoles in this example) and concentration of the *same substance*. Thus, the given number of mmol of K^{1+} ions cannot be divided by the molarity of the K_2HPO_4 . Either the mmol of K^{1+} ions must be converted to the corresponding number of mmol of K_2HPO_4 or the concentration of K_2HPO_4 must be converted into the molarity of K^{1+} ions. We use the latter method here, but either method will work. The chemical equation for dissolving K_2HPO_4 in water is $\text{K}_2\text{HPO}_4(\text{s}) \rightarrow 2\text{K}^{1+} + \text{HPO}_4^{2-}$, so the concentration of K^{1+} ions in 0.0865 M K_2HPO_4 is

$$[\text{K}^{1+}] = \frac{0.0865 \text{ mmol } \text{K}_2\text{HPO}_4}{1 \text{ mL solution}} \times \frac{2 \text{ mmol } \text{K}^{1+}}{1 \text{ mmol } \text{K}_2\text{HPO}_4} = 0.173 \text{ M}$$

The required volume is

$$3.50 \text{ mmol } \text{K}^{1+} \times \frac{1 \text{ mL sol'n}}{0.173 \text{ mmol } \text{K}^{1+}} = 20.2 \text{ mL solution}$$

Thus, 20.2 mL of the solution contains 3.50 mmol of potassium ion.

^{*} The decimal is used to indicate that the zeroes are significant. See Appendix A for more on significant figures.

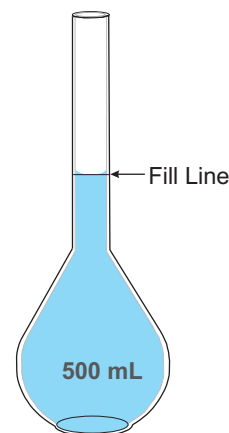


Figure 2.1 Volumetric Flask

The figure shows a 500 mL volumetric flask, so a solution that fills the flask to the fill line would have a volume of 500.0 mL.

Example 2.2

Ocean water is typically 0.53 M in chloride ion. What is the mass of the chloride ion contained in 300. mL of ocean water?

The problem gives the concentration of solute and the volume of solution and asks for the mass of solute. We again use Equation 2.1 to solve for the number of moles of chloride ion. 300 mL = 0.300 L, so

$$n = M \times V = (0.53 \text{ mol}\cdot\text{L}^{-1})(0.300 \text{ L}) = 0.16 \text{ mol Cl}^{-1}$$

Moles of chloride ions are converted to mass by multiplying by the molar mass.

$$(0.16 \text{ mol Cl}^{-1})(35.5 \text{ g}\cdot\text{mol}^{-1}) = 5.6 \text{ g Cl}^{-1}$$

Solutions with concentrations near one molar are considered to be fairly concentrated. While such concentrated solutions are often used in the laboratory, many applications such as biological signaling require only very dilute solutions. Consider that when the concentration of testosterone in the blood reaches 10^{-8} M, it initiates puberty in human males. The following prefixes are typically used to avoid the exponent in expressions for concentration:

- mM (millimolar) $\equiv 10^{-3} \text{ M} = 1 \text{ mmol}\cdot\text{L}^{-1}$
- μM (micromolar) $\equiv 10^{-6} \text{ M} = 1 \mu\text{mol}\cdot\text{L}^{-1}$
- nM (nanomolar) $\equiv 10^{-9} \text{ M} = 1 \text{ nmol}\cdot\text{L}^{-1}$

Thus, male puberty is initiated when the concentration of testosterone reaches 10 nM. Note that a prefix to a concentration unit indicates a change in the numerator of the ratio of Equation 2.1 but not in the denominator.

Example 2.3

What total mass of testosterone ($\text{C}_{19}\text{H}_{28}\text{O}_2$, $M_m = 288 \text{ g}\cdot\text{mol}^{-1}$) is in 5.7 liters of blood that has a testosterone concentration of 12.5 nM?

Use Equation 2.1 and the fact that 12.5 nM = $12.5 \times 10^{-9} \text{ M}$ to solve for the moles of testosterone,

$$n = M \times V = (12.5 \times 10^{-9} \text{ mol}\cdot\text{L}^{-1})(5.7 \text{ L}) = 7.1 \times 10^{-8} \text{ mol}$$

which is converted to mass by multiplying by the molar mass.

$$(7.1 \times 10^{-8} \text{ mol})(288 \text{ g}\cdot\text{mol}^{-1}) = 2.1 \times 10^{-5} \text{ g} = 21 \mu\text{g testosterone}$$

The number of moles determined in the first step, not the rounded answer, was used to avoid rounding errors (see Appendix A.4).

PRACTICE EXAMPLE 2.1

What are the ion concentrations in a solution prepared by dissolving 2.10 g of $\text{Ba}(\text{OH})_2$ in enough water to make 250. mL of solution?

$$M_m \text{ of } \text{Ba}(\text{OH})_2 = \text{_____} \text{ g}\cdot\text{mol}^{-1}$$

$$n = \text{_____} \text{ mol Ba}(\text{OH})_2$$

Molarity of $\text{Ba}(\text{OH})_2$

$$M = \text{_____} = \text{_____} \text{ M}$$

Ion concentrations

$$[\text{OH}^{-1}] = \text{_____} \times \text{_____} = \text{_____} \text{ M}$$

$$[\text{Ba}^{2+}] = \text{_____} \times \text{_____} = \text{_____} \text{ M}$$

How many millimoles of hydroxide ion are contained in 175 mL of this solution?

How many milliliters of solution would be required to deliver 3.00 mmol of barium ion?

Example 2.4

Express the following concentrations in units such that the magnitude lies between 1 and 100. See the list of SI prefixes inside the back cover.

- a) The concentration of CN^{1-} ion in 0.1 M HCN is 2.0×10^{-5} M

The closest SI prefix that is smaller than 10^{-5} is micro. Multiplying the given cyanide ion concentration by 10^6 , we obtain $(2.0 \times 10^{-5} \text{ M})(10^6) = 20 \text{ } \mu\text{M}$.

- b) The concentration of Ag^{1+} ion in a saturated AgI solution is 9.1×10^{-9} M

10^{-9} is nano, so the concentration is 9.1 nM.

- c) The hydronium ion concentration is 0.026 M

Multiply by 1000 to convert to the milli prefix. $[\text{H}_3\text{O}^{1+}] = (0.026 \text{ M})(10^3) = 26 \text{ mM}$

MOLE FRACTION (X) AND MASS FRACTION

As expressed in Equation 2.2, the **mole fraction** of substance A (X_A) in a mixture is the number of moles A divided by the total number of moles in the mixture.

$$X_A = \frac{\text{moles of A in mixture}}{\text{total number of moles in mixture}} \quad \text{Eq. 2.2}$$

The sum of the mole fractions of all of the components in the mixture is 1, so $X_{\text{solvent}} = 1 - X_{\text{solute}}$ in solutions containing a single solute. Although it can be used for liquid solutions, *mole fractions are most commonly used for solutions in which the solvent is not clearly defined*. Thus, the concentrations of solutions of gases (Practice Example 2.2) and solids (Example 2.5) are frequently given as mole fractions. Mole fractions are moles divided by moles, so they are unitless. However, when they are used in problems, the substances are specified, which makes the numerator and denominator different. Therefore, units of (moles of A)/(total moles) can be used for X_A .

The mass fraction of a solute is the mass of the solute divided by the mass of the mixture.

$$\text{mass fraction of A} = \frac{\text{mass of A in mixture}}{\text{total mass of mixture}} \quad \text{Eq. 2.3}$$

Mass fractions are also unitless, but units of (mass of A)/(total mass of mixture) can be used in problems. Thus, a mass fraction of 0.2 for A can be expressed as (0.2 g A)/(1 g mixture). Like molarity, mass fractions can be very small, but prefixes cannot be used for mass fractions because they are unitless. However, mass fractions are the number of parts of solute present in 1 part (the whole) of mixture, so the number used for the mass fraction

can be increased by simply considering the number of parts present in a larger number of parts of mixture. Consequently, small mass fractions are frequently given as the number of parts of solute in some larger number of parts of solvent. This is done by multiplying the mass fraction by the number of parts required to produce a convenient number. The common multipliers, their names, and the units that can be used in problems are given in Table 2.1. For example, a mass fraction can be expressed as a mass percent by multiplying it by 100, so a mass fraction of 0.2 is a mass percent of 20%, which can be expressed as (20 g A)/(100 g mixture). A mass fraction of 2.3×10^{-5} would ordinarily be expressed as 23 ppm to avoid the negative exponent.

Percents in solutions prepared from two or more liquids can also refer to volume percent, which is (volume of A)/(total volume of solution) \times 100, rather than a mass percent. To distinguish between the mass and volume percents, the percent can be followed by (w/w) for solute weight/solution weight or (v/v) for solute volume/solution volume.

Table 2.1 Common multipliers used with mass fractions

Name	Multiplier	Useful Units
mass fraction	1	g A/g mixture
mass percent	100	g A/100 g mixture
parts per million (ppm)	10^6	g A/ 10^6 g mixture
parts per billion (ppb)	10^9	g A/ 10^9 g mixture

Example 2.5

Matrix alloy is 40.8% Bi, 24.5% Pb, 13.1% Sb, and 21.6% Sn by mass. What are the mole fractions of the elements in the alloy?

First determine the number of moles of each element present in a sample. We are given the mass percents, so we assume a 100.0-g sample, in which case the mass percents equal the masses.

$$40.8 \text{ g Bi} \times \frac{1 \text{ mol Bi}}{209.0 \text{ g Bi}} = 0.195 \text{ mol Bi}; \quad 24.5 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 0.118 \text{ mol Pb};$$

$$13.1 \text{ g Sb} \times \frac{1 \text{ mol Sb}}{121.8 \text{ g Sb}} = 0.108 \text{ mol Sb}; \quad 21.6 \text{ g Sn} \times \frac{1 \text{ mol Sn}}{118.7 \text{ g Sn}} = 0.182 \text{ mol Sn}$$

Determine the total number of moles in 100 g of matrix alloy.

$$0.195 \text{ mol Bi} + 0.118 \text{ mol Pb} + 0.108 \text{ mol Sb} + 0.182 \text{ mol Sn} = 0.603 \text{ mol}$$

Calculate the mole fractions with Equation 2.2.

$$X_{\text{Bi}} = \frac{0.195 \text{ mol Bi}}{0.603 \text{ mol}} = 0.323; \quad X_{\text{Pb}} = \frac{0.118 \text{ mol Pb}}{0.603 \text{ mol}} = 0.196;$$

$$X_{\text{Sb}} = \frac{0.108 \text{ mol Sb}}{0.603 \text{ mol}} = 0.179; \quad X_{\text{Sn}} = \frac{0.182 \text{ mol Sn}}{0.603 \text{ mol}} = 0.302$$

Note that the sum of all mole fractions in the mixture is 1.00. Multiplication of each mole fraction by 100 produces the mole percent. Thus, 32.3% of the atoms in the matrix alloy are bismuth atoms.

PRACTICE EXAMPLE 2.2

A mixture contains 6.0 g N₂, 16.0 g O₂ and 2.0 g He. What is the mole fraction of each gas?

$$\text{Moles of N}_2 = \quad = \quad \text{mol}$$

$$\text{Moles of O}_2 = \quad = \quad \text{mol}$$

$$\text{Moles of He} = \quad = \quad \text{mol}$$

$$\text{Total} = \quad \text{mol}$$

$$X_{\text{N}_2} = \quad = \quad$$

$$X_{\text{O}_2} = \quad = \quad$$

$$X_{\text{He}} = \quad = \quad$$

EXAMPLE 2.6

What is the mass fraction of sulfate ion in drinking water if 1.24 kg of the water is found to contain 68.6 mg of sulfate ion?

The mass fraction of sulfate ion equals its mass divided by the mass of the solution. However, both masses must have the same units, so we convert both to grams.

$$\text{mass fraction} = \frac{0.0686 \text{ g SO}_4^{2-}}{1.24 \times 10^3 \text{ g solution}} = 5.53 \times 10^{-5}$$

The fraction is the number of parts of sulfate per one part of solution. In order to arrive at a more convenient number, we multiply the answer by 10^6 to obtain ppm.

$$(5.53 \times 10^{-5})(10^6 \text{ ppm}) = 55.3 \text{ ppm}$$

Example 2.7

A 0.40-L glass of very sweet iced tea contains 3 heaping teaspoons of sugar. Assume that the density of the iced tea is $\sim 1.0 \text{ g}\cdot\text{mL}^{-1}$ and that a heaping teaspoon of sugar has a mass of 8.0 g to calculate the mass percent of sugar in the tea.

First calculate the mass of three teaspoons of sugar.

$$(3 \text{ tsp})(8.0 \text{ g}\cdot\text{tsp}^{-1}) = 24 \text{ g sugar}$$

Next, use the density of the iced tea to calculate the mass of the solution.

$$(4.0 \times 10^2 \text{ mL})(1.0 \text{ g}\cdot\text{mL}^{-1}) = 4.0 \times 10^2 \text{ g solution}$$

The composition of the solution expressed as a mass percent is

$$\frac{24 \text{ g sugar}}{4.0 \times 10^2 \text{ g sol'n}} \times 100\% = 6.0\% \text{ sugar}$$

Example 2.8

What mass of NaF must be dissolved in 250. mL of deionized water to produce a solution that is 7.0 ppm F^{1-} , a level comparable to that in drinking water?

The density of water is $1.0 \text{ g}\cdot\text{mL}^{-1}$, so the mass of water is 250. g. At such dilute levels, the mass of NaF is negligible compared to the mass of the solvent, so the mass of the solution is also 250. g. Use the concentration of 7.0 ppm to convert the total mass to the mass of fluoride ion present.

$$250. \text{ g sol'n} \times \frac{7.0 \text{ g F}^{1-}}{10^6 \text{ g sol'n}} \times \frac{1000 \text{ mg}}{\text{g}} = 1.75 \text{ mg F}^{1-} \text{ ion}$$

PRACTICE EXAMPLE 2.3

Determine the mass fractions of the solutes in the following solutions. Express each fraction as a mass percent, ppm, or ppb such that your answer is between 1 and 1,000.

a) 1.0 kg of solution contains 200. g of solute.

mass fraction =

answer = _____

b) 3.0 mg of solute is dissolved in 1.0 kg of water

mass fraction =

answer = _____

c) 65 μg of solute is dissolved 2.6 kg of water

mass fraction =

answer = _____

PRACTICE EXAMPLE 2.4

The solubility of AgCN in water at 25°C is $1.1 \times 10^{-8} \text{ M}$. What is the Ag^{1+} ion concentration expressed in ppb in a saturated AgCN solution?

Determine masses present in 1.0 L of solution

Ag^{1+} = _____ g

Solution = _____ g

Then determine their ratio

mass fraction = _____ = _____

mass fraction in ppb = _____

The mass of NaF ($M_m = 42.0 \text{ g}\cdot\text{mol}^{-1}$) is then determined to be

$$1.75 \text{ mg F}^{1-} \text{ ion} \times \frac{1 \text{ mmol F}^{1-}}{19.0 \text{ mg F}^{1-}} \times \frac{1 \text{ mmol NaF}}{1 \text{ mmol F}^{1-}} \times \frac{42.0 \text{ mg NaF}}{\text{mmol NaF}} = 3.9 \text{ mg NaF}$$

MOLALITY (m)

Molality (m) is the number of moles of solute in a kilogram of solvent,

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \quad \text{Eq. 2.4}$$

A solution that has a concentration of 1 m is said to be "one molal". Neither mass nor moles depends upon the temperature, so *molality is temperature independent*. However, the volume of a solution does depend upon the temperature, so the molarity of a solution does depend upon the temperature. Consequently, *molality is commonly used in applications involving changes in temperature*.

Example 2.9

A solution is prepared by mixing 3.75 g of the sugar glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, and 25.0 g of water. What is the molality of the resulting glucose solution?

First, determine the number of moles of glucose and the number of kilograms of water, then use Equation 2.2 to determine the molality of the solution.

$$3.75 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180. \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.0208 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$25.0 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0250 \text{ kg H}_2\text{O}$$

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.0208 \text{ mol C}_6\text{H}_{12}\text{O}_6}{0.0250 \text{ kg H}_2\text{O}} = 0.832 \text{ m}$$

Example 2.10

How many grams of ethanol ($\text{C}_2\text{H}_5\text{OH}$) must be added to 29.3 g of water to prepare a 1.22 m solution?

Rearrange Equation 2.4 to solve for moles of solute (ethanol):

$$\text{moles ethanol} = (\text{molality})(\text{kg water}) = (1.22 \text{ m})(0.0293 \text{ kg}) = 0.0357 \text{ mol ethanol}$$

Multiply moles by molar mass to obtain the mass of ethanol.

$$(0.0357 \text{ mol})(46.07 \text{ g}\cdot\text{mol}^{-1}) = 1.65 \text{ g ethanol}$$

PRACTICE EXAMPLE 2.5

How many grams of water should be added to 23.7 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, $M_m = 62.1 \text{ g}\cdot\text{mol}^{-1}$) to make a solution that is 4.85 m in ethylene glycol?

moles ethylene glycol used = _____ mol

mass of water required = _____ g

2.2 CHANGING CONCENTRATION UNITS

Changing concentration units is a task that must be performed routinely in the chemistry laboratory because concentrations of stock solutions are frequently not the most useful for the experiment in which the solution is to be used. The easiest way to accomplish a conversion is to convert the numerator and denominator independently. The numerator is always moles or mass of solute, so conversion of the given numerator to the desired numerator can be accomplished with the molar mass of the solute. Converting the given denominator into the desired denominator is often more challenging because the denominator can represent either solution or solvent and mass or volume. Examples 2.11 - 2.13 and Practice Example 2.6 demonstrate three of the more common concentration unit conversions.

Example 2.11

Concentrated sulfuric acid is 18.0 M and has a density of 1.839 g·cm⁻³. What percent of the mass of this aqueous solution is due to H₂SO₄?

We are asked to convert molarity to mass percent.

$$\frac{18.0 \text{ mol H}_2\text{SO}_4}{1 \text{ L sol'n}} \Rightarrow \frac{\text{g H}_2\text{SO}_4}{\text{g sol'n}} \times 100\%$$

Once the problem is setup as above, it is much easier to see how to proceed.

1. Convert 18.0 mol H₂SO₄ to grams H₂SO₄ (M_m = 98.1 g·mol⁻¹).

$$18.0 \text{ mol H}_2\text{SO}_4 \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} = 1.766 \times 10^3 \text{ g H}_2\text{SO}_4$$

Note that extra figures have been kept to avoid rounding errors in the answer.

2. Convert 1 liter of solution to grams of solution using the solution density.

$$1000 \text{ mL sol'n} \times \frac{1.839 \text{ g sol'n}}{\text{mL sol'n}} = 1.839 \times 10^3 \text{ g sol'n}$$

3. Take the ratio to obtain the percent by mass, which must be reported to three significant figures because the mass is good to only 3 significant figures.

$$\frac{1.766 \times 10^3 \text{ g H}_2\text{SO}_4}{1.839 \times 10^3 \text{ g sol'n}} \times 100\% = 96.0\%$$

Only 4.0% of the mass is due to water, which is inconsistent with our definition of the solvent as the material present in the greater amount. However, H₂SO₄ is made by dissolving SO₃ in water (SO₃ + H₂O → H₂SO₄). The reaction is extensive and consumes much of the water.

PRACTICE EXAMPLE 2.6

A 30.0% (w/w) solution of sulfuric acid has a density of 1.218 g·mL⁻¹. Recall that w/w is used to indicate that it is a mass (weight) percent.

What is the mole fraction of H₂SO₄?

Masses in a liter of solution:

$$= \text{_____ g sol'n}$$

$$= \text{_____ g H}_2\text{SO}_4$$

$$= \text{_____ g H}_2\text{O}$$

Moles in a liter of solution:

$$= \text{_____ mol H}_2\text{SO}_4$$

$$= \text{_____ mol H}_2\text{O}$$

$$n_{\text{total}} = \text{_____ mol}$$

Mole fractions:

$$X_{\text{H}_2\text{SO}_4} = \text{_____}$$

$$X_{\text{H}_2\text{O}} = \text{_____}$$

What is the molarity of the H₂SO₄?

$$\text{_____ M}$$

What is the molality of the H₂SO₄?

$$\text{_____ m}$$

Example 2.12

What is the molality of the sulfuric acid solution discussed in Example 2.11?

We are asked to convert a molarity (18.0 M) to a molality:

$$\frac{18.0 \text{ mol H}_2\text{SO}_4}{1 \text{ L sol'n}} \Rightarrow \frac{\text{mol H}_2\text{SO}_4}{\text{kg solvent}}$$

The numerators are the same, so we must only convert 1 L of solution into kg of solvent. We know from Example 2.11 that one liter of solution has a mass of 1.839 kg and contains 1.77 kg H₂SO₄ (18.0 mol). We get the solvent mass by difference.

$$\text{solvent mass} = \text{solution mass} - \text{solute mass} = 1.839 - 1.766 = 0.073 \text{ kg}$$

Note that we have again retained an extra significant figure in the mass of H₂SO₄ to minimize rounding errors. The mass of solvent should be reported as 0.07 kg. Thus, the molality, which is good to only one significant figure because the mass of water is good to only one significant figure, is determined to be

$$\frac{18.0 \text{ mol H}_2\text{SO}_4}{0.073 \text{ kg H}_2\text{O}} = 2 \times 10^2 \text{ m}$$

In this example, the molality and molarity are very different. That is not usually the case. The difference in this example arises because the solution is very concentrated. The density of a dilute aqueous solution is ~1 g·mL⁻¹, so the mass of a liter of solution is essentially 1 kg, and the molarity and molality are nearly the same.

Example 2.13

What is the molarity of a 7.0 ppm F¹⁻ ion solution described in Example 2.8?

1) Restate the question in units

(ppm to molarity)

$$\frac{7.0 \text{ g F}^{1-}}{10^6 \text{ g sol'n}} \Rightarrow \frac{\text{mol F}^{1-}}{\text{L sol'n}}$$

2) convert the numerator

(7.0 g F¹⁻ to mol F¹⁻)

$$7.0 \text{ g F}^{1-} \times \frac{1 \text{ mol F}^{1-}}{19.0 \text{ g F}^{1-}} = 0.37 \text{ mol F}^{1-}$$

3) Convert the denominator

(10⁶ g of a dilute solution with a density of 1.0 g·mL⁻¹ to liters of solution.)

$$10^6 \text{ g sol'n} \times \frac{1.0 \text{ mL sol'n}}{1.0 \text{ g sol'n}} \times \frac{1 \text{ L}}{10^3 \text{ mL}} = 10^3 \text{ L}$$

4) Take the appropriate ratio

$$\frac{0.37 \text{ mol F}^{1-}}{1000 \text{ L sol'n}} = 3.7 \times 10^{-4} \text{ M or } 0.37 \text{ mM}$$

2.3 DILUTIONS

When additional solvent is added to a solution, the volume of the solution and the mass of the solvent are increased, *but the amount of solute is unchanged*. In the process, the concentration of the solute is reduced; that is, *the solution is diluted by the addition of solvent*. The key point is that the amount of *solute* is the same in the initial and final solutions, which is expressed quantitatively in Equation 2.5*:

$$C_i V_i = C_f V_f \quad \text{Eq. 2.5}$$

$C_i V_i$, the product of concentration and volume of the initial solution, is the amount of solute in the initial solution, while $C_f V_f$ is the amount of solute in the final solution.* Equation 2.5 can be rearranged to solve for the final concentration as follows:

$$C_f = C_i \times \frac{V_i}{V_f} \quad \text{Eq. 2.6}$$

Equation 2.6* shows that the final concentration equals the initial concentration times the ratio of the initial to final volume, which is unitless and called the **dilution factor**. Dilution factors depend only on the ratio of volumes not on the volumes themselves. Consequently, they are often given in terms of the ratio. For example, diluting 20 mL to 60 mL would be referred to as a 1:3 dilution, and diluting 20 mL to 50 mL would be a 2:5 dilution.

* Equations 2.5 and 2.6 are valid only if the concentration units involve the volume of solution. Thus, they hold for concentrations such as g/mL and molarity, but they cannot be used with molality or percent. However, they can usually be applied to solutions whose concentrations are given in ppm or ppb because the concentrations are generally so low in such solutions that their densities are $1.0 \text{ g}\cdot\text{mL}^{-1}$, which makes the mass of the solution in grams numerically equal to its volume in mL.

Example 2.14

- a) 30.0 mL of concentrated H_2SO_4 (18.0 M) is added slowly[†] to 400 mL of H_2O . After the solution has cooled, its volume is adjusted to 500.0 mL with more water. What is the molarity of the resulting sulfuric acid solution?

Use Equation 2.6 to determine the final concentration.

$$C_f = C_i \times \frac{V_i}{V_f} = 18.0 \text{ M} \times \frac{30.0 \text{ mL}}{500.0 \text{ mL}} = 1.08 \text{ M H}_2\text{SO}_4$$

- b) How would 300. mL of 1.5 M H_2SO_4 be prepared from the concentrated acid?

We are given the final volume and concentration as well as the initial concentration (18.0 M), so we solve Equation 2.5 for the initial volume.

$$V_i = V_f \times \frac{C_f}{C_i} = 300. \text{ mL} \times \frac{1.5 \text{ M}}{18 \text{ M}} = 25 \text{ mL H}_2\text{SO}_4$$

The solution would be prepared by adding 25 mL of the acid to some volume (~200 mL) of water. After the solution has cooled, the volume would be adjusted to 300. mL with H_2O .

[†] Sulfuric acid must be added to water slowly because the dilution is very exothermic, and the acid is much denser than water. If water is added to the more dense acid, the water stays on top and boils, which causes splattering. However, when the acid is added to the water, the acid sinks to the bottom of the solution, which cools the reaction.

Example 2.15

2.00 mL of a 500. ppm Zn^{2+} solution is diluted to a total volume of 1.00 L. What is the final concentration in ppm?

This is a very dilute solution, so the concentration in Equation 2.5 can be expressed with the mass fraction.

$$C_f = \frac{C_i V_i}{V_f} = \frac{(500. \text{ ppm})(2.00 \text{ mL})}{1000 \text{ mL}} = 1.00 \text{ ppm}$$

Frequently, unknown solutions must be diluted to a certain level in order to run an experiment. Since the solution concentration is unknown, the required dilution factor is also unknown. In cases like this, several *successive dilutions* may be required to obtain a solution concentration that is appropriate for the experiment. As shown in Equation 2.7, the concentration of the final solution after a series of successive dilutions is equal to the initial concentration times the product of the dilution factors used in the successive dilutions.

$$C_f = C_i \times \frac{V_1}{V_2} \times \frac{V_3}{V_4} \times \frac{V_5}{V_6} \times \dots \quad \text{Eq. 2.7}$$

In Equation 2.7, V_1 mL of a solution with concentration C_i is diluted to a volume of V_2 mL. V_3 mL of the resulting solution is then diluted to V_4 mL to make a third solution. The process is continued until the desired concentration is made. Example 2.16 and Practice Example 2.7 demonstrate the procedure.

Example 2.16

50.00 mL of an unknown solution A is diluted to 500.00 mL to make solution B. 25.00 mL of solution B is then diluted to 750.00 mL to prepare solution C. 15.00 mL of solution C is diluted to 1.000 L. The concentration of solution C is found to be 1.47 μM . What is the concentration of solution A?

We are asked to determine the initial concentration from the final concentration ($C_c = 1.47 \times 10^{-6} \text{ M}$) and the dilution factors. We substitute into Equation 2.7 as follows:

$$1.47 \times 10^{-6} \text{ M} = C_A \times \frac{50.00}{500.00} \times \frac{25.00}{750.00} \times \frac{15.00}{1000} = (C_A)(5.000 \times 10^{-5})$$

Solving for the initial concentration, we obtain the following:

$$C_A = \frac{1.47 \times 10^{-6} \text{ M}}{5.000 \times 10^{-5}} = 0.0294 \text{ M}$$

PRACTICE EXAMPLE 2.7

Solution C is prepared by diluting a 0.100 M HCl stock solution as follows:

1. Solution A is prepared by diluting 20.0 mL of the stock solution to 50.0 mL.
2. Solution B is prepared by diluting 10.0 mL of Solution A to 75.0 mL.
3. Dilution of 20.0 mL of Solution B to 250.0 mL produces Solution C.

Solution A:

$$[\text{HCl}] = \quad = \quad \text{M}$$

Solution B:

$$[\text{HCl}] = \quad \times \quad = \quad \text{M}$$

Solution C:

$$[\text{HCl}] = \quad \times \quad = \quad \text{M}$$

Alternatively, use Equation 2.7 and determine the concentration of HCl in Solution C from the initial concentration and the dilution factors.

$$[\text{HCl}] = \quad \times \quad \times \quad \times$$

2.4 DETERMINING CONCENTRATIONS

We treat two of the more common methods used for determining the concentration of a solution: spectrophotometry and solution stoichiometry.

SPECTROPHOTOMETRY

Colored solutions absorb light that is the complementary color of the color they appear. As shown in the color wheel in Figure 2.2, orange is the complement of blue, so a blue solution is one that absorbs orange light. The amount of light that it absorbs depends upon the concentration of the absorbing solute, so measuring the amount of light absorbed by a solution is an easy way to determine the concentration of the absorbing solute.

The amount of light absorbed by a sample at a particular wavelength is known as the sample's **absorbance** at that wavelength (Figure 2.3). Beer's law (Equation 2.8) relates the absorbance (**A**) of a solution to the molar concentration (**c**) of the solute that absorbs the light, the cell's path length (**l**) in centimeters, and the molar absorptivity of the absorbing substance (**ε**), which is a measure of how strongly absorbing the solute is.

$$A = \epsilon lc$$

Eq. 2.8

Absorbance is unitless, so the units of **molar absorptivity** (**ε**) are $M^{-1} \cdot cm^{-1}$. Both **l** and **c** are defined by the experiment, but **ε** depends only on the absorbing species. Absorption is a nearly ideal way to measure concentration because it is easily done and the measured parameter, the absorbance, is directly proportional to the concentration.

Experimentally, the absorbance of a solution of known concentration is determined first to establish the value of **ε**. Although only one such measurement is required to determine the value of **ε**, several are usually done in order to construct a calibration curve (a plot of absorbance versus concentration). The absorbance of the unknown is then measured and its concentration determined using the value of **ε** or the calibration curve obtained for the known solution. However, if the concentration of one component of a mixture is to be measured by absorption spectroscopy, there must be a wavelength of light where only that one component absorbs. Solvent absorbance can also be a problem because the concentration of the solvent is so much greater than that of the solute that a significant absorbance can occur even at wavelengths where **ε** of the solvent is quite small. To correct for this problem, spectroscopists measure the absorbance of a sample that contains all of the components in the mixture except the solute of interest. This sample is called the **blank**. The absorbance of the blank is subtracted from the solution absorbance to obtain the absorbance of the solute of interest.

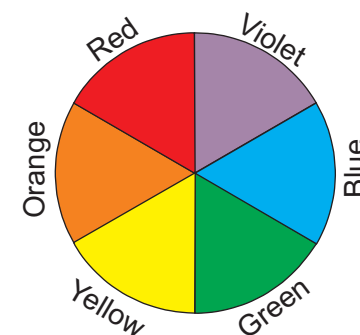


Figure 2.2 Color Wheel

A color and its complement contain all colors, so a solution appears a color because it absorbs its complement. Complementary colors are opposite one another in a color wheel, so orange is the complement of blue. This means that a solution that is blue absorbs orange light and a solution that appears orange absorbs blue light.

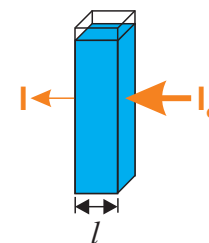


Figure 2.3 Absorbance and Beer's Law

Orange light is absorbed by a blue solution. The amount of light that is absorbed by the solution is called the absorbance of the solution: $A = -\log I/I_0$, where I_0 is the intensity of the incoming light and I is the intensity of the outgoing light. The absorbance depends upon the concentration of the absorbing substance (**c**), the distance the light travels through the sample (**l**), and the molar absorptivity of the solute at the wavelength of the light (**ε**) as given by Beer's law.

Example 2.17

The concentration of a solution containing a cyanine dye in a 1.00 cm cell is determined as follows:

- 1) The absorbance of a solution in which a dye concentration is 86.9 μM is too high to be measured, but the absorbance after a 1:100 dilution is 0.185.
- 2) The absorbance of the unknown after a 1:20 dilution is 0.352.

What is the concentration of the unknown, undiluted cyanine dye solution?

Account for the 1:100 dilution of the original sample to obtain the concentration of the solution whose absorbance was measured.

$$c_f = c_i \times \frac{V_i}{V_f} = 86.9 \mu\text{M} \times \frac{1}{100} = 0.869 \mu\text{M} = 8.69 \times 10^{-7} \text{ M}$$

Determine the molar absorptivity of the dye from the absorbance of the known sample.

$$\varepsilon = \frac{A}{lc} = \frac{0.185}{(1.00 \text{ cm})(8.69 \times 10^{-7} \text{ M})} = 2.13 \times 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$$

Use the above molar absorptivity to determine the concentration of the unknown solution whose absorbance was measured.

$$c = \frac{A}{l\varepsilon} = \frac{0.352}{(1.00 \text{ cm})(2.13 \times 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1})} = 1.65 \times 10^{-6} \text{ M} = 1.65 \mu\text{M}$$

Account for the 1:20 dilution to determine the concentration of the initial sample.

$$c_i = c_f \times \frac{V_f}{V_i} = 1.65 \mu\text{M} \times \frac{20}{1} = 33.0 \mu\text{M}$$

Example 2.18

The concentration of Fe^{3+} in an aqueous solution is determined by the addition of an excess *o*-phenanthroline (phen), which forms a blue complex with the Fe^{3+} that absorbs at 610 nm.* The following solutions are prepared:

- 1) *Blank*: 2.0 mL of iron-free water mixed with 0.001 mL of phen solution.
- 2) *Standard*: 2.0 mL of water that is 5.0 ppm Fe^{3+} mixed with 0.001 mL of phen.
- 3) *Sample*: 2.0 mL of unknown mixed with 0.001 mL of phen.

The spectrometer was adjusted to read 0.000 absorbance with the blank at the 610 nm wavelength, thereby eliminating problems due to the solvent. The absorbance of the standard solution was then measured to be 0.730 and that of the sample to be 0.562. What is the concentration of Fe^{3+} in this sample?

PRACTICE EXAMPLE 2.8

A 1.86 μM solution of β -carotene, the precursor to vitamin A and the source of the orange color in carrots, has an absorbance of 0.259 in a 1-cm cell at 450 nm. What is the molar absorptivity of β -carotene at 450 nm?

What is the concentration of β -carotene in a solution that has an absorbance of 0.187 at 450 nm?

* Farmers with sandy soils often need to apply iron (Fe^{3+}) to their fields, and they check for the level of iron by testing the runoff water in drainage ditches with this procedure.

Because the absorbance of the same complex is being measured, the value of ϵ is the same in both the standard and the sample solutions. All measurements are made under identical circumstances, so l is also the same in both experiments. Thus, we can express the two absorbances as

$$A_{\text{std}} = \epsilon l c_{\text{std}} \quad \text{and} \quad A_{\text{sample}} = \epsilon l c_{\text{sample}}$$

where A_{std} is the absorbance of the standard and A_{sample} is the absorbance of the sample. ϵ and l have no subscripts because their values do not change in the two experiments. Dividing the two expressions eliminates ϵ and l .

$$\frac{A_{\text{std}}}{A_{\text{sample}}} = \frac{c_{\text{std}}}{c_{\text{sample}}}$$

Solving for the concentration of the sample, we obtain

$$c_{\text{sample}} = c_{\text{std}} \times \frac{A_{\text{sample}}}{A_{\text{std}}} = 5.0 \text{ ppm} \times \frac{0.562}{0.730} = 3.8 \text{ ppm Fe}^{3+}$$

REACTION STOICHIOMETRY

Another way to determine an unknown concentration is to measure the amount of a known reactant that is required to completely react with the solute. The determination can be **gravimetric** (mass is measured) or **volumetric** (volume is measured). We now combine the concepts of stoichiometry presented in Chapter 1 with those dealing with solutions presented in this chapter to discuss solution stoichiometry. The calculations are generally identical to those presented in Chapter 1 except that solution reactions are often written as net ionic equations and the given amounts are expressed as concentrations and volumes rather than masses. However, these two differences do not change the fundamentals of the calculations. We consider two types of solution stoichiometry problems: precipitation (gravimetric) and titrations (volumetric).

Precipitation Reactions (gravimetric)

Precipitation reactions occur when ions in solution combine to produce an insoluble salt. The rules used to predict whether or not a salt is insoluble are given in Table 2.2. However, the *solubility rules* in Table 2.2 are only rough guidelines, and there are many exceptions.

Table 2.2 Solubility rules for ionic compounds in water

Rule 1	Compounds of NH_4^{1+} and group 1A metal ions are soluble.
Rule 2	Compounds of NO_3^{1-} , ClO_4^{1-} , ClO_3^{1-} and $\text{C}_2\text{H}_3\text{O}_2^{1-}$ are soluble.
Rule 3	Compounds of Cl^{1-} , Br^{1-} , and I^{1-} are soluble <i>except</i> those of Ag^{1+} , Cu^{1+} , Tl^{1+} , Hg_2^{2+} and Pb^{2+} .
Rule 4	Compounds of SO_4^{2-} are soluble <i>except</i> those of Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{2+} .
Rule 5	<i>Most</i> other ionic compounds are insoluble.

PRACTICE EXAMPLE 2.9

What is the silver ion concentration in a solution of AgNO_3 if the addition of an excess of K_3PO_4 to 50.00 mL of the AgNO_3 solution produces 0.3634 g of precipitate?

Identity of precipitate: _____

Molar mass of precipitate: _____ $\text{g} \cdot \text{mol}^{-1}$

millimoles of silver ion present in 50.00 mL of solution

_____ mmol Ag^{1+}
concentration of Ag^{1+} ion

$[\text{Ag}^{1+}] = \text{_____ M}$

Example 2.19

What is the I^- ion concentration in a solution if the addition of an excess of 0.100 M $\text{Pb}(\text{NO}_3)_2$ to 25.0 mL of the I^- solution produces 987 mg of PbI_2 ?

This is a gravimetric determination of iodide. Use the factor-label method and the molar mass of PbI_2 ($461.0 \text{ g}\cdot\text{mol}^{-1}$) to convert the given mass of PbI_2 into the number of moles of I^- ion that it contains.

$$987 \text{ mg PbI}_2 \times \frac{1 \text{ mmol PbI}_2}{461.0 \text{ mg PbI}_2} \times \frac{2 \text{ mmol I}^-}{1 \text{ mmol PbI}_2} = 4.28 \text{ mmol I}^-$$

25.0 mL of solution contained 4.28 mmol I^- , so the concentration of I^- in the unknown solution is determined to be

$$[\text{I}^-] = \frac{4.28 \text{ mmol I}^-}{25.0 \text{ mL solution}} = 0.171 \text{ M}$$

Example 2.20

Determine the amount of precipitate that forms and the concentration of the excess reactant present in a solution after 75.0 mL of 0.0856 M AgNO_3 solution and 100.0 mL of a 0.0315 M K_3PO_4 solution have been mixed.

Step 1. Write a balanced chemical equation. AgNO_3 and K_3PO_4 are strong electrolytes, so we use the net equation. Referring to the solubility rules, we conclude that K^{1+} and NO_3^{1-} ions are spectator ions, but Ag_3PO_4 is insoluble (Rule 5). The net equation for the reaction is $3\text{Ag}^{1+} + \text{PO}_4^{3-} \rightarrow \text{Ag}_3\text{PO}_4$.

Step 2. Determine the limiting reactant. The limiting reactant is that reactant with the smallest mole/coefficient ratio. The amount of each reactant is given in terms of its molarity and its volume in mL, so Equation 2.1 is used to determine the number of mmoles of each.

$$(75.0 \text{ mL})(0.0856 \text{ mmol}\cdot\text{mL}^{-1}) = 6.42 \text{ mmol Ag}^{1+}$$

$$(100.0 \text{ mL})(0.0315 \text{ mmol}\cdot\text{mL}^{-1}) = 3.15 \text{ mmol PO}_4^{3-}$$

Divide the mmoles of each by the coefficient in the balanced chemical equation to obtain

$$\frac{6.42 \text{ mmol Ag}^{1+}}{3 \text{ mmol Ag}^{1+}} = 2.14; \quad \frac{3.15 \text{ mmol PO}_4^{3-}}{1 \text{ mmol PO}_4^{3-}} = 3.15$$

$2.14 < 3.15$, so Ag^{1+} is the limiting reactant.

Step 3. Construct the reaction table. All quantities on the Δ line are based on the amount of limiting reactant, 6.42 mmol Ag^{1+} .

	3Ag^{1+}	+	PO_4^{3-}	\rightarrow	Ag_3PO_4	
Initial	6.42		3.15		0	mmol
Δ	-6.42		-2.14		+2.14	mmol
Final	0		1.01		2.14	mmol

PRACTICE EXAMPLE 2.10

32.0 mL of 0.112 M $\text{Pb}(\text{NO}_3)_2$ is mixed with 58.0 mL of 0.0886 M KCl . Determine the mass of precipitate that forms and assume additive volumes to determine the concentration of the excess reactant.

Net reaction: _____

Limiting reactant: _____

Reaction Table:

+ \rightarrow

in

Δ

fin

Mass of precipitate

Concentration of excess reactant

Use the moles and molar mass of Ag_3PO_4 to determine the mass of precipitate

$$(2.14 \text{ mmol Ag}_3\text{PO}_4)(418.6 \text{ mg}\cdot\text{mmol}^{-1}) = 896 \text{ mg or } 0.896 \text{ g}$$

We assume additive volumes; *i.e.*, the final volume is the sum of the two initial volumes: $75.0 + 100.0 = 175.0 \text{ mL}$. The molar concentration of phosphate ion remaining in the solution is then determined to be

$$[\text{PO}_4^{3-}] = \frac{1.01 \text{ mmol}}{175.0 \text{ mL}} = 0.00577 \text{ M or } 5.77 \text{ mM}$$

In Chapter 8, we will show that the final concentration of the limiting reactant is small, but it is not zero because equilibrium is established.

Titration (volumetric)

A titration is an analytical procedure in which the stoichiometric volume of one reactant, the **titrant** that is required to react with a known amount of another reactant, the **analyte**, is determined. The experimental setup is shown in Figure 2.4. The **buret**, which contains the titrant, is calibrated so that the volume of solution it delivers can be determined precisely (usually to 0.01 mL). The rate of delivery of the titrant is adjusted with the stopcock. In a common titration, the concentration of the titrant is known and the amount of the analyte is determined. A known amount of volume or dissolved mass of analyte is placed in the reaction flask, and the titrant is added slowly until the stoichiometric volume has been delivered. This point, known as the **equivalence point**, is usually approximated by a color change produced by one of the reactants or by an indicator that is added to the analyte solution. The point at which the color change occurs is called the **end point** of the titration. Typically, the equivalence point is approximated by an end point.

Example 2.21

3.86 g of impure NaOH pellets are dissolved in sufficient water to make 1.00 L of solution. What is the purity of the pellets if the titration of 30.0 mL of 0.107 M HCl required 38.6 mL of the resulting solution?

1) Determine the number of millimoles of H_3O^{1+} :

$$30.0 \text{ mL H}_3\text{O}^{1+} \times \frac{0.107 \text{ mmol H}_3\text{O}^{1+}}{\text{mL H}_3\text{O}^{1+}} = 3.21 \text{ mmol H}_3\text{O}^{1+}$$

2) Convert mmol H_3O^{1+} to mmol OH^{1-} using $\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$

$$3.21 \text{ mmol H}_3\text{O}^{1+} \times \frac{1 \text{ mmol OH}^{1-}}{1 \text{ mmol H}_3\text{O}^{1+}} = 3.21 \text{ mmol OH}^{1-}$$

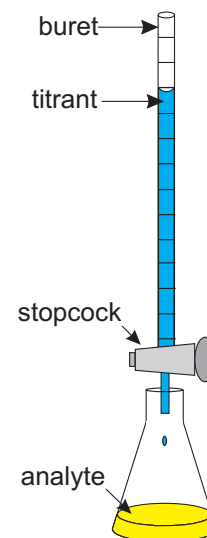
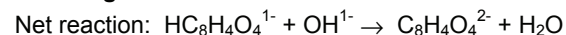


Figure 2.4 Titration apparatus

PRACTICE EXAMPLE 2.11

Dissolving $\text{KHC}_8\text{H}_4\text{O}_4$ (KHP, $M_m = 204.2 \text{ g}\cdot\text{mol}^{-1}$) in water produces the $\text{HC}_8\text{H}_4\text{O}_4^{1-}$ ion, which is a weak monoprotic acid that is used to determine the concentrations of strong base solutions. What is the hydroxide ion concentration in a NaOH solution if 33.26 mL of the solution was required to react with 764.3 mg of KHP?



mmoles of KHP

= _____ mmol KHP

mmol of hydroxide reacting =

= _____ mmol OH^{1-}

$[\text{OH}^{1-}] =$

= _____ M

3) Convert the mmol of OH^{1-} in 38.6 mL of solution to mass of NaOH.

$$3.21 \text{ mmol OH}^{1-} \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol OH}^{1-}} \times \frac{40.0 \text{ mg NaOH}}{\text{mmol NaOH}} = 128 \text{ mg NaOH}$$

4) Use the amount of NaOH in 38.6 mL to determine the amount in original 1.00 L

$$128 \text{ mg NaOH} \times \frac{1000 \text{ mL solution}}{38.6 \text{ mL solution}} = 3.32 \times 10^3 \text{ mg NaOH} = 3.32 \text{ g NaOH}$$

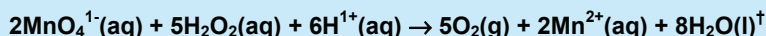
5) Use the mass of NaOH and the mass of pellets to determine the purity.

$$\frac{3.32 \text{ g NaOH}}{3.86 \text{ g pellets}} \times 100\% = 85.9\% \text{ pure}$$

Only 85.9% of the mass of the pellets is actually NaOH.

Example 2.22

What is the percent H_2O_2 in a sample if 20.00 g of the H_2O_2 solution* required titration with 40.85 mL of 0.1728 M KMnO_4 ?



The number of mmols of H_2O_2 in the sample is determined from the number of mmols of MnO_4^{1-} required for the titration and the stoichiometric ratio between H_2O_2 and MnO_4^{1-} .

$$40.85 \text{ mL MnO}_4^{1-} \times \frac{0.1728 \text{ mmol MnO}_4^{1-}}{\text{mL MnO}_4^{1-}} \times \frac{5 \text{ mmol H}_2\text{O}_2}{2 \text{ mmol MnO}_4^{1-}} = 17.65 \text{ mmol H}_2\text{O}_2$$

The mass of the H_2O_2 in the sample is

$$17.65 \text{ mmol H}_2\text{O}_2 \times \frac{34.014 \text{ mg H}_2\text{O}_2}{\text{mmol H}_2\text{O}_2} = 600.2 \text{ mg H}_2\text{O}_2$$

Note that the result of the calculation for the number of millimoles of H_2O_2 is used in the above, not the rounded value, which does change the last significant figure. The percentage of the total mass of the sample that is H_2O_2 is then

$$\% \text{ H}_2\text{O}_2 = \frac{0.6002 \text{ g H}_2\text{O}_2}{20.00 \text{ g sol'n}} \times 100\% = 3.001\% \text{ H}_2\text{O}_2$$

Hydrogen peroxide that is purchased in a drug store is also 3%.

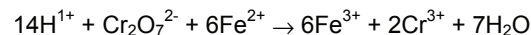
* H_2O_2 decomposes by the reaction $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g})$. Even if the bottle is sealed to keep O_2 from escaping, some decomposition occurs and the concentration of H_2O_2 drops.

† MnO_4^{1-} is a deep purple color, while Mn^{2+} is colorless. Excess H_2O_2 in the flask converts the added MnO_4^{1-} to Mn^{2+} , so the solution remains colorless, but as soon as the H_2O_2 has been consumed, additional MnO_4^{1-} causes the solution to turn pink. Thus, the end point is reached when the solution first retains a light pink color.

PRACTICE EXAMPLE 2.12

A 0.8564-g sample of iron ore is dissolved in acid to produce Fe^{2+} ion. The resulting solution was then titrated with 0.03448 M $\text{K}_2\text{Cr}_2\text{O}_7$. What is the mass percent iron in the ore if the titration required 21.52 mL of $\text{Cr}_2\text{O}_7^{2-}$?

Titration reaction:



1. determine mmol of $\text{Cr}_2\text{O}_7^{2-}$ required

= _____

mmol

2. convert mmol of $\text{Cr}_2\text{O}_7^{2-}$ to mmol of Fe^{2+} in sample

= _____ mmol

3. convert mmol Fe^{2+} to mg of Fe in ore sample

= _____ mg

4. mass percent of iron in ore

= _____ %

2.5 COLLIGATIVE PROPERTIES

Colligative properties depend on the concentration of the solute *particles*, not their identity, so a sodium ion has the same effect on these properties as does a sugar molecule. In this section, we discuss the quantitative relationships between solute particle

concentrations and the effects that they cause.

Colligative properties depend upon the concentration of particles, so particle concentrations are often referred to as colligative concentrations. For example, the molarity of all particles in a solution is often referred to as the **colligative molarity**, M_c . This is not an important distinction for nonelectrolytes, but it is very important for electrolytes. Consider that a 0.020 M solution of the strong electrolyte CaCl_2 is 0.020 M in Ca^{2+} and $2(0.020) = 0.040$ M in Cl^{1-} . Consequently, the colligative molarity of a 0.020 M solution of CaCl_2 is $M_c = [\text{Ca}^{2+}] + [\text{Cl}^{1-}] = 0.020 + 0.040 = 0.060$ M. The **colligative molality**, m_c , is defined analogously. The difference between the concentration of a solution and its colligative concentration is shown in Equation 2.9.

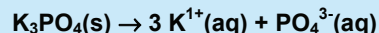
$$M_c = i M \quad \& \quad m_c = i m \quad \text{Eq. 2.9}$$

i is the van't Hoff factor. In this text, we assume that the van't Hoff factor is simply the number of moles of particles produced when one mole of a solute dissolves. However, because of interactions between the ions, i is usually somewhat less than this ideal number. Practice Example 2.13 gives more examples of van't Hoff factors.

Example 2.23

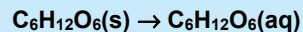
Determine the colligative molarity of each of the following solutions:

a) 0.080 M K_3PO_4



$$i = 3 \text{ K}^{1+} \text{ ions} + 1 \text{ PO}_4^{3-} \text{ ion} = 4 \text{ ions} \Rightarrow M_c = i M = 4M = 4(0.080) = 0.32 \text{ M}$$

b) 0.042 M $\text{C}_6\text{H}_{12}\text{O}_6$



This organic compound is a nonelectrolyte so $i = 1 \Rightarrow M_c = M = 0.042 \text{ M}$

As shown in Figure 2.5, adding a solute to a solvent depresses the freezing point by ΔT_f , elevates the boiling point by ΔT_b , and lowers the vapor pressure at temperature T by ΔP . The effect is to increase the temperature-pressure range of the liquid state. The amount by which the liquid state is extended (shown in blue in the figure) depends only on the concentration of the solute particles, so freezing point depression, boiling point elevation, and vapor pressure lowering are all colligative properties, and we now examine the relationship between particle concentrations and their effect on each of these colligative properties. We then define a fourth colligative property, the osmotic pressure.

PRACTICE EXAMPLE 2.13

Determine the van't Hoff factor for each of the following.

CaSO_4 : _____

$\text{Ba}(\text{OH})_2$: _____

CH_3OH : _____

HCl : _____

NH_4ClO : _____

SF_4 : _____

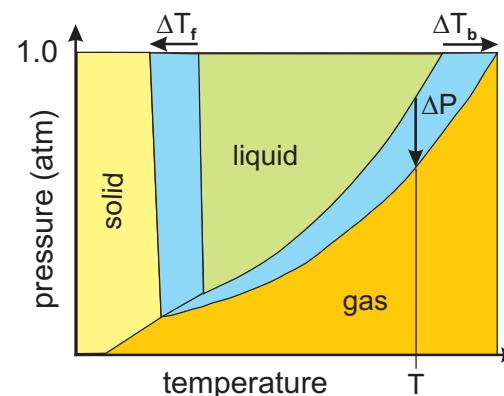


Figure 2.5 Phase diagram of a pure solvent and a solution

The green region is the liquid region of the pure solvent. The blue region is liquid in the solution but solid or gas in the solvent. The arrows indicate the changes in the freezing point (freezing point depression, ΔT_f), the normal boiling point (boiling point elevation, ΔT_b), and the vapor pressure at temperature T (vapor pressure lowering, ΔP) caused by the addition of a solute to a pure solvent.

VAPOR PRESSURE LOWERING

The liquid \rightleftharpoons vapor equilibrium is a dynamic equilibrium that is established when the rate of evaporation equals the rate of condensation. The pressure of the vapor in equilibrium with the liquid at a given temperature is the **vapor pressure** of the liquid at that temperature. Evaporation occurs from the surface of the liquid, so the rate of evaporation depends upon the concentration of particles at the surface. Figure 2.6 compares a pure solvent with a solution in which the mole fraction of a nonvolatile solute is 0.2. A solute mole fraction of 0.2 means that 20% of the particles in solution are solute particles, so 20% of the sites on the surface are occupied by nonvolatile solute particles. Consequently, evaporation can occur from only 80% of the surface sites, which results in a 20% reduction in the rate of evaporation, which in turn, causes a 20% reduction in the vapor pressure. We conclude that ΔP , the amount by which the vapor pressure of the solvent at some temperature is lowered by the addition of a solute with a mole fraction of X_{solute} , is

$$\Delta P = X_{\text{solute}} P^{\circ} \quad \text{Eq. 2.10}$$

ΔP is the vapor pressure lowering; it is always positive because the *vapor pressure of a solution is always lower than that of the pure solvent*. P° is the vapor pressure of the pure solvent at the temperature under consideration. The vapor pressure of water is given at several temperatures in Table 2.3. The vapor pressure of the solution is lower than that of the solvent by ΔP , so $P = P^{\circ} - \Delta P = P^{\circ} - X_{\text{solute}} P^{\circ} = (1 - X_{\text{solute}}) P^{\circ}$. However, $1 - X_{\text{solute}} = X_{\text{solvent}}$, so we can rewrite Equation 2.10 as

$$P = X_{\text{solvent}} P^{\circ} \quad \text{Eq. 2.11}$$

Equation 2.11 indicates that the vapor pressure of a solution is equal to the vapor pressure of the pure solvent times the fraction of the surface sites occupied by the solvent; *i.e.*, the *mole fraction of the solvent*. Thus far, we have determined mole fractions of solutes rather than solvents, so be careful not to use the wrong mole fraction in Equation 2.11.

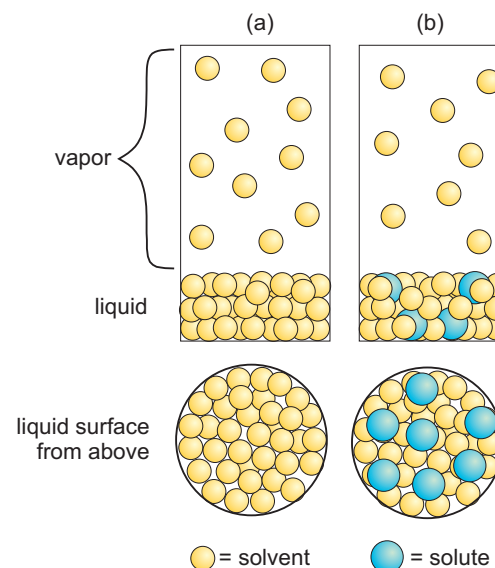


Figure 2.6 Vapor Pressure Lowering

- Solvent:** All of the surface sites are occupied by solvent molecules, which produces ten molecules in the vapor.
- Solution:** The mole fraction of the solute in the solution is ~ 0.2 , so nonvolatile solute particles (blue spheres) occupy $\sim 20\%$ of the surface sites, which reduces the vapor pressure by $\sim 20\%$ as shown by the presence of only eight molecules in the vapor.

Example 2.24

What is the vapor pressure of a solution prepared by dissolving 10.0 g of NaCl in 100. g of water at 25 °C?

The van't Hoff factor for NaCl is $i=2$ ($\text{Na}^{1+} + \text{Cl}^{1-}$), so there are two moles of ions (particles) for each mole of NaCl. The total number of moles of solute in solution is

$$10.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol NaCl}} = 0.342 \text{ mol ions}$$

The number of moles of solvent (water) in the solution is

$$100. \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 5.56 \text{ mol H}_2\text{O}$$

The total number of moles of particles is $0.34 \text{ mol ions} + 5.56 \text{ mol H}_2\text{O} = 5.90 \text{ mol}$. The mole fraction of the solvent is then calculated to be

$$X_{\text{solvent}} = \frac{5.56 \text{ mol H}_2\text{O}}{5.90 \text{ mol total}} = 0.942$$

The vapor pressure of water is found to be $P^\circ = 23.8 \text{ torr}$ (Table 2.3), so the vapor pressure of the solution can be determined with Equation 2.11 to be

$$P = X_{\text{solvent}}P^\circ = (0.942)(23.8 \text{ torr}) = 22.4 \text{ torr}$$

Dissolving NaCl in water lowers the vapor pressure of the water by $23.8 - 22.4 = 1.4 \text{ torr}$ or 5.9%, which is the mole percent of NaCl. This is the same result that would have been obtained had we used Equation 2.10.

Table 2.3 Vapor pressure of water at various temperatures

T (°C)	P° (torr) ^a	T (°C)	P° (torr) ^a
0	4.6	50	92.5
5	6.5	55	118.0
10	9.2	60	149.4
15	12.8	65	187.5
20	17.5	70	233.7
25	23.8	75	289.1
30	31.8	80	355.1
35	41.2	85	433.6
40	55.3	90	525.8
45	71.9	95	633.9

^a 1 torr = 1 mm Hg.

BOILING POINT ELEVATION

The **normal boiling point** of a liquid is the temperature at which its vapor pressure is 1 atm. Although this is the definition of the *normal* boiling point, it is common to refer to it as simply the *boiling point*. The boiling point of water is 100 °C, so its vapor pressure at 100 °C is 1 atm, but the vapor pressure of an aqueous solution is less than 1 atm at 100 °C due to vapor pressure lowering. Consequently, an aqueous solution must be heated to a higher temperature to achieve a vapor pressure of 1 atm, so the boiling point of an aqueous solution is always higher than that of pure water. This reasoning can be applied to any solution, so we conclude that *the boiling point of a solution is always higher than the boiling point of the pure solvent*. The amount by which the boiling point of the solvent is increased by the addition of a nonvolatile solute is known as the **boiling point elevation**, ΔT_b . The magnitude of the increase is proportional to the colligative molality of the solute:

$$\Delta T_b = k_b m_c = i k_b m \quad \text{Eq. 2.12}$$

k_b is the **boiling point elevation constant** of the solvent; it has units °C·m⁻¹ (degrees per molal). The boiling point elevation constants and boiling points of some common solvents are included in Table 2.4. ΔT_b is the amount by which the boiling point of the solvent (T_b°) is raised, so the boiling point of the solution is given as

$$T = T_b^\circ + \Delta T_b$$

Table 2.4 Freezing point depression and boiling point elevation data for some solvents

Solvent	Freezing Point (°C)	k_f (°C·m ⁻¹)	Boiling Point (°C)	k_b (°C·m ⁻¹)
Acetic Acid	16.6	3.90	117.9	3.07
Benzene	5.5	4.90	80.1	2.53
Chloroform	-63.5	4.70	61.7	3.63
Cyclohexane	6.6	20.0	80.7	2.79
Ethanol	-117.3	1.99	78.5	1.22
<i>para</i> -Xylene	11.3	4.30		
Water	0.0	1.86	100.0	0.512

FREEZING POINT DEPRESSION

Spreading salt on icy streets and sidewalks melts the ice because solute particles reduce the freezing point of a solvent in much the same way as they reduce its vapor pressure. That is, solute particles block sites on the solid where solvent molecules might otherwise freeze, thereby reducing the rate of freezing. The amount by which the freezing point is lowered is called the **freezing point depression**, ΔT_f , and is shown in Equation 2.13:

$$\Delta T_f = k_f m_c = i k_f m$$

Eq. 2.13

In Equation 2.13, k_f is the freezing point depression constant, which has units of $^{\circ}\text{C}\cdot\text{m}^{-1}$ and depends on the solvent, and m_c is the colligative molality of the solute. The freezing point depression constants and freezing points of some common solvents are listed in Table 2.4. ΔT_f is the amount by which the freezing point of the solvent (T_f°) is lowered, so the freezing point of the solution is given as

$$T = T_f^{\circ} - \Delta T_f$$

Example 2.25

Antifreeze is ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$ [$M_m=62.1 \text{ g}\cdot\text{mol}^{-1}$; $d=1.11 \text{ g}\cdot\text{mL}^{-1}$]. What are the boiling and freezing points of a 50.% (v/v) aqueous solution?

Ethylene glycol has a very low vapor pressure, so we can assume that it is a nonvolatile solute for our calculation. The first step is to determine the molality. 50.% (v/v) denotes a volume/volume percent, which means that 50.% of the *volume* of the antifreeze is ethylene glycol and 50.% of the *volume* is water. We need a quantity of solution for which the number of moles of solute and kg of solvent can be determined, but we are free to choose any amount. For simplicity, we base our calculations on 1 L = 1000. mL of antifreeze. The mixture is a 50/50 mixture, so we can write

$$1000. \text{ mL of mixture} = 500. \text{ mL H}_2\text{O} + 500. \text{ mL C}_2\text{H}_6\text{O}_2$$

Use the densities of the two liquids and the molar mass of ethylene glycol to determine the mass of water and the number of moles of ethylene glycol.

$$500. \text{ mL H}_2\text{O} \times \frac{1.00 \text{ g H}_2\text{O}}{\text{mL H}_2\text{O}} = 500. \text{ g H}_2\text{O} = 0.500 \text{ kg H}_2\text{O}$$

$$500. \text{ mL C}_2\text{H}_6\text{O}_2 \times \frac{1.11 \text{ g C}_2\text{H}_6\text{O}_2}{\text{mL C}_2\text{H}_6\text{O}_2} \times \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.1 \text{ g C}_2\text{H}_6\text{O}_2} = 8.94 \text{ mol C}_2\text{H}_6\text{O}_2$$

The molality of ethylene glycol in the 50.% mixture is

$$\text{molality} = \frac{8.94 \text{ mol C}_2\text{H}_6\text{O}_2}{0.500 \text{ kg H}_2\text{O}} = 17.9 \text{ m}$$

The freezing point *depression* caused by the undissociated ($i = 1$) ethylene glycol is

PRACTICE EXAMPLE 2.14

The salt that is commonly used to melt ice on roads and sidewalks is CaCl_2 ($M_m = 111 \text{ g}\cdot\text{mol}^{-1}$). What are the melting point, boiling point, and vapor pressure at 20°C of a solution of CaCl_2 made by dissolving 62.3 g of CaCl_2 in 100. mL of H_2O ?

$$= \text{_____ mol CaCl}_2$$

$$\text{in _____ kg H}_2\text{O}$$

$$\text{molality of CaCl}_2: \text{_____ m}$$

$$\text{van't Hoff factor for CaCl}_2 \text{ is } i = \text{_____}$$

$$\text{colligative molality} = \text{_____} \times \text{_____} = \text{_____ m}$$

Freezing point and boiling point

$$\Delta T_f = \text{_____ } ^{\circ}\text{C}\cdot\text{m}^{-1} \times \text{_____ m} = \text{_____ } ^{\circ}\text{C}$$

$$\Delta T_b = \text{_____ } ^{\circ}\text{C}\cdot\text{m}^{-1} \times \text{_____ m} = \text{_____ } ^{\circ}\text{C}$$

$$\text{Freezing point: } T_f = \text{_____ } ^{\circ}\text{C}$$

$$\text{Boiling point: } T_b = \text{_____ } ^{\circ}\text{C}$$

Moles and mole fraction of water in solution

$$= \text{_____ mol H}_2\text{O}$$

$$X(\text{H}_2\text{O}) = \text{_____}$$

$$\text{Vapor pressure of water at } 20^{\circ}\text{C} \text{ from Table 2.2} = \text{_____ torr}$$

The vapor pressure of the solution at 20°C is

$$\text{_____} \times \text{_____} = \text{_____ torr}$$

$$\Delta T_f = (1.86\text{ }^{\circ}\text{C}\cdot\text{m}^{-1})(17.9\text{ m}) = 33.3\text{ }^{\circ}\text{C}.$$

where $1.86\text{ }^{\circ}\text{C}\cdot\text{m}^{-1}$ is the freezing point depression constant of water from Table 2.4. The freezing point of pure water is $0\text{ }^{\circ}\text{C}$, so the freezing point of the antifreeze is $-33\text{ }^{\circ}\text{C}$ ($-27\text{ }^{\circ}\text{F}$), a substantial protection. The protection against boil-over is not as good.

$$\Delta T_b = (0.512\text{ }^{\circ}\text{C}\cdot\text{m}^{-1})(17.9\text{ m}) = 9.16\text{ }^{\circ}\text{C}$$

where $0.512\text{ }^{\circ}\text{C}\cdot\text{m}^{-1}$ is the boiling point elevation constant for water. The boiling point *elevation* is $9\text{ }^{\circ}\text{C}$. Because water boils at $100\text{ }^{\circ}\text{C}$, the boiling point of the antifreeze is $109\text{ }^{\circ}\text{C}$ ($228\text{ }^{\circ}\text{F}$). The pressure in your car's cooling system is elevated above 1 atm, however, which also increases the boiling point.

Colligative properties depend only on the concentration of the solute particles, so they can be used to determine the number of moles of solute particles present in a solution. If the mass of the solute is known, then its molar mass can also be determined. Example 2.26 demonstrates the use of freezing point depressions in determining a molar mass, once a common procedure.

Example 2.26

1.00 g of an unknown, non-dissociating ($i = 1$) solute is added to 10.00 g of *para*-xylene. The freezing point of the solution is $1.95\text{ }^{\circ}\text{C}$ lower than that of the pure solvent. What is the molar mass of the unknown?

From Table 2.4, we find that $k_f = 4.30\text{ }^{\circ}\text{C}\cdot\text{m}^{-1}$ for *para*-xylene. This is a good solvent for this experiment because of its relatively large k_f . The freezing point depression of *para*-xylene is over twice that for the same sample in water.

- Equation 2.11 is used to determine the molality of the solution.

$$m = \frac{\Delta T_f}{k_f} = \frac{1.95\text{ }^{\circ}\text{C}}{4.30\text{ }^{\circ}\text{C}\cdot\text{m}^{-1}} = 0.453\text{ m}$$

- The number of moles of solute present is determined from the mass of the solvent and the molality.

$$(0.453\text{ mol}\cdot\text{kg}^{-1})(0.0100\text{ kg}) = 4.53\times 10^{-3}\text{ mol}$$

- The molar mass is determined from the number of moles and the mass of the sample.

$$M_m = \frac{\text{grams of sample}}{\text{moles of sample}} = \frac{1.00\text{ g}}{4.53\times 10^{-3}\text{ mol}} = 221\text{ g}\cdot\text{mol}^{-1}$$

OSMOTIC PRESSURE

A *semipermeable membrane* is a membrane that allows solvent molecules (usually water) to pass through while denying passage to solute particles. The movement of the solvent molecules through the membrane is called **osmosis**. The rate of osmosis depends upon the rate at which the solvent molecules collide with the membrane. The presence of a solute reduces the rate at which solvent molecules pass through the membrane by reducing the concentration of the solvent and blocking solvent access to portions of the membrane.

Figure 2.7a shows two containers (I and II) filled with water and separated by a semipermeable membrane. The concentration of water on both sides is identical, so the rate of osmosis is the same in both directions, $I \rightleftharpoons II$. However, a solute (larger blue spheres) has been added to container II in Figure 2.7b. The presence of the solute reduces the solvent concentration, which reduces the rate at which solvent molecules collide with and penetrate the membrane. Consequently, the rate of passage of solvent molecules in direction $I \leftarrow II$ drops below that in the $I \rightarrow II$ direction, so there is a net passage of solvent from I into II, which dilutes the solution in side II. We conclude that

When solutions with different concentrations are separated by a semipermeable membrane, solvent molecules pass from the more dilute solution into the more concentrated solution. The result is a dilution of the more concentrated solution.

In Figure 2.8, a semipermeable membrane separates pure water and a concentrated aqueous solution. Initially, the two levels are the same, but there is a net movement of water molecules from the pure water into the solution. As a result, the solution level rises and the pure water level drops. The rising column on the solution side exerts an increasing pressure on the membrane that increases the rate at which water molecules pass from the solution pass back into the pure water. Equilibrium is established when the pressure is sufficient to drive the water molecules out of the solution at the same rate that they leave the pure water. The pressure exerted by the column at equilibrium is the **osmotic pressure**. The osmotic pressure developed by a solution is given by Equation 2.14.

$$\pi = M_c RT = i MRT$$

Eq. 2.14

In Equation 2.14, π is the osmotic pressure in atmospheres, M_c is the colligative molarity, T is the absolute temperature, and $R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the ideal gas law constant. Note that $\text{L}\cdot\text{mol}^{-1} = \text{M}^{-1}$, so the constant R can also be expressed as $0.0821 \text{ atm}\cdot\text{K}^{-1}\cdot\text{M}^{-1}$.

If a pressure exceeding the osmotic pressure is applied to the concentrated side of Figure 2.8, water can be forced from the solution side into the pure water in a process

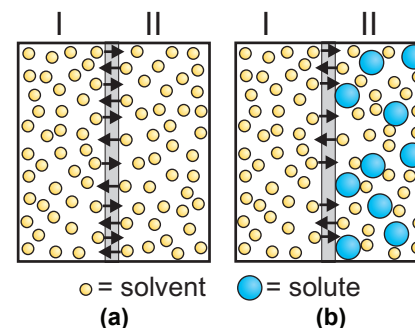


Figure 2.7 Osmosis

- a) The rate of osmosis is equal in both directions when the solutions are identical.
b) The rate of osmosis from $I \leftarrow II$ is decreased because the solute particles block rather than penetrate the membrane.

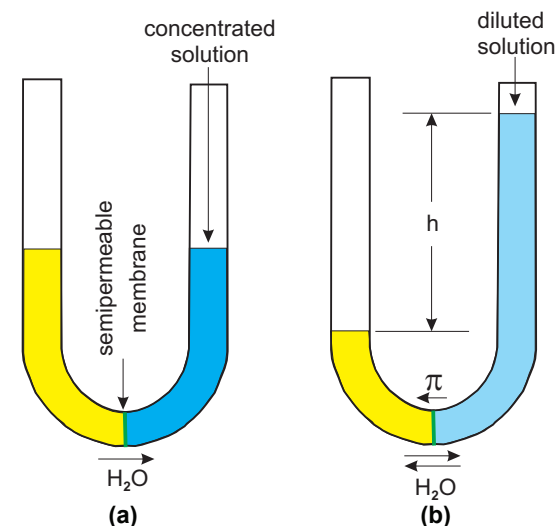


Figure 2.8 Osmotic Pressure

The solution and solvent levels are identical, but there is net passage of water from solvent to solution.

When the height difference between the two levels, h , produces sufficient pressure, the rate of flow through the membrane is the same in both directions, and the system reaches equilibrium. The pressure exerted by the water column of height h at equilibrium is the *osmotic pressure*, π .

called *reverse osmosis*. Reverse osmosis has been used to purify seawater on ships and in the Middle East.

Example 2.27

Assume sea water is 0.53 M NaCl and determine what minimum pressure is required to purify sea water by reverse osmosis at 25 °C.

Using $i = 2$ for NaCl and 298 K for 25 °C in Equation 2.14, we determine the osmotic pressure of sea water to be:

$$\pi = iMRT = 2(0.53 \text{ M})(0.0821 \text{ atm}\cdot\text{K}^{-1}\cdot\text{M}^{-1})(298 \text{ K}) = 26 \text{ atm}$$

The applied pressure in reverse osmosis must exceed the osmotic pressure, so a pressure over 26 times that of atmospheric pressure must be applied. The biggest challenge preventing the general use of reverse osmosis to obtain drinking water from sea water is finding membranes that can withstand such high pressures.

Osmotic pressure has many applications in biology because cell membranes are semipermeable. When the solution around a cell has the same colligative concentration as within the cell, water enters and leaves the cell at the same rate and the cell maintains its size and shape. However, when a cell is placed in pure water, it expands and eventually ruptures as water flows into the cell faster than it flows out. Placing a cell in a solution with a greater colligative concentration causes the cell to shrink as water flows out faster than it flows in. This is the reason that drinking salt water does not quench your thirst and actually makes you thirstier. Osmotic pressure is responsible for the transport of water from the roots to the tops of plants. Water enters a tree through the membranes in its roots, but evaporates from the leaves resulting in a substantial concentration difference between the roots and the leaves. The large concentration difference can develop osmotic pressures of up to ~20 atm in very tall trees. As demonstrated in Example 2.28, osmotic pressure can also be used to determine molar mass.

Example 2.28

0.75 L of an aqueous solution containing 0.40 g of a peptide has an osmotic pressure of 3.74 torr at 27 °C. What is the molar mass of the peptide?

The procedure followed in this problem is very similar to that used in Example 2.26. We begin by realizing that peptides do not dissociate in water, so $i = 1$.

1. Convert the given pressure to atmospheres by dividing the given pressure in torr by 760 torr·atm⁻¹, then solve Equation 2.13 for the molarity of the solution.

$$M = \frac{\pi}{RT} = \frac{(3.74/760) \text{ atm}}{(0.0821 \text{ atm} \cdot \text{K}^{-1} \cdot \text{M}^{-1})(300 \text{ K})} = 2.0 \times 10^{-4} \text{ M}$$

2. Determine the number of moles of peptide in 0.75 L of solution.

$$n = (0.75 \text{ L})(2.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}) = 1.5 \times 10^{-4} \text{ mol}$$

3. Calculate the molar mass from the number of moles and mass of peptide.

$$M_m = \frac{\text{grams peptide}}{\text{moles peptide}} = \frac{0.40 \text{ g}}{1.5 \times 10^{-4} \text{ mol}} = 2.7 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$$

PRACTICE EXAMPLE 2.15

What osmotic pressure would develop between the solution described in Practice Example 2.14 and pure water at 298K? Assume that the solution has a density of 1.2 g·mL⁻¹.

Volume of solution

$$V = \underline{\hspace{2cm}} \text{ L}$$

Colligative Molarity

$$M_c = \underline{\hspace{2cm}} \text{ M}$$

Osmotic Pressure

$$\pi = \underline{\hspace{2cm}} \text{ atm}$$

2.6 COLLOIDS

Sometimes materials will suspend as small aggregates rather than dissolve. For example, sand will stay suspended in water as long as the water is stirred; but soon after the stirring has stopped, the sand settles to the bottom of the container. Because these mixtures do not meet the rigorous criterion of a solution, they are called **dispersions** or **suspensions**.

Suspensions in which the particle size is very small (1 nm to 1 μm) are called colloidal suspensions or simply **colloids**. White paint is a colloidal suspension of SiO₂ and TiO₂ particles, which are used to make the paint opaque and white, respectively. Colloidal suspensions, which can be stable for years, are classified according to their composition. Whipped cream is a **foam**: a gas suspended in a liquid. Jellies and starch solutions are **sols**: solids suspended in a liquid. Milk is an **emulsion**: a liquid suspended in a liquid. **Aerosols** can be liquids suspended in a gas (hair sprays) or solids suspended in a gas (smoke). **Fog** is also an aerosol (water in air) and **smog**, the combination of *smoke* and *fog*, is also a colloidal suspension.

2.7 CHAPTER SUMMARY AND OBJECTIVES

Several concentration units were defined:

$$\begin{aligned} \text{Molarity of A} \quad M_A &= \frac{\text{mol A}}{\text{L solution}} = \frac{\text{mmol A}}{\text{mL solution}} \\ \text{Mole Fraction of A} \quad X_A &= \frac{\text{mol A}}{\text{total mol of all substances in mixture}} \\ \text{Mass Fraction of A} \quad \text{mass fraction} &= \frac{\text{mass A}}{\text{total mass of mixture}} \\ \text{Molality of A} \quad m_A &= \frac{\text{mol A}}{\text{kg solvent}} \end{aligned}$$

Mass percent, parts per million, and parts per billion were also defined. Concentrations and volumes give us yet another way to determine the number of moles of a sample and can be applied to the stoichiometry of reactions occurring in solution. An easy way to convert from one concentration unit to another is to put the given and desired units side-by-side and convert the numerators and the denominators independently.

Addition of a solvent to a solution dilutes the solution. Calculations of resulting concentrations or required volumes can be done by using the dilution formula: $C_i V_i = C_f V_f$ (Equation 2.5) where $C_i V_i$ is the amount (moles or mass) of solute in the initial solution, and $C_f V_f$ is the amount of solute in the final solution. It is important to remember that dilution changes the volume of the solution and the concentration of the solute, but it does *not* change the amount of solute.

Concentrations can be determined by measuring the absorbances of a blank, a standard, and the sample. Beer's law relates the absorbance (A) of a sample to its molar absorptivity (ϵ), its concentration (c), and to the path length (l) that the light travels through the sample: $A = \epsilon l c$ (Equation 2.8).

Colligative properties are those properties of a solution that depend on the concentration but not on the identity of the solute particles. The colligative concentration of a solution is the total concentration of all particles in the solution. For example, in a solution consisting of only one solute, the colligative molarity is $M_c = iM$ (Equation 2.9) where i , the van't Hoff factor, is the number of moles of particles that results when one mole of solute dissolves. i is one for nonelectrolytes but is greater than one for electrolytes.

There are four colligative properties:

ANSWERS TO PRACTICE EXAMPLES

- 2.1 $[\text{Ba}^{2+}] = 0.0490 \text{ M}$; $[\text{OH}^{1-}] = 0.0980 \text{ M}$;
17.1 mmol OH^{1-} ; 61.2 mL
- 2.2 Mole fractions: $\text{N}_2 = 0.17$; $\text{O}_2 = 0.41$; $\text{He} = 0.41$
- 2.3 a) 20.% b) 3.0 ppm c) 25 ppb
- 2.4 1.2 ppb Ag^{1+}
- 2.5 78.8 g H_2O
- 2.6 Mole fractions: $\text{H}_2\text{SO}_4 = 0.0730$; $\text{H}_2\text{O} = 0.927$
molarity = 3.73 M; molality = 4.37 m
- 2.7 $A = 40.0 \text{ mM}$; $B = 5.33 \text{ mM}$; $C = 0.427 \text{ mM}$
- 2.8 $\epsilon = 1.39 \times 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$; $c = 1.34 \mu\text{M}$
- 2.9 Ag_3PO_4 ; 418.58 mg/mmol; 2.605 mmol; 0.0521 M
- 2.10 $\text{Pb}^{2+} + 2\text{Cl}^{1-} \rightarrow \text{PbCl}_2$; 714 mg PbCl_2 ; $[\text{Pb}^{2+}] = 11.2 \text{ mM}$
- 2.11 3.743 mmol OH^{1-} ; $[\text{OH}^{1-}] = 0.1125 \text{ M}$
- 2.12 4.452 mmol Fe^{2+} ; 28.73%
- 2.13 $\text{CaSO}_4 = 2$; $\text{Ba}(\text{OH})_2 = 3$; $\text{CH}_3\text{OH} = 1$;
 $\text{HCl} = 2$; $\text{NH}_4\text{ClO} = 2$; $\text{SF}_4 = 1$
- 2.14 $T_f = -31.3^\circ\text{C}$; $T_b = 108.6^\circ\text{C}$; $P = 13.4 \text{ torr}$
- 2.15 $V = 0.14 \text{ L}$; $M_c = 12 \text{ M}$; $\pi = 3.1 \times 10^2 \text{ atm}$

- | | |
|------------------------------|--|
| 1. vapor pressure lowering | $\Delta P = X_{\text{solute}} P^{\circ}$ |
| 2. boiling point elevation | $\Delta T_b = k_b m_c = i k_b m$ |
| 3. freezing point depression | $\Delta T_f = k_f m_c = i k_f m$ |
| 4. osmotic pressure | $\pi = M_c RT = i MRT$ |

Colloids are suspensions of very small (1 nm to 1 μm) particles that can stay suspended for years.

After studying the material in this chapter, you should be able to:

1. determine the molarity, molality, mole fraction, and mass fraction of a solution from the amounts of solute and solvent or solution (Section 2.1);
2. determine the number of moles in a volume of solution of known molarity (Section 2.1);
3. prepare a solution given the volume and concentration of the solution (Section 2.1);
4. use prefixes m (milli), μ (micro) and n (nano) (Section 2.1);
5. convert between different concentration units (Section 2.2);
6. calculate the concentration of a solution after a dilution (Section 2.3);
7. dilute solution of known concentration to one of a desired concentration (Section 2.3);
8. use Beer's Law to determine the concentration of a solution (Section 2.4);
9. determine the limiting reactant from a balanced chemical equation and the concentrations and volumes of the reactants (Section 2.4);
10. determine the volume of one reactant of known concentration that reacts with a known volume of another of known concentration (Section 2.4);
11. determine the concentrations of the excess reactants (Section 2.4);
12. describe the causes of the colligative properties at the molecular level (Section 2.5);
13. determine the van't Hoff factor (i) for a compound (Section 2.5);
14. convert normal concentrations into colligative concentrations (Section 2.5);
15. calculate the vapor pressure of a solution given the mole fraction of the solute and the vapor pressure of the solvent (Section 2.5);
16. determine the boiling and freezing points of a solution from the solute concentration and the boiling and freezing point depression constants of the solvent (Section 2.5);
17. determine the osmotic pressure of a solution of known concentration (Section 2.5);
18. explain how osmosis is important in biological systems (Section 2.5);
19. explain the utility of reverse osmosis (Section 2.5);
20. distinguish between a colloid and a solute (Section 2.6); and
21. name the five classes of colloids and give an example of each (Section 2.6).

2.7 EXERCISES

CONCENTRATION UNITS

1. How many grams of CuSO_4 are required to make 650. mL of a 0.115 M solution?
2. How many grams of NaCl are required to prepare 250. mL of a 0.241 M solution?
3. How many grams of Na_2SO_4 are required to make 90.0 mL of a solution that is 0.200 M in Na^{1+} ?
4. How many mmols of each ion are present in 325 mL of a 0.0817 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$?
5. How many mmols of chloride ion are in 55.0 mL of 0.0688 M BaCl_2 solution?
6. How many mL of a 0.338 M Na_3PO_4 are required to deliver 23.6 mmol of sodium ion?
7. How many mL of 0.124 M $\text{Ba}(\text{OH})_2$ are required to deliver 38.6 mmol of hydroxide ion?
8. How many mL of a 0.125 M aqueous solution of NaNO_3 could be made from 3.50 g of NaNO_3 ?
9. How many grams of sodium should be added to 15.0 g Hg to make a mixture in which the mole fraction of sodium is 0.800?
10. Drinking water in the USA cannot exceed 0.5 ppm mercury. What mass of mercury is present in 1.0 L of water at this concentration? What is the molar concentration of mercury?
11. The density of a 1.140 M solution of NH_4Cl at 20 °C is 1.0186 $\text{g}\cdot\text{mL}^{-1}$. What mass of water does 100. mL of this solution contain?
12. What is the mass percent sucrose in a 0.180 m aqueous solution of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$, $M_m = 342 \text{ g}\cdot\text{mol}^{-1}$)?
13. What mass of $\text{Fe}(\text{ClO}_4)_3$ is required to make 275 mL of a solution that is 0.100 M in ClO_4^{1-} ?
14. How many grams of Na_2SO_4 should be added to 285 g of water to make a solution with a colligative molality of 0.500 m?
15. How many grams of CaCl_2 should be added to 50.0 g of water to make a solution in which the mole fraction of Cl^{1-} is 0.150?

CHANGING CONCENTRATION UNITS

16. The label on a bottle of vinegar indicates that it is 4.2% acetic acid (CH_3COOH). If the density of the solution is 1.01 $\text{g}\cdot\text{mL}^{-1}$, what is the molarity of the solution?
17. Concentrated H_3PO_4 is 75% and has a density of 1.57 $\text{g}\cdot\text{mL}^{-1}$.
 - a) What is the molarity of concentrated phosphoric acid?
 - b) How many mL of the concentrated acid would be required to prepare 1.5 L of a 0.20 M solution of H_3PO_4 ?
18. The concentration of grain alcohol ($\text{C}_2\text{H}_5\text{OH}$) in whisky is given in ‘proof’, which is twice the percent alcohol by volume (v/v). What are the mole fraction and molality of $\text{C}_2\text{H}_5\text{OH}$ in 90 proof vodka? Assume that vodka is a solution of only $\text{C}_2\text{H}_5\text{OH}$ and water and that the volumes are additive. The density of $\text{C}_2\text{H}_5\text{OH}$ is 0.79 $\text{g}\cdot\text{mL}^{-1}$.
19. A 60/40 solder is a solution that is 60% Pb and 40% Sn. What are the two mole fractions in the solder?
20. The solubility of $\text{Mg}_3(\text{PO}_4)_2$ is 6 μM . How many ppm of *magnesium ion* are in a saturated solution?
21. What is the molality of a sucrose solution if its mole fraction is 0.025?
22. Cisplatin, $(\text{NH}_3)_2\text{Cl}_2\text{Pt}$, is a chemotherapy agent for the treatment of some cancers. Determine the mass of cisplatin in 100. mL of each of the following solutions:
 - a) 1.0 μM $(\text{NH}_3)_2\text{Cl}_2\text{Pt}$
 - b) 1.0 ppm $(\text{NH}_3)_2\text{Cl}_2\text{Pt}$
 - c) 1.0 ppm $(\text{NH}_3)_2\text{Cl}_2\text{Pt}$
23. Pure, crystalline Si is a poor conductor, but it can be converted into a p-type semiconductor by dissolving 1.0 ppm Ga in the Si crystal. This is a process called “doping” in the semiconductor industry. Given that the molar mass of Si is 28.086 and of Ga is 69.72, what is the mole fraction of Ga in the crystal? The density of the p-type Si semiconductor is 2.33 $\text{g}\cdot\text{cm}^{-3}$.
24. What is the concentration of CaCl_2 expressed as percent in an aqueous solution that is 0.820 M in CaCl_2 and has a density of 1.070 $\text{g}\cdot\text{mL}^{-1}$.
25. What is the molality of a 2.06 M solution of H_2SO_4 ($d = 1.124 \text{ g}\cdot\text{mL}^{-1}$)?

DILUTION

26. 265 mL of a 0.125 M NaCl solution is left uncovered. What is the molarity of the solution if evaporation reduces the volume to 186 mL?
27. What is the molarity of a solution prepared by adding 30.0 mL of water to 57.0 mL of a 0.114 M CuSO₄ solution? Assume additive volumes.
28. To what volume should 10 mL of 12 M HF be diluted to make 0.50 M HF?
29. What volume of an 18.0 M stock solution of H₂SO₄ is needed in order to make 100. mL of 3.0 M H₂SO₄ solution?
30. How many mL of 9.85 M H₂SO₄ are needed to prepare 500. mL of 0.0850 M H₂SO₄?
31. What is the [H⁺] in a solution prepared by diluting 20.0 mL of 12.0 M HCl to 350. mL?
32. What is the [H⁺] in a solution prepared by mixing 1.0 L of 2.0 M HCl, 1.6 L of 0.80 M HCl, 0.50 L of 3.0 M HCl, and 1.4 L of water?
33. What is the molarity of the chloride ion in a solution prepared by mixing 75 mL of 0.20 M NaCl and 55 mL of 0.15 M MgCl₂? Assume that volumes are additive.
34. 20.0 mL of 2.50 M stock solution is diluted to 50.0 mL. A 15.0-mL sample of the resulting solution is then diluted to 45.0 mL. A 20.0-mL sample of this solution is then diluted to 75.0 mL. What is the concentration of sucrose in the final solution?
35. 100.0 mL of a stock solution of hydrochloric acid was diluted to 250.0 mL. A 10.0-mL sample of the resulting solution was then diluted to 250.0 mL. The final solution was prepared by diluting 30.0 mL of this solution to 100.0 mL. A 40.0-mL sample of the final solution was titrated with 0.0887 M NaOH. If the titration required 32.6 mL of the base, what is the concentration of the original stock solution?
36. A solution, which is prepared by four consecutive 1:4 dilutions of a stock solution, has a concentration of 0.244 mM. What is the concentration of the stock solution?
37. A stock solution that is 0.4762 M undergoes the following successive dilutions: 1:3, 2:5, 1:10, and 2:15. What is the concentration of the final solution?

BEER'S LAW

38. The manganese concentration in steel can be determined spectrophotometrically by dissolving the steel in acid and oxidizing Mn to MnO₄¹⁻. The resulting solution is purple and the absorbance at 525 nm can be monitored. A standard solution that is 0.228 mM in MnO₄¹⁻ has an absorbance of 0.343 in a 1.00-cm cell. The absorbance of an unknown manganese solution in the same cell is 0.468. What is the molar concentration of Mn in the unknown solution?
39. Formaldehyde, CH₂O (M_m = 30.03 g·mol⁻¹), is an atmospheric pollutant that can be measured in aqueous solutions by reaction with 1,3,5-trihydroxy-benzene to produce a red-orange dye. A standard solution was prepared by dissolving 1.50 mL of formaldehyde gas (at 1.00 atm pressure and 25 °C) in 1.00 L of water. This solution was treated with an excess of 1,3,5-trihydroxy-benzene. A couple of milliliters of the resulting solution was placed in a spectrophotometric cell with a thickness of 1.00 cm and the absorbance was found to be 0.967 at 470 nm. A 1.00-L sample of rainwater was similarly treated and the absorbance, measured in the same cell, was determined to be 0.426. What is the concentration of formaldehyde in the rainwater? Express your answer in both molar and ppm units.
40. A 2.78×10⁻⁴ M solution has an absorbance of 0.449 at 520 nm in a 1.00-cm cell. The solvent's absorbance under the same conditions is 0.012.
 - a) What is the molar absorptivity of the solute?
 - b) What is the solute concentration in a solution with an absorbance of 0.368 in a 1.00-cm cell at 520 nm?
41. Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine) was investigated for its possible use in solar energy conversion. A solution was prepared by dissolving 58.2 mg Ru(bpy)₃(ClO₄)₂ (M_m = 612 g·mol⁻¹) in enough water to make 100.0 mL of solution. However, the resulting solution absorbed too strongly at 450 nm to be measured, so 5.0 mL of the solution was diluted to 100.0 mL. The absorbance of the final solution at 450 nm in a 1.00-cm cell was determined to be 0.571.
 - a) What is the molar absorptivity of Ru(bpy)₃²⁺ at 450 nm?
 - b) What is the concentration of Ru(bpy)₃²⁺ in a solution with an absorbance of 0.885 at 450 nm?

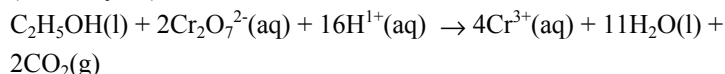
42. Ammonia can be determined spectrophotometrically by reaction with phenol ($\text{C}_6\text{H}_5\text{OH}$) in the presence of OCl^- ion. The product of the reaction absorbs at 625 nm. The nitrogen in a protein was determined in the following manner.
- Reference: A solution was made by dissolving 10.0 mg NH_4Cl in water. Phenol and KOC were then added. After reaction, the solution was diluted to 1.00 L. 20.0 mL of the solution was then diluted to 100.0 mL, and the absorbance was found to be 0.168 at 625 nm. What is the molar absorptivity of the product of the reaction between ammonia and phenol in the presence of hypochlorite?
 - Sample: All of the nitrogen in 5.02 mg of a protein was converted into ammonia. Then phenol and KOC were added. After the reaction, the solution was diluted to 500. mL and the absorbance was measured to be 0.564 at 625 nm. How many mmols of nitrogen were in the original sample? What is the mass percent of nitrogen in the protein?

COLLIGATIVE PROPERTIES

- What is the colligative molality of a solution prepared by dissolving 15.2 g of AlCl_3 ($M_m = 133.3 \text{ g}\cdot\text{mol}^{-1}$) in 155 mL of water?
- List the freezing points of 0.10 m aqueous solution of the following in decreasing order. Explain your reasoning.
 $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ CaCl_2 CaSO_4
- What is the freezing point of a 0.11 m aqueous CaCl_2 solution?
- What is the osmotic pressure of a 0.056 M aqueous NaCl at 298 K?
- What is the osmotic pressure of a 0.20 M CaCl_2 solution at 298 K?
- As a very rough general rule, increasing the temperature of a reaction by 10 °C doubles the rate of reaction. Approximately how many grams of salt should be added to 1.5 qts (~ 1.5 L) of water to increase the boiling water by 10 °C? Would this be a satisfactory way in which to reduce the time required to make “boiled potatoes”?
- A solution is prepared by dissolving 1.0 g of CaCl_2 in 100. mL of water to produce a solution with a density $1.1 \text{ g}\cdot\text{mL}^{-1}$.
 - What is the vapor pressure of the solution at 20 °C? The vapor pressure of water at 20 °C is 17.5 mm Hg?
 - What is the boiling point of the solution?
 - What is the freezing point of the solution?
 - What osmotic pressure would develop at 25 °C when the solution is placed in contact with pure water at a semipermeable membrane?
- The colligative molality of seawater is about 1.10 m, and its density is about $1.05 \text{ g}\cdot\text{mL}^{-1}$.
 - What is the vapor pressure of the solution at 20 °C? The vapor pressure of water at 20 °C is 17.5 mm Hg.
 - What is the normal boiling point of seawater?
 - What is the freezing point of seawater?
- The colligative molarity of living cells is typically 0.3 M. What osmotic pressure would develop when the cells are placed in pure water at 37 °C? What effect would this have on the cell?
- Pepsin is the principal digestive enzyme of gastric juice. A 1.50-g sample of pepsin is dissolved in enough water to make 5.00 mL of solution. The osmotic pressure of the solution is found to be 0.213 atm at 25 °C. What is the molar mass of pepsin?
- 15.8 mg of a protein is dissolved in enough water to make a 5.00-mL solution. What is the molar mass of the protein if the osmotic pressure of the solution at 15 °C is 4.65 torr?
- A solution is prepared by dissolving 1.63 g of an unknown organic compound in 15.00 g of cyclohexane. What is the molar mass of the compound if the solution has a melting point of -5.1 °C? See Table 2.4 for information about cyclohexane.
- Vitamin K is involved in normal blood clotting. When 1.00 g of vitamin K is dissolved in 20.0 g of camphor, ($k_f = 40.0 \text{ }^\circ\text{C}\cdot\text{m}^{-1}$) the freezing point of the solution is lowered by 4.43 °C. What is the molar mass of vitamin K?

SOLUTION STOICHIOMETRY

56. Alcohol levels can be determined by reaction with dichromate (breathalyzer).



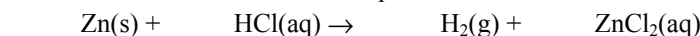
What is the alcohol level expressed in parts per thousand of a blood plasma if a 30.0-g sample of plasma requires 27.43 mL of a 0.02226-M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ for complete reaction?

57. What is the concentration of the excess reactant in a solution prepared by mixing 25.0 mL of 0.242 M HCl with 36.3 mL of 0.167 M $\text{Ba}(\text{OH})_2$? Is this solution acidic, basic or neutral?
58. Given the *unbalanced* chemical equation:
 $\text{Al}(\text{OH})_3(\text{s}) + \text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 How many mL of 2.00 M HCl are required to react completely with 50.0 g of $\text{Al}(\text{OH})_3$?
59. Determine the amount of precipitate that will form if 50.0 mL of 0.100 M $\text{Na}_2\text{SO}_4(\text{aq})$ and 100. mL of 0.300 M BaCl_2 are mixed.
60. Construct the reaction table for the *net* reaction resulting when 45.0 mL of 0.0886 M AgNO_3 and 35.0 mL of 0.106 M K_2CrO_4 are mixed.
 a) What mass of precipitate would form?
 b) Assume additive volumes and determine the concentration of the excess reactant after the reaction is complete?
61. Construct the reaction table for the *net* reaction of 36.6 mL of 0.0668 M FeCl_3 and 24.2 mL of 0.100 K_2S .
 a) What mass of Fe_2S_3 precipitates?
 b) What is the concentration of the excess reactant after complete reaction? Assume additive volumes.

MISCELLANEOUS PROBLEMS

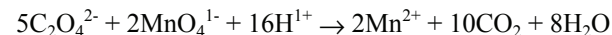
62. Trichloroethylene, C_2HCl_3 is used as a dry cleaning solvent and an industrial extraction agent. The EPA (Environmental Protection Agency) has set a limit of 5.0 ppb C_2HCl_3 in drinking water. Assuming that the average person consumes 2.0 L of drinking water in a day, what is the maximum mass of trichloroethylene to which a person could be exposed through drinking water? Drinking water has a density of $1.0 \text{ g}\cdot\text{mL}^{-1}$.

63. Given the *unbalanced* chemical equation:



If 130. mL of $\text{HCl}(\text{aq})$ reacts with an excess of Zn, the reaction produces 7.00 L of $\text{H}_2(\text{g})$ at 273 K and 1.00 atm. What is the molarity of the HCl?

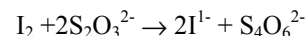
64. A 0.250 m aqueous solution of $\text{Co}(\text{NH}_3)_4\text{Cl}_3$ freezes at -0.93°C . Determine the van't Hoff factor for the complex ion.
65. A solution is prepared by dissolving 5.863 g of impure NaOH in sufficient water to make 1.000 L of solution. The solution is added to a buret and used to titrate 25.00 mL of a 0.1173 M solution of HCl.
 a) What is the molarity of the NaOH solution if the titration requires 28.04 mL of base.
 b) What is the percent purity of the original NaOH sample?
66. A 0.5843-g sample of impure $\text{Ca}(\text{OH})_2$ is dissolved in 50.00 mL of water. 20.00 mL of the resulting solution is then titrated with 0.1164 M HCl. What is the percent purity of the $\text{Ca}(\text{OH})_2$ if the titration requires 22.18 mL of acid?
67. A 10.00-mL sample of blood was diluted to 100.00 mL. 10.00 mL of the resulting solution was analyzed for calcium by precipitating all of the calcium as calcium oxalate, CaC_2O_4 . The solid CaC_2O_4 was then re-dissolved in H_2SO_4 and titrated with KMnO_4 . What is the Ca^{2+} ion concentration in the blood sample expressed as (milligrams Ca^{2+})/(mL blood) if the endpoint was reached with the addition of 1.14 mL of 0.00886 M KMnO_4 ?



68. Vitamin C or ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) can be analyzed by first oxidizing it with an excess of I_2 by the following reaction:



and then determining the amount of excess I_2 by titration with $\text{S}_2\text{O}_3^{2-}$.



A tablet that is supposed to contain 500-mg of vitamin C was dissolved in water and 100.00 mL of 0.06246 M I_2 was added. After complete oxidation of the ascorbic acid, the solution was titrated with $\text{S}_2\text{O}_3^{2-}$. How many milligrams of vitamin C were in the tablet if the titration required 63.69 mL of 0.1127 M $\text{K}_2\text{S}_2\text{O}_3$?

69. All of the iron in 1.314 g of an ore was converted to Fe^{2+} , which was then analyzed by titration with dichromate. What is the mass percent of iron in the ore if 38.64 mL of 0.02063 M $\text{K}_2\text{Cr}_2\text{O}_7$ was required to reach the equivalence point? The chemical equation for the titration is
- $$14\text{H}^{1+} + \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$
70. The chloride ion concentration in a sample of seawater was analyzed by titration with 0.1126 M AgNO_3 to precipitate AgCl . What is the chloride ion concentration in a 10.00-mL sample, if the titration required 46.78 mL of 0.1126 M AgNO_3 to reach the endpoint? If the density of seawater is $1.012 \text{ g}\cdot\text{mL}^{-1}$, what is the mass percent of chloride ion in the sample?
71. The concentration of a stock solution of Rhodamine B, a commercial dye ($\epsilon = 1.060 \times 10^5 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at 543 nm) is determined spectrophotometrically, but the absorbance of the stock solution was too great to read on a spectrometer, so 15.00 mL of the solution was diluted to 250.00 mL. The resulting solution was still too concentrated, so 10.00 mL of that solution was diluted to 500.00 mL, but the solution was still too concentrated. However, a dilution of 25.00 mL of the resulting solution to a final volume of 500.00 mL provided an acceptable solution with an absorbance of 0.1814 in a 1.000-cm cell. What is the concentration of the stock solution? What volume of stock solution would be required to make 2.000 L of a solution with an absorbance of 1.000 in a 1.000-cm cell?
72. What is the iron(III) concentration in an acidified solution if adding an excess of hydroxide to 20.00 mL of the solution produced 181 mg of $\text{Fe}(\text{OH})_3$?
73. How many grams of NaCl must be added to 120 mL of water at 25°C to prepare a solution with a vapor pressure of 20.0 torr? At 25°C , the density of water is $1.0 \text{ g}\cdot\text{mL}^{-1}$, and its vapor pressure is 23.8 torr.

CHAPTER 3

The First Law of Thermodynamics

3.0 Introduction

3.1 Some Definitions and Conventions

3.2 Work, Heat, and Energy

3.3 The First Law of Thermodynamics

3.4 Enthalpy

3.5 Standard States & Properties of ΔH

3.6 Hess' Law of Heat Summation

3.7 Enthalpies (or Heats) of Formation

3.8 Bond Dissociation Energies

3.9 Calorimetry

3.10 Combustion: Food as Fuel

3.11 Chapter Summary and Objectives

3.12 Exercises

3.0 INTRODUCTION

Almost all reactions involve energy changes because the potential energy of the products and the reactants usually differ. If the potential energy of the products is greater than that of the reactants, energy must be supplied to the reaction to make the reaction proceed. However, if the products are at lower potential energy, energy is released during reaction. The released energy can be used to drive turbines and pistons, run batteries, and even supply the energy used by our bodies while we work and play. An understanding of the energy changes that take place during a reaction allows us to determine how best to run the reaction and even how much product we can expect under various conditions. The study of the energy changes that accompany chemical reactions is known as thermochemistry, which is a branch of the more general field of thermodynamics - the study of energy and its transformations. In this chapter, we discuss the first law of thermodynamics, define some important terms, and demonstrate some valuable tools that can be used to determine the energy requirements of reactions.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- define energy, heat, and work and to show the relationship between them;
- discuss the first law of thermodynamics and apply it to some simple systems;
- define state functions;
- relate the enthalpy of reaction to the energy change of the reaction;
- define standard states;
- discuss Hess' law and demonstrate its use;
- define enthalpies of formation and bond energies and demonstrate their use;
- explain how the energy content in food is determined; and
- discuss how enthalpies of reaction are determined experimentally.

3.1 SOME DEFINITIONS AND CONVENTIONS

In our study of thermodynamics, we will be interested in the *changes* in the thermodynamic properties that accompany a process. A change is designated by the symbol “ Δ ”. For example, “ ΔX ” means a change in the quantity X . The sign of ΔX indicates the direction of the change because $\Delta X \equiv X_{\text{final}} - X_{\text{initial}}$. Consequently, $\Delta E = 50 \text{ J}$ means that the final energy is 50 J greater than the initial energy (*i.e.*, the energy increased by 50 J). Similarly, $\Delta E = -50 \text{ J}$ means that the energy of the final state is 50 J lower than the initial state or that the energy decreased by 50 J.

Indicating that the energy changed by 50 J means little without knowledge of what it is that experienced the change. Consequently, an important part of any thermodynamic problem is precisely defining the **system**, the reference object or process. Everything that interacts with the system is known as the **surroundings**. Together, the system and its surroundings comprise the **thermodynamic universe**; that is, thermodynamic universe = system + surroundings. Thus, we can write $\Delta E_{\text{univ}} = \Delta E + \Delta E_{\text{sur}}$. Note that subscripts are used to specify changes in the universe and the surroundings, but none are used for the system. Thus, $\Delta E = -50 \text{ J}$ implies that the *energy of the system* dropped by 50 J, while $\Delta E_{\text{sur}} = +50 \text{ J}$ means that the energy of the surroundings increased by 50 J.

Let’s apply these ideas to a cash flow problem in which you write a check to a friend for \$50. The first step in “setting up the books” is to define the system, which is taken as your account. Only your friend’s account interacts with (accepts money from) the system, so it can be thought of as the surroundings. If ΔB is the change in the balance of your account (the system), then $\Delta B = -\$50$ because money transferred out of the system, which caused your balance to decrease by \$50. Similarly, $\Delta B_{\text{sur}} = +\50 because money transferred into the surroundings, which increased the balance in your friend’s account by \$50. Money was *conserved* in the process because money was neither created nor destroyed, $\Delta B_{\text{univ}} = \Delta B + \Delta B_{\text{sur}} = -50 + 50 = 0$. Money was simply transferred from the system to the surroundings. Note that, $\Delta B = +\$50$ if the system is defined as your friend’s account, and, if both accounts are in the same bank, $\Delta B = 0$ if the bank is the system. Consequently, it is very important to clearly define the system in any process.

3.2 WORK, HEAT, AND ENERGY

Work is a force through a distance and is represented by the symbol w . As shown in Figure 3.1, the sign of w simply indicates whether the work was done on or by the system.

w = work done on the system

$-w$ = work done by the system

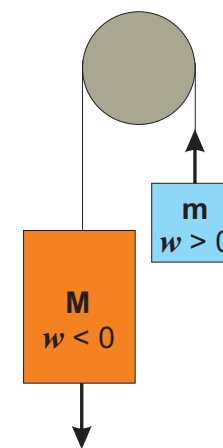


Figure 3.1 Work and the sign of w

As the large mass M drops, its potential energy decreases. Part of the lost potential energy is used to do work as the smaller mass m is lifted. If mass m is the system, $w > 0$ as work is done on it, but if mass M is the system, $w < 0$ as work is done by it.

Thus, $w = +50 \text{ J}$ is read ‘50 joules of work was done on the system’. However, a minus sign is not read explicitly, rather it is indicated by the use of the word *by*. Consequently, $w = -50 \text{ J}$ is usually read as ‘50 joules of work was done by the system.’

Heat is that form of energy that is transferred as a result of temperature differences and is represented by the symbol q . The sign of q indicates the direction of the heat flow.

q = heat absorbed by the system $-q$ = heat given off by the system

Thus, $q = +50 \text{ J}$ is read ‘50 J of heat was absorbed by the system.’ Once again, a minus sign is not read explicitly, and $q = -50 \text{ J}$ is read ‘50 J of heat was given off by the system.’ When $q > 0$, heat enters the system, and the process is said to be **endothermic**. Endothermic processes increase the energy of the system (Figure 3.2a). When $q < 0$, heat exits the system, and the process is said to be **exothermic**. Exothermic processes reduce the energy of the system (Figure 3.2b).

When heat is added to a chemical system, it usually results in either a temperature rise or a phase change (vaporization, sublimation, or melting). If the *heat results only in a temperature rise*, then the amount of heat absorbed by a system is proportional to the temperature change it undergoes. The proportionality constant is called the **heat capacity, C** , of the system. Equation 3.1 is used to determine the amount of heat transferred when the temperature of a system with a heat capacity C changes by ΔT degrees.

$$q = C\Delta T$$

Eq. 3.1

In Equation 3.1, the temperature change ΔT ($T_{\text{final}} - T_{\text{initial}}$) has the same numerical value in either Celsius or Kelvin, and the most common units for the heat capacity are $\text{J}\cdot^\circ\text{C}^{-1}$. The heat capacity depends not only on the substance but on its mass as well. Water does not have a unique heat capacity but a specified mass of water does. For example, the heat capacity of 12 g of water is $50 \text{ J}\cdot^\circ\text{C}^{-1}$. Tabulated values are usually given for the heat capacities of one gram of material. This quantity is called the **specific heat, s** . Specific heats are normally given in $\text{J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$. Table 3.1 shows the specific heats of several substances. A high specific heat implies that the substance can absorb a substantial amount of heat with a relatively small temperature rise. Heat capacity (C) is related to the specific heat (s) and mass (m) of the sample by Equation 3.2.

$$C = ms$$

Eq. 3.2

The **molar heat capacity, \bar{C}** , is the heat capacity of a mole of substance and has units of $\text{J}\cdot\text{mol}^{-1}\cdot^\circ\text{C}^{-1}$.

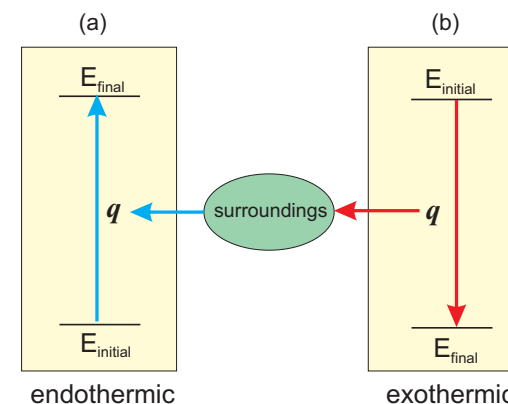


Figure 3.2 Heat and the sign of q

- In an endothermic process, $q > 0$ as heat flows from the surroundings into the system, thereby increasing the energy of the system, $\Delta E = E_{\text{final}} - E_{\text{initial}} = q > 0$.
- In an exothermic process, $q < 0$ as heat flows from the system into the surroundings, thereby decreasing the energy of the system, $\Delta E = E_{\text{final}} - E_{\text{initial}} = q < 0$.

Table 3.1. Specific heats of selected substances

Substance	Specific Heat ($\text{J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$)
Al(s)	0.90
Cu(s)	0.38
Fe(s)	0.44
Hg(l)	0.14
Kr(g)	0.25
$\text{N}_2(\text{g})$	1.04
$\text{CCl}_4(\text{l})$	0.86
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	2.46
$\text{H}_2\text{O}(\text{l})$	4.18
$\text{H}_2\text{O}(\text{s})$	2.0
$\text{H}_2\text{O}(\text{g})$	2.0

Example 3.1

How much heat is required to heat 17 g of ice from $-12\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$? The specific heat of ice is $2.0\text{ J}\cdot\text{g}^{-1}\cdot^{\circ}\text{C}^{-1}$.

Combining Equations 3.1 and 3.2 we can write

$$q = ms\Delta T$$

where $\Delta T = T_{\text{final}} - T_{\text{initial}} = 0 - (-12) = +12\text{ }^{\circ}\text{C}$, so

$$q = (17\text{ g})(2.0\text{ J}\cdot\text{g}^{-1}\cdot^{\circ}\text{C}^{-1})(12\text{ }^{\circ}\text{C}) = +4.1 \times 10^2\text{ J} = 0.41\text{ kJ}$$

If 0.41 kJ of heat is added to 17 g of ice at $-12\text{ }^{\circ}\text{C}$, the ice would warm to $0\text{ }^{\circ}\text{C}$, but more heat would be required to melt it.

Energy is the capacity to do work or to transfer heat. It can take the form of either kinetic or potential energy. **Kinetic energy (KE)** is energy of motion. Any particle that is moving has the capacity to do work or to transfer heat. For example, the kinetic energy of a moving truck has the capacity to do work by simply colliding with another object and moving the object through a distance. It also has the capacity to transfer heat through the brake drums and tires when the brakes are applied. Recall that one of the postulates of the kinetic molecular theory of gases is that temperature is a measure of the average kinetic energy of the molecules. Thus, increasing the temperature of a system increases the kinetic energy (speed) of the particles in the system.

Potential energy is energy of position. A truck parked at the top of a hill has potential energy due to its position. It has no kinetic energy when it is parked, but when the brake is released, it begins to move as its potential energy is converted into kinetic energy. The truck rolls downhill because doing so reduces its potential energy. Similarly, chemical bonds form because the potential energy of the bound atoms is lower than the potential energy of the separated atoms. Molecules like trinitrotoluene (TNT), sugar, and octane (a component of gasoline) release energy when they react with oxygen because the potential energy of the bonds they form is lower than the potential energy of the original bonds. Gases also condense to liquids because the potential energy of the molecules is lower in the liquid (intermolecular interactions) than in the gas (no interactions).

PRACTICE EXAMPLE 3.1

A person lifts a 70 kg mass to a height of 2.0 m. The effort requires 1.4 kJ of work.

If the person is the system, $w =$ _____.

If the mass is the system, $w =$ _____.

Fill in the following blanks with on or by.

1.4 kJ of work was done _____ the person, and 1.4 kJ of work was done _____ the mass.

A piece of metal is placed into hot water. 120 J of heat is transferred from the water to the metal.

If the metal is the system, $q =$ _____ and the process is said to be _____ thermic.

If the water is the system, $q =$ _____ and the process is said to be _____ thermic.

Fill in the following blanks with absorbed or given off

120 J of heat were _____ by the metal and

120 J of heat were _____ by the water.

3.3 THE FIRST LAW OF THERMODYNAMICS

The **first law of thermodynamics** states that energy is conserved in all processes.*

$$\Delta E_{\text{univ}} = 0 \quad \text{Eq. 3.3}$$

Another common statement is that energy cannot be created or destroyed. The energy change in the universe is simply the sum of the energy changes in the system and its surroundings, so Equation 3.3 can also be expressed in the following form:

$$\Delta E + \Delta E_{\text{sur}} = 0$$

Solving for the energy change in the system, we arrive at Equation 3.4.

$$\Delta E = -\Delta E_{\text{sur}} \quad \text{Eq. 3.4}$$

Energy cannot be created or destroyed, but it can be transferred between a system and its surroundings (Equation 3.4). We conclude that *all energy leaving a system enters the surroundings, and all energy entering a system comes from the surroundings.*

Heat and work are the two most common ways of transferring energy between a system and its surroundings. The energy of a system increases when work is done on it ($w > 0$) and/or it absorbs heat ($q > 0$), but its energy decreases when it does work ($w < 0$) and/or gives off heat ($q < 0$). These relationships are summarized in Equation 3.5, which is another common expression of the first law of thermodynamics.

$$\Delta E = q + w \quad \text{Eq. 3.5}$$

Example 3.2

What energy change is experienced by a system that absorbs 358 J of heat and does 412 J of work?

The energy of a system increases when it absorbs heat, but its energy decreases when it does work, so the energy change of the system equals the heat absorbed by the system minus the work done by the system: $\Delta E = 358 - 412 = -54$ J.

Alternatively, we can use Equation 3.5. The system absorbs 358 J of heat so $q = +358$ J. The system also does 412 J of work, so $w = -412$ J. Thus, we obtain the following:

$$\Delta E = q + w = 358 - 412 = -54 \text{ J}$$

The energy of the system drops by 54 J, which means that the energy of the surroundings increases by 54 J.

As an example of energy transfer with heat and work, consider the experiment shown in Figure 3.3. A green object of mass **M** falls a distance **d** from a table to the floor while

* Due to the equivalence of mass and energy, $E = mc^2$, the statement should indicate that 'mass-energy' is conserved. However, mass-energy considerations are only important in nuclear reactions, the topic of Chapter 11.

lifting a smaller red object with mass **m**. We assume that all of the kinetic energy of mass **M** is converted into heat when it strikes the floor.* We divide the surroundings into a thermal and mechanical components. The **thermal surroundings** exchange energy with a system in the form of heat. The floor is the thermal surroundings in Figure 3.3. The faster the system (mass **M**) hits the floor, the greater is the amount of energy that is transferred to the thermal surroundings. The **mechanical surroundings** exchange energy with a system in the form of work. The red mass **m** is the mechanical surroundings in Figure 3.3. The amount of energy transferred to the mechanical surroundings increases as **m** increases.

Consider the how energy transfer varies as a function of the smaller mass **m** when mass **M** falls a distance **d** as shown in Figure 3.3. We assume that $\Delta E = -100 \text{ J}$ for the fall.

- If **m** = 0 (no smaller mass), no work is done ($w = 0$) and the entire 100 J is transferred to the thermal surroundings, $\Delta E = q = -100 \text{ J}$.
- If **m** is such that the system must do 70 J of work to lift the smaller mass ($w = -70 \text{ J}$), then only 30 J can be transferred to the thermal surroundings: $q = \Delta E - w = -100 - (-70) = -30 \text{ J}$.
- If **m** = **M**, all of the energy change would be transferred to the mechanical surroundings ($\Delta E = w = -100 \text{ J}$) leaving none to transfer to the thermal surroundings. No work could actually be done because a system cannot move without kinetic energy. This system is at equilibrium.

In the above experiments, we examined the transition between the same initial and final states by three different thermodynamic *paths* that differed in their distributions of q and w . ΔE was the same for each path because ΔE depends only upon the initial and final states - not on how they were achieved: $\Delta E = E_{\text{final}} - E_{\text{initial}}$. Properties, like energy, that depend only upon the state of the system are called **state functions**.† The fact that energy is a state function means that ΔE for a chemical process depends only upon the states of the reactants and products, not on the manner in which they react! This is an important property because it allows us to determine ΔE for a reaction using any path - even one that is unreasonable - as long as the reactants and products remain the same. Both q and w are path dependent, so they are not state functions. q and w for a reaction depend not only on the reactants and products; they also depend on how the reaction is carried out.

Almost all chemical reactions that are not insulated from their surroundings exchange energy with the thermal surroundings, but those that consume or produce gases can also exchange energy with the mechanical surroundings. We now show how to partition the energy change of such reactions into their heat and work components. We begin by expressing the ideal gas law for a mixture of gases.

$$PV = n_g RT$$

* The kinetic energy of the system is transferred to the molecules in the floor, which causes their temperature to rise. Cars are stopped by brakes in a similar manner as the kinetic energy of the car is converted into heat by the friction in the brake pads.

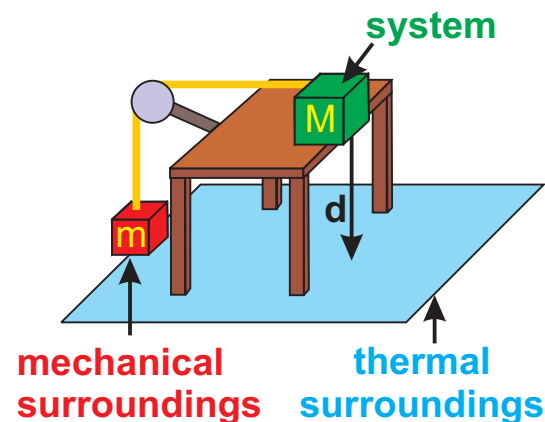


Figure 3.3 Energy is transferred as heat and/or work
As the green mass (the system) falls, it transfers energy to the mechanical surroundings by doing work on the red mass. When the system hits the floor, its remaining energy is transferred to the thermal surroundings. $\Delta E = q + w$, so as more energy is transferred to the mechanical surroundings (w), less energy is transferred to the thermal surroundings (q).

† n , P , V , and T are also state functions. Any property whose change is denoted with a “ Δ ” is a state function. Thus, a volume change is represented as ΔV because it depends only upon the initial and final volumes.

n_g is the total number of moles of gas in the mixture. If the mixture is a reaction mixture, then n_g may vary during the reaction as gases are either consumed or produced. However, most reactions are carried out at constant temperature and pressure,* so P, T, and R are all constant. Thus, the change in the number of moles of gas requires a change in the volume, which is expressed in Equation 3.6.

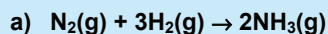
$$P\Delta V = \Delta n_g RT \quad \text{Eq. 3.6}$$

ΔV is the volume change caused by a change in the number of moles of gas, which is determined as follows:

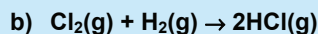
$$\Delta n_g = \text{moles of gas produced} - \text{moles of gas consumed} \quad \text{Eq. 3.7}$$

Example 3.3

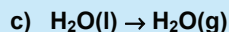
Determine Δn_g for each of the following processes.



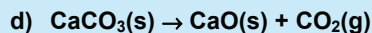
$$\Delta n_g = 2 \text{ mol produced (2NH}_3\text{)} - 4 \text{ mol consumed (1N}_2 + 3\text{H}_2\text{)} = -2 \text{ mol gas}$$



$$\Delta n_g = 2 \text{ mol produced (2HCl)} - 2 \text{ mol consumed (1Cl}_2 + 1\text{H}_2\text{)} = 0$$



$$\Delta n_g = 1 \text{ mol produced} - 0 \text{ mol gas consumed (reactant is a liquid)} = 1 \text{ mol gas}$$



$$\Delta n_g = 1 \text{ mol produced (CO}_2\text{)} - 0 \text{ mol consumed} = 1 \text{ mol gas}$$

Δn_g , which is moles of gas-phase products – moles of gas-phase reactants, is the actual change in the number of moles of gas during the process, not necessarily the number determined from the balanced chemical equation. Thus, $\Delta n_g = -2$ moles as determined in Example 3.3a is the change in the number of moles of gas when 1 mol N_2 reacts with 3 mol H_2 to produce 2 mol NH_3 . The fact that it is negative means that gas is consumed during the reaction. Δn_g for the process in which 4.0 g H_2 react would be determined as follows:

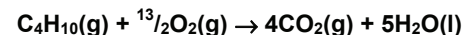
$$\Delta n_g = 4.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2} \times \frac{-2 \text{ mol gas change}}{3 \text{ mol H}_2 \text{ reacting}} = -1.3 \text{ mol gas change}$$

We next consider the transfer of energy between a reaction and its surroundings by examining the combustion of propane carried out at constant temperature and pressure

* Conditions of constant temperature and pressure are so common in chemical reactions that we restrict our discussions in this and the next chapter to the thermodynamics of systems at these conditions.

PRACTICE EXAMPLE 3.2

Consider the combustion of butane at 25 °C.



What is Δn_g for the reaction as written?

$$\Delta n_g =$$

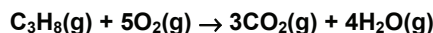
What is Δn_g for the combustion of 5.000 g of butane?

$$M_m = \text{_____ g} \cdot \text{mol}^{-1}$$

$$\text{mols C}_4\text{H}_{10} = \text{_____ mol}$$

$$\Delta n_g =$$

inside of a cylinder and piston (Figure 3.4). The reaction is



$\Delta n_g = +1$ mol (7 mol gas produced - 6 mol gas consumed), so one mole of gas is created during the reaction of one mole of propane. The reaction temperature is high enough to assure that the water is a gas. We make two observations during the reaction: 1) the reaction vessel gets very hot;* and 2) the volume of the container increases (the piston rises). The first observation indicates that the reaction is exothermic ($q < 0$), and the second observation indicates that work is being done by the piston ($w < 0$). Thus, the energy change of the reaction is transferred to the surroundings as both heat and work. We now focus on the work term.

The surroundings exert an opposing pressure (P_{op}) on the piston, which results in an opposing force (F_{op}) that is equal to the opposing pressure times the cross-sectional area of the piston (A). The piston does work when it moves a distance (d) against the opposing force.

$$\text{work done by the piston} = (F_{\text{op}})(d) = (P_{\text{op}}A)(d) = (P_{\text{op}})(Ad)$$

Ad is the cross-sectional area times the distance moved by the piston, which is the volume change of the gas; *i.e.*, $Ad = \Delta V$. The piston is being moved by the system, so

$$\text{work done by the system} = P_{\text{op}}\Delta V$$

We use the fact that w is the work done on (not by) the system to arrive at Equation 3.8.

$$w = -P_{\text{op}}\Delta V \quad \text{Eq. 3.8}$$

Equation 3.8 indicates that $w < 0$ when $\Delta V > 0$, which means that work is done by a system during an expansion. Similarly, work is done on a system during a compression ($\Delta V < 0$). The reaction is run at constant temperature and pressure, so the volume change in Figure 3.4 is due to an increase in the number of moles of gas inside the cylinder ($\Delta n_g = 1$ mol gas), so Equation 3.6 applies. Substitution of $\Delta n_g RT$ for $P\Delta V$ into Equation 3.8 yields Equation 3.9, which relates the work done on the system (w) as the result of changing the number of moles of gas.

$$w = -\Delta n_g RT \quad (R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \quad \text{Eq. 3.9}$$

Thus, work is done by a system ($w < 0$) that produces more gas than it consumes, work is done on a system ($w > 0$) that consumes more gas than it produces, and no work is done during reactions that do not change the number of moles of gas. In the combustion of propane given above, $\Delta n_g = 1$ mol gas. The positive sign of Δn_g means that $w < 0$ and work is done by the gas as it pushes the piston against the opposing atmospheric pressure.

* The cylinder gets very hot during the reaction, but the reaction can still be considered at constant temperature because energy is a state function. ΔE depends only on the initial and final states, so temperatures that are reached during the reaction are irrelevant so long as the temperatures are the same when the initial and final measurements are made.

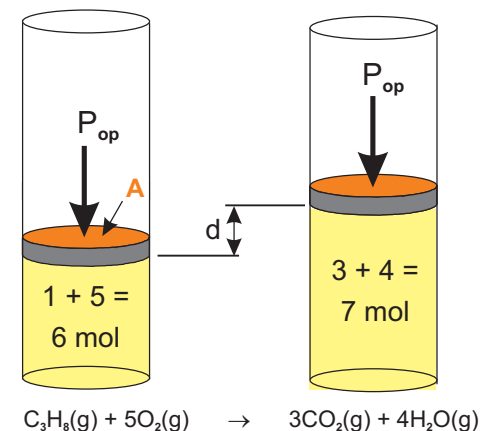


Figure 3.4 Work due to Δn_g

A piston with cross sectional area A moves a distance d because the number of moles of gas increases by a factor of 7/6 during the reaction. The piston does work as it moves against an opposing pressure of P_{op} .

Example 3.4

How much work is done during the ...

a) combustion of 25.0 g of propane at 298 K?

At 298 K, the water that is produced would be a liquid not a gas.* The reaction is



$\Delta n_g = 3 \text{ mol gas formed} - 6 \text{ mol gas consumed} = -3 \text{ mol gas/mole propane}$. We determine Δn_g for the reaction of 25 g as follows:

$$\Delta n_g = 25.0 \text{ g C}_3\text{H}_8 \times \frac{1 \text{ mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{-3 \text{ mol gas}}{1 \text{ mol C}_3\text{H}_8} = -1.70 \text{ mol gas}$$

Next use Equation 3.9 to determine w .

$$w = -\Delta n_g RT = -(-1.70 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) = 4.21 \times 10^3 \text{ J} = 4.21 \text{ kJ}$$

4.21 kJ of work is done on the gases ($w > 0$) by the atmosphere as the piston is pushed down by the atmosphere, decreasing the volume ($\Delta V < 0$).

b) evaporation of 12 g of water at 25 °C?

$\Delta n_g = +1 \text{ mol}$ for the evaporation of 1 mol H_2O : $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$, Δn_g for the evaporation of 12 g of water is determined as follows:

$$\Delta n_g = 12 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol gas}}{1 \text{ mol H}_2\text{O}} = 0.67 \text{ mol}$$

Next, use Equation 3.9 to determine the work.

$$w = -\Delta n_g RT = -(0.67 \text{ mol})(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298 \text{ K}) = -1.7 \times 10^3 \text{ J}.$$

1.7 kJ of work is done by 0.67 mole of escaping water molecules.

* The water would be produced as a gas due to the large amount of heat produced during the reaction, but after the reaction cooled to room temperature, the water would liquefy. Remember, it is only the initial and final conditions that matters.

PRACTICE EXAMPLE 3.3

Refer to the results for Practice Example 3.2 to determine the value of w for the combustion of 5.000 g of butane at 298 K?

$$w = \text{_____ J}$$

Thus, in the combustion of 5.00 g of butane _____ J of work are done (on or by) the system because of the change in the number of moles of gas.

3.4 ENTHALPY

The work described in Equation 3.9 is only one part of the energy change of reaction, and we now consider the other, heat. The heat absorbed[†] by a reaction at constant pressure (q_p) is called the **enthalpy of reaction**, ΔH ; *i.e.*, $\Delta H = q_p$. The enthalpy (heat) of reaction can be related to the energy change by substituting ΔH for q and $-\Delta n_g RT$ for w into $\Delta E = q + w$.

$$\Delta E = \Delta H - \Delta n_g RT \quad \text{Eq. 3.10a}$$

Solving for the enthalpy change, we obtain Equation 3.10b.

$$\Delta H = \Delta E + \Delta n_g RT \quad \text{Eq. 3.10b}$$

According to Equations 3.10a and 3.10b, $\Delta E = \Delta H$ for reactions in which the number of

[†] Defining enthalpy as the heat absorbed by the reaction allows us to specify the direction of the heat flow with the sign of the enthalpy change. When $\Delta H > 0$, the reaction absorbs heat, but when $\Delta H < 0$, the reaction releases heat.

moles of gas does not change; that is, $\Delta E = \Delta H$ for reactions in which $\Delta n_g = 0$.

Reactions are often run in sealed containers that do not undergo volume change (referred to as *bombs*). If there is no volume change, no work is done. The generation or consumption of gas results in a pressure change but not work. We may then substitute $q = q_v$, the heat absorbed at constant volume, and $w = 0$ into $\Delta E = q + w$ to obtain $\Delta E = q_v$.

To summarize, the *enthalpy of reaction is the heat absorbed when a process is carried out at constant pressure ($\Delta H = q_p$)*, while the *energy change is the heat absorbed when the same process is carried out at constant volume ($\Delta E = q_v$)*. Equation 3.10a can then be read as: the heat absorbed by a reaction carried out at constant volume (ΔE) is equal to the heat absorbed when the reaction is carried out at constant pressure (ΔH) plus the work done on the reaction as a result of a change in the number of moles of gas ($-\Delta n_g RT$).

Example 3.5

The enthalpy of vaporization of water at 25 °C is 44.0 kJ·mol⁻¹. What is ΔE for the vaporization of 12 g of water at 25 °C?

The thermochemical expression for the evaporation of one mole of H₂O at 25 °C is



The amount of work done by the gas is $\Delta n_g RT = 2.5\text{ kJ}$ (see Example 3.4). Applying Equation 3.10a to this process, we obtain

$$\Delta E = \Delta H - \Delta n_g RT = 44.0 - 2.5 = 41.5\text{ kJ}$$

Thus, a mole of water vapor at 25 °C has 41.5 kJ more energy than does a mole of liquid water at 25 °C, but the vaporization of a mole of water requires 44.0 kJ of heat because 2.5 kJ is extracted by the escaping molecules doing work as they push back the atmosphere. The work done by the gases is of no use to us; it is lost. What is important is that we must supply 44.0 kJ of energy to vaporize a mole of water.

We now take into account the fact that only 0.67 mole (12 g) of water actually evaporated. Although the units of ΔE as determined above are kJ, it is implied from the balanced equation that 41.5 kJ of energy are absorbed in the evaporation of one mole of water. Consequently, we can write

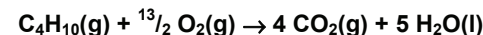
$$\Delta E = (41.5\text{ kJ}\cdot\text{mol}^{-1})(0.67\text{ mol}) = 28\text{ kJ}$$

The energy of 12 g H₂O is 28 kJ greater in the gas phase than in the liquid phase.

The remainder of this chapter is devoted to discussing ways of obtaining enthalpies of reaction and showing how they are used.

PRACTICE EXAMPLE 3.4

$\Delta E = -244.9\text{ kJ}$ for the combustion of 5.000 g of butane at 25 °C. What is ΔH_{comb} for a mole of butane?



moles of butane ($M_m = 58.12\text{ g}\cdot\text{mol}^{-1}$)

n = _____ mol

ΔE_{comb} per mole

$\Delta E_{\text{comb}} =$ _____ = _____ kJ·mol⁻¹

work term

$\Delta n_g =$

$\Delta n_g RT =$

$\Delta n_g RT =$

= _____ kJ·mol⁻¹

ΔH_{comb}

$\Delta H_{\text{comb}} =$ _____ kJ·mol⁻¹

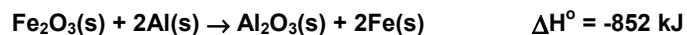
3.5 STANDARD STATES AND PROPERTIES OF ENTHALPY CHANGE

Enthalpy tables can be very useful when trying to make predictions about a reaction, but thermodynamic properties, such as enthalpy, vary with the state of the substance, its concentration if it is in solution, or its pressure if it is a gas. To assure that tabulated enthalpies are consistent, they are typically reported for processes in which the reactants and products are all in their **standard states**.

- The standard state of a pure substance is its most stable form at 1 atm pressure and the specified temperature. Unless indicated otherwise, it is assumed that solids and liquids are pure. Gases can be assumed pure even in mixtures because the molecules in the gas are far apart and have no significant effect on one another. Thus, the standard state of a gas is the gas at 1 atm pressure.
- The standard state of a dissolved substance is the substance at a concentration of 1 M at 1 atm pressure and the specified temperature.

There is no standard temperature, so the temperature should be specified. If no temperature is specified, then exactly 25 °C (298.15 K) should be assumed. However, 25 °C is simply the most common temperature; it is not the standard temperature. The standard state of a substance depends upon the temperature. For example, the standard state of water is a liquid at 1 atm and 25 °C, but it is a solid at 1 atm and -25 °C and a gas at 1 atm and 125 °C. A superscript zero is used to indicate that the thermodynamic property corresponds to the standard state value. Hence, ΔH° indicates the **standard enthalpy** of the process, which is the enthalpy of reaction when all reactants and products are in their standard states. All values of enthalpy given in this chapter are standard enthalpies.

A **thermochemical equation** is a chemical equation that also indicates a thermodynamic property of the reaction. Consider the thermochemical equation for the *thermite* reaction



The value of ΔH in the above equation indicates that 852 kJ of heat are *liberated* ($\Delta H < 0$) when one mole of solid Fe_2O_3 reacts with two moles of solid Al to produce one mole of solid Al_2O_3 and two moles of solid Fe. No temperature is given, so we assume a temperature of 298 K. The enthalpy change of the reaction is the standard enthalpy of reaction (as indicated by the superscript $^\circ$) because all of the substances are solids, and the solid is the standard state of each at 298 K.

The units of ΔH in a thermochemical equation are kJ, but it is important to realize that

the value applies to the reaction of the number of moles specified in the balanced equation. Some enthalpy changes are associated with the reaction of one mole of a named substance. In these cases, the enthalpy change is given in $\text{kJ}\cdot\text{mol}^{-1}$ when the reaction is not written. Thus, we would say that the heat of vaporization of water is $44.0 \text{ kJ}\cdot\text{mol}^{-1}$, but we write the thermochemical equation for the vaporization as



That is, the *per mole* is not included when the reaction is written because the chemical equation shows that the 44.0 kJ corresponds to the heat absorbed when 1 mol evaporates.*

Example 3.6

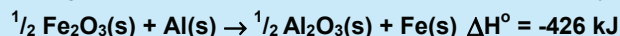
Use the thermochemical equation for the thermite reaction to determine the standard enthalpies for the following:

a) The reaction of 1.0 mol of Al with an excess of Fe_2O_3 .

We recognize that $\Delta H^\circ = -852 \text{ kJ}$ for the reaction of 2 mol Al, so we write

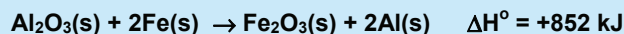
$$1 \text{ mol Al} \times \frac{-852 \text{ kJ}}{2 \text{ mol Al}} = -426 \text{ kJ}$$

Rewriting the thermochemical equation for the new quantity, we obtain



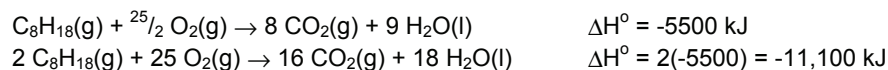
b) The reaction of 2.0 mol of Fe with an excess of Al_2O_3 .

Enthalpy is a state function, so the amount of energy required to convert the products of the original reaction back to the reactants, must be the same as the energy released when the reactants were first converted to products. The thermochemical equation is



Example 3.6 demonstrates two important properties of ΔH .

- 1) If a reaction is multiplied by a number, so too, is the enthalpy change.



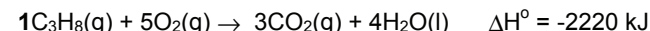
The amount of energy released is doubled when the amount of octane is doubled.

- 2) If a reaction is reversed, then the sign of the enthalpy of reaction is changed.



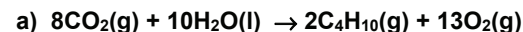
Thus, 6 kJ are absorbed when one mole of ice melts at its melting point, but 6 kJ are released ($\Delta H < 0$) when one mole of water freezes.

* The heat or enthalpy of combustion is another important example that we will use frequently. The **heat of combustion** of a substance is defined as the heat absorbed when one mole of the substance reacts with oxygen at constant pressure. The statement, "The standard heat of combustion of propane is $-2220 \text{ kJ}\cdot\text{mol}^{-1}$ at 298K," implies the following thermochemical equation:



PRACTICE EXAMPLE 3.5

Use the thermochemical equation for the combustion of butane from Practice Example 3.4 to determine ΔH for the following at 298 K:



$$\Delta H = \text{_____ kJ}$$

b) combustion of 25.0 g of butane ($M_m = 58.12 \text{ g}\cdot\text{mol}^{-1}$).

$$\Delta H = \text{_____ kJ}$$

3.6 HESS' LAW OF HEAT SUMMATION

Enthalpy is a state function, so the enthalpy of reaction is independent of the path used to convert the reactants into products. This means that we can choose any path, even one that is unrealistic as long as it takes the initial state (reactants) to the final state (products). This fact coupled with **Hess' law of heat summation** allows us to determine enthalpies of reactions from tabulated data.

Hess' Law of heat summation. If a process can be expressed as the sum of several steps, then the enthalpy change of the process is the sum of the enthalpy changes of the steps.

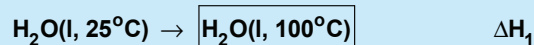
Example 3.7 is an application of this very useful thermodynamic law.

Example 3.7

How much heat is required to convert 20.0 g of water at 25 °C to steam at 150 °C?

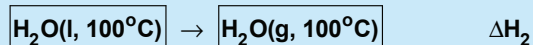
Refer to Table 3.2 for the thermal properties of water. The overall process can be expressed as $\text{H}_2\text{O}(\text{l}, 25\text{ }^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{g}, 150\text{ }^\circ\text{C})$, which can be broken down into three steps as shown in the heating curve in Figure 3.5 and by the following three steps:

1. Warm the liquid to the boiling point



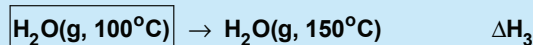
Heating the liquid increases the temperature to the boiling point.

2. Vaporize the liquid at its boiling point



Heating at the boiling point vaporizes the liquid without changing its temperature.

3. Warm the steam to 150 °C



Heating beyond the boiling point again results in a temperature increase.

When the three steps are summed, the boxed items cancel* and are, therefore, not included in the net reaction. Thus, the liquid at 100 °C formed in Step 1 is consumed in Step 2, and the gas at 100 °C formed in Step 2 is consumed in Step 3. Only the initial and final states do not cancel.

Addition of the three steps results in the overall reaction. Hess' law of heat summation tells us that the enthalpy of the overall reaction is the sum of the three enthalpies:

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

We must now determine the three enthalpies.

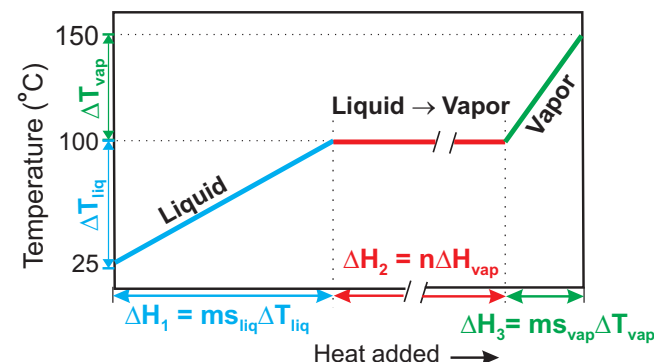


Figure 3.5 Heating curve for water from 25 °C to 150 °C

Read in the opposite direction, the curve is a cooling curve. The system contains n moles = m grams of H_2O . For water, $s_{\text{liq}} \sim 2s_{\text{vap}}$, so the slope of the vapor line is about twice that of the liquid line. The break in the heat added line is due to the fact that ΔH_2 is much larger than either ΔH_1 or ΔH_3 . See Example 3.7 for details.

* A substance can never appear as both a reactant and a product in a balanced chemical equation. Each molecule that is formed cancels one molecule that reacts. Thus, if a reaction shows 3A on the reactant side and 1A on the product side, the net equation would show $(3-1)A = 2A$ as reactants. We will use this fact many times.

Step 1 is a 75 °C temperature rise, and the heat absorbed is determined in a manner similar to Example 3.1. Using, the specific heat of liquid water in Table 3.2, we obtain

$$\Delta H_1 = ms\Delta T = (20.0 \text{ g})(4.18 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1})(75^\circ\text{C}) = 6.3 \times 10^3 \text{ J} = 6.3 \text{ kJ}$$

Step 2 is vaporization. The heat of vaporization of water is 40.7 kJ·mol⁻¹ at its boiling point (Table 3.2). The molar heat of vaporization must be multiplied by the number of moles to obtain the enthalpy of the process.

$$\Delta H_2 = 20.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \times \frac{40.7 \text{ kJ}}{\text{mol H}_2\text{O}} = 45.2 \text{ kJ}$$

Step 3 is a 50 °C temperature increase, and the heat absorbed is determined in a manner similar to Step 1. The specific heat of steam is 2.0 J·g⁻¹·°C⁻¹ (Table 3.2).

$$\Delta H_3 = ms\Delta T = (20.0 \text{ g})(2.0 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1})(50^\circ\text{C}) = 2.0 \times 10^3 \text{ J} = 2.0 \text{ kJ}$$

We obtain the answer by summing the three contributions:

$$\Delta H = 6.3 + 45.2 + 2.0 = 53.5 \text{ kJ}$$

Table 3.2 Some thermal properties of water

	Specific Heats (J·g ⁻¹ ·°C ⁻¹)
H ₂ O(l)	4.18
H ₂ O(s)	2.0
H ₂ O(g)	2.0

Enthalpies of phase changes (kJ·mol⁻¹)

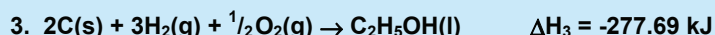
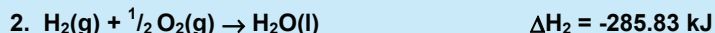
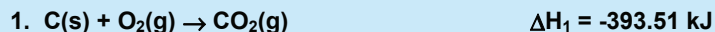
$$\Delta H_{\text{fus}} = 6.01 \text{ (at 273 K)}$$

$$\Delta H_{\text{vap}} = 40.7 \text{ (at 373 K)}$$

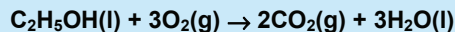
These data can also be found inside the back cover for quick reference.

Example 3.8

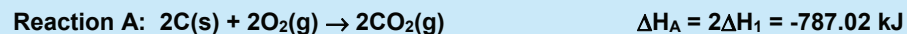
Use the following three thermochemical reactions:



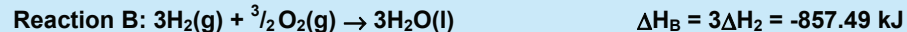
and Hess' Law to determine the enthalpy of combustion of ethanol:



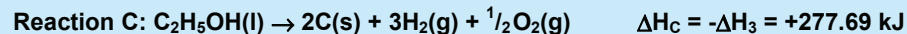
Our goal is to arrange the three given reactions in such a way that their sum is the combustion reaction. The combustion produces two moles of CO₂ while Reaction 1 produces only one. Reaction 1 must therefore be multiplied by two, which means that its enthalpy change must also be multiplied by two.



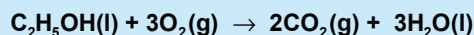
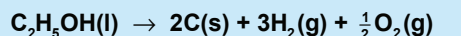
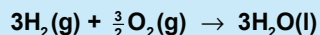
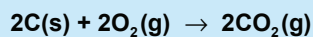
Reaction 2 must be multiplied by three to supply the required three moles of water.



Reaction 3 forms one mole of ethanol, but the combustion consumes one mole, so Reaction 1 must be written in the reverse direction. When the direction of a reaction is reversed, the sign of the enthalpy change is also reversed. Thus we write,



Summing Reactions A, B and C results in the desired combustion reaction:



Consequently, the enthalpy of combustion is the sum of the three enthalpies.

$$\Delta H = \Delta H_A + \Delta H_B + \Delta H_C = 2\Delta H_1 + 3\Delta H_2 - \Delta H_3 = -787.02 - 857.49 + 277.69$$

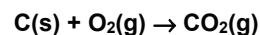
$$\Delta H = -1366.82 \text{ kJ}$$

3.7 ENTHALPIES (OR HEATS) OF FORMATION

Hess' law is a valuable tool in thermodynamics, but finding a set of thermochemical reactions that sum to the desired reaction can be a formidable task. The task is simplified with the use of a series of thermochemical reactions known as formation reactions. The **standard enthalpy (or heat) of formation**, ΔH_f° , is defined as follows:

The standard heat of formation of a substance is the enthalpy change for the reaction that produces one mole of the substance from its elements in their standard states.

The enthalpies given for reactions 1, 2 and 3 in Example 3.8 are the standard enthalpies of formation of $\text{CO}_2\text{(g)}$, $\text{H}_2\text{O(l)}$, and $\text{C}_2\text{H}_5\text{OH(l)}$, respectively. Heats of formation are given for substances, but it is important to realize that the heat of formation is the enthalpy change *for the formation reaction*. For example, the statement that the heat of formation of $\text{CO}_2\text{(g)}$ is $-393.51 \text{ kJ}\cdot\text{mol}^{-1}$ implies the following thermochemical equation:

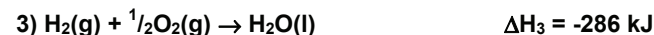
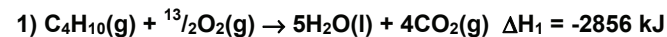


$$\Delta H = -393.51 \text{ kJ}$$

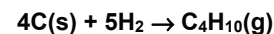
The standard state of carbon is graphite, which is represented as C(s) , and the standard state of oxygen is $\text{O}_2\text{(g)}$. Note that the *heat of formation of any element in its standard state is zero* because there is no change in the formation of an element in its standard state. Consider the formation reaction of oxygen gas, $\text{O}_2\text{(g)} \rightarrow \text{O}_2\text{(g)}$. Clearly there is no enthalpy change in a reaction with the same initial and final states. Selected standard enthalpies of formation at 25°C can be found in Appendix B.

PRACTICE EXAMPLE 3.6

Given the following thermochemical equations for combustion,



determine the enthalpy change for the following reaction, which is known as the enthalpy of formation of butane:



Rearrange and/or multiply each of the given chemical equations by an integer so that their sum equals the formation reaction.

Rewrite Equation 1 so that the correct number of butane molecules appear in the correct place and determine the enthalpy of reaction for the resulting equation A.

Eq A.

$$\Delta H_A = \text{_____ kJ}$$

Rewrite Equation 2 so that the correct number of carbon atoms appear in the correct place and determine the enthalpy of reaction for the resulting equation B.

Eq B.

$$\Delta H_B = \text{_____ kJ}$$

Rewrite Equation 3 so that the correct number of water molecules appear in the correct place and determine the enthalpy of reaction for the resulting equation C.

Eq C.

$$\Delta H_C = \text{_____ kJ}$$

Sum equations A,B, and C to obtain Equation D, which should be the formation reaction of butane, and use Hess' Law to determine the enthalpy of formation (ΔH_f) of butane.

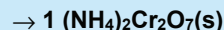
Eq D.

$$\Delta H_f = \text{_____ kJ}$$

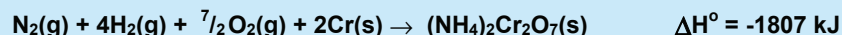
Example 3.9

The standard heat of formation of ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{s})$, is $-1807 \text{ kJ}\cdot\text{mol}^{-1}$. Write the process to which this number applies.

The heat of formation is the enthalpy change when one mole of the substance is formed. We therefore start with



The coefficient of one is not normally used, but it is placed in the above for emphasis; the coefficient of the product cannot be changed. The substance is formed from its elements in their standard states. The standard states of nitrogen, hydrogen and oxygen are the diatomic gases at 1 atm pressure while that of chromium is the solid metal. The process to which the heat of formation of $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7(\text{s})]$ applies is



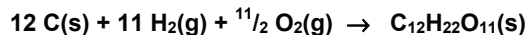
Multiplying the above equation by two to get rid of the fraction results in a reaction with an enthalpy equal to the heat of formation of $2(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. The reaction must be balanced using a coefficient of one for the substance whose heat of formation is being reported!

Tabulated standard enthalpies of formation can be used to calculate standard enthalpies of a large number of reactions by the application of Hess' law of heat summation as demonstrated in Example 3.8. The procedure can be simplified by using the expression given in Equation 3.11.

$$\Delta H = \sum_{\text{products}} c[\text{product}] \times \Delta H_f^\circ[\text{product}] - \sum_{\text{reactants}} c[\text{reactant}] \times \Delta H_f^\circ[\text{reactant}] \quad \text{Eq. 3.11}$$

$c[\text{product}]$ is the coefficient of the product in the balanced equation whose heat of formation is $\Delta H_f^\circ[\text{product}]$. Thus, the enthalpy of any reaction can be determined as the sum of the heats of formation of the products, each multiplied by its coefficient in the balanced equation, minus the sum of the heats of formation of the reactants, each multiplied by its coefficient in the balanced equation.*

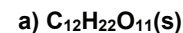
The enthalpies of formation of most compounds cannot be determined directly. As an example, consider the reaction pertaining to the heat of formation of sucrose:



Under no circumstances would $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$ be the sole product of the reaction of carbon, hydrogen and oxygen. Rather, a large number of compounds containing those elements would result, and the enthalpy of reaction could not be associated with any single compound. Consequently, enthalpies of formation are often determined indirectly as shown in Example 3.11 and Practice Example 3.9.

PRACTICE EXAMPLE 3.7

Write the formation reactions for the following.

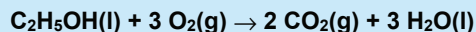


* Tabulated values of heats of formation are given in $\text{kJ}\cdot\text{mol}^{-1}$, but each coefficient is the number of moles of the substance in the balanced equation. Therefore, the product of the coefficient and the enthalpy of formation of the substance has units of kJ. Thus, enthalpy changes for reactions determined with Equation 3.11 have units of kJ.

Example 3.10

Determine the standard heat of combustion of $\text{C}_2\text{H}_5\text{OH}$ using Equation 3.11.

This is the same problem done in Example 3.8. This time, however, we use Equation 3.11 instead of rearranging a series of reactions. The chemical equation for the combustion reaction is



We apply Equation 3.11 to the above as follows:

$$\Delta H^\circ = 2\Delta H_f^\circ[\text{CO}_2(\text{g})] + 3\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - \Delta H_f^\circ[\text{C}_2\text{H}_5\text{OH}(\text{l})] - 3\Delta H_f^\circ[\text{O}_2(\text{g})]$$

Inserting the tabulated values for the heats of formation, we obtain:

$$\Delta H = 2(-393.51) + 3(-285.83) - (-277.69) - 3(0) = -1366.82 \text{ kJ}$$

The above is the same value as obtained in Example 3.8. Thus, the application of Equation 3.11 is equivalent to rearranging the formation reactions so that they sum to the desired reaction; i.e., Equation 3.11 is just an application of Hess' law.

PRACTICE EXAMPLE 3.8

Determine the heat of combustion of propane gas (C_3H_8) from tabulated heats of formation.

The chemical equation for the combustion of propane at 298 K:

The relevant heats of formation:

$$\Delta H_f^\circ[\text{CO}_2(\text{g})] = -393.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^\circ[\text{C}_3\text{H}_8(\text{g})] = -103.8 \text{ kJ}\cdot\text{mol}^{-1}$$

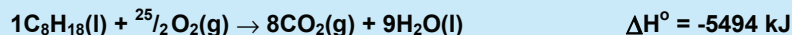
The heat of combustion of propane as determined from heats of formation:

$$\Delta H_{\text{comb}} = \text{_____} \text{ kJ}\cdot\text{mol}^{-1}$$

Example 3.11

The standard enthalpy of combustion of octane (C_8H_{18}) is $-5494 \text{ kJ}\cdot\text{mol}^{-1}$. What is the standard enthalpy of formation of octane?

The enthalpy of combustion is the heat absorbed when one mole of a substance reacts with oxygen at constant pressure.



Applying Equation 3.11 to the combustion reaction we obtain

$$\Delta H^\circ = -5494 = 8\Delta H_f^\circ[\text{CO}_2(\text{g})] + 9\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - 1\Delta H_f^\circ[\text{C}_8\text{H}_{18}(\text{l})] - 12.5\Delta H_f^\circ[\text{O}_2(\text{g})]$$

We next solve for the enthalpy of formation of octane.

$$1\Delta H_f^\circ[\text{C}_8\text{H}_{18}(\text{l})] = 8\Delta H_f^\circ[\text{CO}_2(\text{g})] + 9\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - 12.5\Delta H_f^\circ[\text{O}_2(\text{g})] - \Delta H^\circ$$

We are given ΔH° and values for the standard enthalpies of formation of CO_2 , H_2O , and O_2 can be obtained from Appendix B. Consequently, the standard enthalpy of formation of octane is:

$$1\Delta H_f^\circ[\text{C}_8\text{H}_{18}(\text{l})] = 8(-393.51) + 9(-285.83) - 12.5(0) - (-5494) = -227 \text{ kJ}$$

Divide by the one mole to obtain the heat of formation of octane, $\Delta H_f^\circ = -227 \text{ kJ}\cdot\text{mol}^{-1}$. It is through reactions like combustion that most enthalpies of formation are determined.

PRACTICE EXAMPLE 3.9

The standard heat of combustion of butane at 298 K is $-2856 \text{ kJ}\cdot\text{mol}^{-1}$. Use other tabulated heats of formation to determine the standard heat of formation of C_4H_{10} ?

The combustion reaction is

The standard heat of combustion in terms of the heats of formations of reactants and products is

$$\Delta H^\circ =$$

Solving for the heat of formation of butane yields

$$\Delta H_f^\circ =$$

Inserting the known enthalpies one obtains

$$\Delta H_f^\circ =$$

$$\Delta H_f^\circ = \text{_____} \text{ kJ}\cdot\text{mol}^{-1}$$

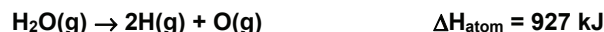
3.8 BOND DISSOCIATION ENERGIES

Heats of formation offer an excellent way to determine enthalpies of reaction. However, it is quite possible that the reaction of interest may involve molecules for which heats of formation have not been reported. In these cases, bond energies can be used to *approximate* enthalpy changes.

The **bond dissociation energy**, which is also referred to as the **bond energy** or **dissociation energy**, is given the symbol **D**. It is the energy required to break one mole of bonds *in the gas phase*. Table 3.3 shows some common bond energies. Note that they are always positive because energy is always required to break bonds. The bond energy of an H-Cl bond is 431 kJ·mol⁻¹, so we can write the following:



In the preceding reaction, the HCl molecule is *atomized*. Atomization is the process of breaking all of the bonds in a molecule to produce the atoms, and the energy required is the **enthalpy of atomization**, ΔH_{atom} . Thus, the bond energy of HCl is the same as its atomization energy. The atomization energy of a large molecule is equal to the sum of the bond energies of all of the bonds in the molecule. Consequently, bond energies can be determined from enthalpies of atomization. Consider the atomization of a water molecule



Atomization requires the breaking of two O-H bonds, so the *average* O-H bond energy is

$$D_{\text{O-H}} = \frac{\Delta H_{\text{atom}}}{\text{moles of bonds}} = \frac{927 \text{ kJ}}{2 \text{ mol}} = 463 \text{ kJ} \cdot \text{mol}^{-1}$$

Enthalpies of atomization can be determined from enthalpies of formation (Example 3.12 and Practice Example 3.10).

Another path that can be used to convert the reactants to the products is to atomize the reactants and then recombine the atoms to make the products. Application of Hess' Law of heat summation to this path produces the following valuable procedure to use in estimating[†] heats of reactions.

$$\Delta H \sim \sum D_{\text{broken bonds}} - \sum D_{\text{formed bonds}} \quad \text{Eq. 3.12}$$

When using Equation 3.12 to determine the enthalpy of a reaction, *you should always draw Lewis structures for the reactants and products to assure that you have the correct number and bond order of each type of bond.*

Table 3.3 Bond energies of some common bonds (kJ/mol)

Single bonds

H-H 436	C-H 413	N-H 391	O-H 463	S-H 347
H-F 565	C-F 485	N-F 272	O-F 190	S-F 327
H-Cl 431	C-Cl 328	N-Cl 200	O-Cl 203	S-Cl 271
H-Br 366	C-Br 276	N-Br 243	O-Br 235	S-Br 218
H-I 299	C-I 234	N-I 159	O-I 234	S-I 170
	C-C 347	N-N 163	O-O 146	S-S 266
F-F 159	C-N 305	N-O 201	O-P 351	
Cl-Cl 243	C-O 358	N-P 209	O-S 265	
Br-Br 193	C-S 259			
I-I 151				

Multiple bonds

C=C 612	C=N 615	N=N 418	O=O 495
C≡C 820	C≡N 891	N≡N 941	
	C=O 799	N=O 607	
	C≡O 1072		

[†] The bond energy of a bond depends upon its environment. Thus, the C-H bond energy in CHF₃ is slightly different from the one in CH₄. Consequently, Equation 3.12 is only an approximation because a tabulated bond energy is usually an average of several different examples of the bond, which may be slightly different than the bond energy in the molecule to which it is applied. In addition, bond energies are sometimes used for reactions in solution, but they apply only to gas-phase reactions.

Example 3.12

- a) Use the data in Appendix B to determine the average P-Cl bond energy.

The easiest way to obtain the P-Cl bond energy is from the enthalpy of atomization of the gas-phase molecule that contains only P-Cl bonds. PCl_3 is a good choice, so we write its atomization equation and use Appendix B to determine its enthalpy of atomization.



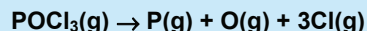
$$\Delta H_{\text{atom}} = \Delta H_f[\text{P}(\text{g})] + 3\Delta H_f[\text{Cl}(\text{g})] - \Delta H_f[\text{PCl}_3(\text{g})] = 316 + 3(122) - (-288) = 970 \text{ kJ}$$

Atomization of PCl_3 requires breaking three P-Cl bonds, so the average P-Cl bond energy in PCl_3 is

$$D_{\text{P-Cl}} = \frac{\Delta H_{\text{atom}}}{\text{moles of bonds}} = \frac{970 \text{ kJ}}{3 \text{ mol}} = 323 \text{ kJ} \cdot \text{mol}^{-1}$$

- b) Use the results of Part a and the data in Appendix B to determine the P-O bond strength in POCl_3 .

Start by determining the enthalpy of atomization.



$$\Delta H_{\text{atom}} = \Delta H_f[\text{P}(\text{g})] + \Delta H_f[\text{O}(\text{g})] + 3\Delta H_f[\text{Cl}(\text{g})] - \Delta H_f[\text{POCl}_3(\text{g})]$$

$$\Delta H_{\text{atom}} = 316 + 249 + 3(122) - (-542) = 1473 \text{ kJ}$$

Atomization of POCl_3 requires breaking 3P-Cl bonds and one P-O bond

$$\Delta H_{\text{atom}} = 3D_{\text{P-Cl}} + 1D_{\text{P-O}} = 1473 \text{ kJ}$$

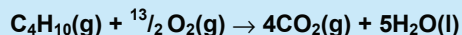
The one is retained in front of $D_{\text{P-O}}$ as a reminder that the bond energy in $\text{kJ} \cdot \text{mol}^{-1}$ is multiplied by one mole to produce units of kJ. The energy of three P-Cl bonds was determined in Example 3.12, so we can solve the above for $D_{\text{P-O}}$.*

$$D_{\text{P-O}} = \frac{\Delta H_{\text{atom}} - 3D_{\text{P-Cl}}}{\text{moles of bonds}} = \frac{(1473 - 970) \text{ kJ}}{1 \text{ mol}} = 503 \text{ kJ} \cdot \text{mol}^{-1}$$

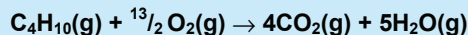
Example 3.13

Use the bond energies in Table 3.3 and the fact that the heat of vaporization of water at 298 K is $44.0 \text{ kJ} \cdot \text{mol}^{-1}$ to estimate the heat of combustion of C_4H_{10} at 298 K:

First write the balance equation for the combustion reaction at 298 K.



Bond energies are valid only for gases, so their use will result in the value of ΔH for the reaction in which the water forms as a gas rather than a liquid.



PRACTICE EXAMPLE 3.10

Use the C-F bond energy in Table 3.3 and the data in Appendix B to determine the C-H bond energy in CHF_3 . The standard heat of formation of CHF_3 is $-695.4 \text{ kJ} \cdot \text{mol}^{-1}$.

The chemical equation for the atomization of CHF_3

The enthalpy of atomization

$$\Delta H_{\text{atom}} = \underline{\hspace{2cm}}$$

The C-H bond energy in CHF_3

$$D_{\text{CH}} = \underline{\hspace{2cm}}$$

* Note that this is much higher than the $351 \text{ kJ} \cdot \text{mol}^{-1}$ given for the P-O bond energy in Table 3.3, which indicates that this bond has substantial double bond character. Indeed, bonds between phosphorus and terminal oxygens are usually drawn as double bonds in Lewis structures even though this places more than eight electrons around the phosphorus.

PRACTICE EXAMPLE 3.11

Estimate the heat of formation of $\text{F}_2\text{N-NF}_2(\text{g})$.

Formation reaction

Energy required to break bonds

Energy released when bonds form

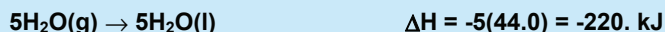
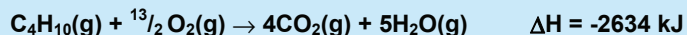
Enthalpy of formation

Drawing Lewis structures for all substances shows that three C-C bonds, ten C-H bonds, and 6.5 O=O bonds must be broken, while eight C=O bonds and ten O-H bonds are formed. Consequently, the enthalpy of the reaction can be estimated as

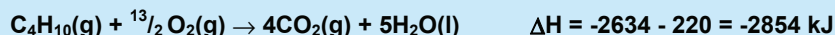
$$\Delta H = 3D_{\text{C-C}} + 10D_{\text{C-H}} + 6.5D_{\text{O=O}} - 8D_{\text{C=O}} - 10D_{\text{O-H}}$$

$$\Delta H = 3(347) + 10(413) + 6.5(495) - 8(799) - 10(463) = -2634 \text{ kJ}$$

The above ΔH is for the reaction producing water gas, so we now use the heat of vaporization and Hess' law of heat summation to obtain the desired enthalpy. We need to convert five moles of gaseous water into liquid water, so we multiply the heat of vaporization by 5, change its sign, and add it to the above reaction.



Summing these two reactions produces the desired result,



which is within 1% of the actual heat of combustion.

3.9 CALORIMETRY

Calorimetry is the measurement of the heat flow of a process, and a schematic of a simple calorimeter is shown in Figure 3.6. The calorimeter consists of a thermally insulated container, a thermometer, and a carefully measured amount of water. The thermal insulation can range from Styrofoam[®] as found in insulated cups to evacuated jackets as found in Thermos[®] bottles. A heat source or sink, which is often a reaction, is then placed in the calorimeter, and the temperature change of the calorimeter is measured. The entire system (reaction + calorimeter) is thermally insulated, so $q = q_{\text{rxn}} + q_{\text{cal}} = 0$, which can be rewritten as

$$q_{\text{rxn}} = -q_{\text{cal}} \quad \text{Eq. 3.13}$$

In other words, no heat enters or leaves the system; it simply flows between the reaction and the calorimeter. Because the calorimeter experiences only a temperature change, we can apply Equation 3.1 to q_{cal} and obtain

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T_{\text{cal}} \quad \text{Eq. 3.14}$$

C_{cal} is the heat capacity of the calorimeter, and ΔT_{cal} is the temperature change experienced by the calorimeter. However, most of the heat absorbed by the calorimeter is absorbed by the water, so it is often assumed that the calorimeter is simply the water. In this approximation, the heat capacity of the calorimeter is equal to the heat capacity of the

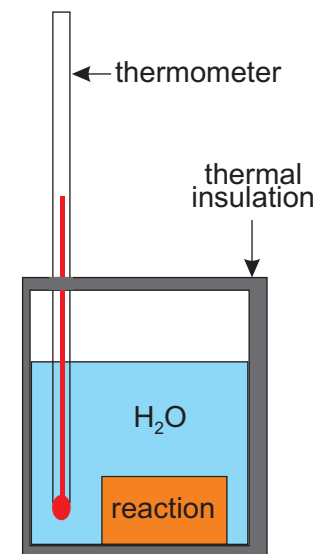


Figure 3.6 Schematic of a calorimeter

water, which is related to the specific heat and mass of the water by the following (see Equation 3.2):

$$C_{\text{cal}} \sim m_{\text{water}} s_{\text{water}}$$

Substitution of the above into Equation 3.14 yields the common approximation of the calorimetry equation.

$$q_{\text{rxn}} = -m_{\text{water}} s_{\text{water}} \Delta T_{\text{water}} \quad \text{Eq. 3.15}$$

The nature of q_{rxn} depends on how the measurement is made. Remember that ΔE is the heat absorbed at constant volume ($\Delta E = q_V$) while ΔH is the heat absorbed at constant pressure ($\Delta H = q_P$). Thus, if the reaction is carried out in an open flask (at constant pressure), $q_{\text{rxn}} = q_P = \Delta H$; but, if the reaction is carried out in a bomb (at constant volume), $q_{\text{rxn}} = q_V = \Delta E$.

Example 3.14

9.0 g of Al at 100.0 °C are placed in 20.0 mL of water at 20.0 °C contained in a Styrofoam® cup. At thermal equilibrium, the temperature of the water/aluminum mixture is 27.1 °C. What is the specific heat of aluminum?

The process occurs in an insulated cup, so Equation 3.13 can be used. But a hot piece of aluminum, rather than a reaction, is the heat source, so we may write

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

The heat flowing out of the aluminum flows into the calorimeter. Because both the calorimeter (water) and the aluminum involve only temperature changes, we write

$$m_{\text{Al}} s_{\text{Al}} \Delta T_{\text{Al}} = -m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \Delta T_{\text{H}_2\text{O}}$$

Consequently, we may express the specific heat of the aluminum as:

$$s_{\text{Al}} = -\frac{m_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \Delta T_{\text{H}_2\text{O}}}{m_{\text{Al}} \Delta T_{\text{Al}}}$$

The aluminum experiences a temperature change of $\Delta T_{\text{Al}} = 27.1 - 100.0 = -72.9$ °C while the water undergoes a temperature change of $\Delta T_{\text{H}_2\text{O}} = 27.1 - 20.0 = +7.1$ °C. Substitution of these temperature changes, the known masses, and the specific heat of water yields the answer.

$$s_{\text{Al}} = -\frac{(20.0 \text{ g})(4.18 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1})(7.1 ^\circ\text{C})}{(9.0 \text{ g})(-72.9 ^\circ\text{C})} = 0.90 \text{ J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$$

Example 3.15

Combustion of 1.00 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) causes the temperature in a bomb calorimeter with a heat capacity of $4.90 \text{ kJ}\cdot^\circ\text{C}^{-1}$ to rise from 24.92 to 28.33°C .

a) What is the standard heat of combustion of sucrose?

We are given the heat capacity of the calorimeter and the temperature change, so we use Equation 3.13 to obtain q_{rxn}

$$q_{\text{rxn}} = -C_{\text{cal}}\Delta T_{\text{cal}} = -(4.90 \text{ kJ}\cdot^\circ\text{C}^{-1})(28.33 - 24.92) = -16.7 \text{ kJ}$$

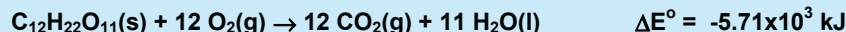
This is typical of the combustion of carbohydrates, which average $17 \text{ kJ}\cdot\text{g}^{-1}$. We will consider this further in the next section on foods and fuels.

The reaction is carried out in a bomb, so it is at constant volume, which means that $q_{\text{rxn}} = \Delta E$. We next divide q_{rxn} by the number of moles of sucrose to get the molar energy change.

$$n = 1.00 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = 0.00292 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$$

$$\Delta E = \frac{-16.7 \text{ kJ}}{0.00292 \text{ mol}} = -5.71 \times 10^3 \text{ kJ}\cdot\text{mol}^{-1}$$

The balanced equation to which this ΔE applies is for the combustion of one mole of sucrose or



Δn_g for the above reaction is $\Delta n_g = 12 - 12 = 0$. Therefore, $\Delta H^\circ = \Delta E^\circ$

The standard heat of combustion of sucrose is $\Delta H_{\text{comb}}^\circ = -5.71 \times 10^3 \text{ kJ}\cdot\text{mol}^{-1}$

b) What is the standard heat of formation of sucrose?

The standard enthalpy of combustion can be expressed in terms of the standard heats of formation of the reactants and products as

$$\Delta H^\circ = 12\Delta H_f^\circ[\text{CO}_2(\text{g})] + 11\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - 1\Delta H_f^\circ[\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})] - 12\Delta H_f^\circ[\text{O}_2(\text{g})]$$

Solving for the heat of formation of sucrose and substituting tabulated values, we obtain

$$1\Delta H_f^\circ[\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})] = -\Delta H^\circ + 12\Delta H_f^\circ[\text{CO}_2(\text{g})] + 11\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] - 12\Delta H_f^\circ[\text{O}_2(\text{g})]$$

$$1\Delta H_f^\circ[\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})] = 5.71 \times 10^3 + 12(-393.5) + 11(-285.8) - 12(0) = -2.16 \times 10^3 \text{ kJ}$$

Divide by the one mole (coefficient) to determine that the standard heat of formation of sucrose is $-2.16 \times 10^3 \text{ kJ}\cdot\text{mol}^{-1}$.

PRACTICE EXAMPLE 3.12

Combustion of 6.346 mmol of liquid toluene (C_7H_8) in a bomb calorimeter with a heat capacity of $8.651 \text{ kJ}\cdot^\circ\text{C}^{-1}$ resulted in a temperature rise of 2.864°C in the calorimeter.

a) What is the heat of combustion of toluene?

Combustion Reaction:

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

$$\Delta E_{\text{comb}} =$$

$$\Delta n_g =$$

$$\Delta n_g RT =$$

$$\Delta H_{\text{comb}} =$$

b) What is the heat of formation of toluene?

heat of combustion in terms of heats of formation of reactants and products:

$$\Delta H_{\text{comb}} =$$

Solve the above for $\Delta H_f(\text{C}_7\text{H}_8)$

$$\Delta H_f = \text{_____ kJ}\cdot\text{mol}^{-1}$$

3.10 COMBUSTION: FOOD AS FUEL

The metabolism of carbohydrates and fats in the body also produces CO_2 and H_2O , and the energy that is derived from their metabolism is essentially the same as would be produced by their combustion in a calorimeter. As indicated in Example 3.15, a typical carbohydrate delivers about $17 \text{ kJ}\cdot\text{g}^{-1}$ in a calorimeter. A *dietary calorie* (Cal, upper case 'C') is actually a kcal of energy and $1 \text{ kcal} = 4.184 \text{ kJ}$. Thus, the combustion of a gram of carbohydrate delivers about 4 Cal. The combustion of fats produces about $38 \text{ kJ}\cdot\text{g}^{-1}$ or $9 \text{ Cal}\cdot\text{g}^{-1}$. The metabolism of proteins, like carbohydrates, averages about $17 \text{ kJ}\cdot\text{g}^{-1}$ or $4 \text{ Cal}\cdot\text{g}^{-1}$. For example, consider the following information for one serving that appears on the nutrition label of a can of soup:

Calories 160	Calories from fat 10
Total Fat 1g	
Total Carbohydrates 31 g	
Total Protein 7 g	

Using our average energies of combustion, we would predict that a total fat of 1g would produce ~ 9 dietary calories, which is consistent with the 10 calories from fat listed on the can. The mass of the carbohydrates and protein is $31 + 7 = 38 \text{ g}$, so the energy derived from their combustion is $(38 \text{ g})(4 \text{ Cal}\cdot\text{g}^{-1}) \sim 150 \text{ Cal}$. The total dietary calorie content is the sum of the 150 Cal from the protein and carbohydrates and the 10 Cal from the fat.

3.11 CHAPTER SUMMARY AND OBJECTIVES

The first law of thermodynamics states that energy is conserved for all processes, $\Delta E_{\text{univ}} = 0$. This means that no process can be devised that will create or destroy energy. Energy, however, can be transferred between the system and the surroundings, $\Delta E = -\Delta E_{\text{sur}}$. This is usually accomplished by a combination of heat (q) and work (w), or $\Delta E = q + w$, the energy change of the system equals the heat absorbed by it plus the work done on it. Thus, heat and work are two ways in which energy can be transferred. Heat is that form of energy that is transferred as the result of a temperature difference only. The amount of heat absorbed by a substance undergoing a temperature change only is $q = C\Delta T = ms\Delta T$ where C is the system's heat capacity, m is its mass and s is its specific heat.

In chemical reactions carried out at constant pressure, some of the energy change may be associated with the production or consumption of gases. However, that part of the energy is not of interest to us; it is the heat we must provide or that we can extract from the

reaction that is relevant. Thus, the enthalpy of reaction, ΔH , is defined as the heat absorbed by a reaction carried out at constant pressure. The enthalpy change of a reaction is related to the energy change of the reaction by the expression $\Delta E = \Delta H - \Delta n_g RT$, where Δn_g is the change in the number of moles of gas during the reaction and $\Delta n_g RT$ is the work done by those gases.

The enthalpy of a reaction can be determined with the use of Hess' law of heat summation if the thermochemical equations that sum to the desired reaction are available. The thermochemical equations most often used are those corresponding to the standard heats of formation. The standard heat of formation of a substance is the heat absorbed when one mole of the substance is formed from its elements in their standard states. The standard enthalpy of a reaction can be determined from the standard enthalpies of formation (ΔH_f°) of the products and reactants as

$$\Delta H = \sum_{\text{products}} c[\text{product}] \times \Delta H_f^\circ[\text{product}] - \sum_{\text{reactants}} c[\text{reactant}] \times \Delta H_f^\circ[\text{reactant}]$$

$c[\text{product}]$ is the coefficient in the chemical equation of the product that has a heat of formation of $\Delta H_f^\circ[\text{product}]$.

Bond energies can be determined from atomization energies and used to estimate the enthalpies of gas-phase reactions by subtracting the energy that is released when the product bonds form from the energy required to break the reactant bonds.

Calorimetry is the measurement of heat flow. Since no heat enters or leaves the calorimeter, the heat of a reaction is simply transferred to or from the calorimeter, $q_{\text{rxn}} = -q_{\text{cal}}$. Since most of the heat capacity of the calorimeter is due to the water, the calorimetry equation is often expressed as $q_{\text{rxn}} = -m_w S_w \Delta T_w$, where "w" signifies water. If the reaction is carried out in an open container (constant pressure), $q_{\text{rxn}} = \Delta H$, but if the reaction is carried out in a bomb calorimeter (constant volume), $q_{\text{rxn}} = \Delta E$.

ANSWERS TO PRACTICE EXAMPLES

- 3.1 a) $w_{\text{person}} = -1.4 \text{ kJ}$ $w_{\text{mass}} = +1.4 \text{ kJ}$
work is done by the person on the mass
b) $q_{\text{metal}} = +120 \text{ J}$ endothermic
 $q_{\text{water}} = -120 \text{ J}$ exothermic
heat is absorbed by the metal and
given off by the water
- 3.2 a) $\Delta n_g = -3.5 \text{ mol}$ b) $\Delta n_g = -0.3011 \text{ mol}$
- 3.3 746 J done on gas
- 3.4 $\Delta E_{\text{comb}} = -2847 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta H_{\text{comb}} = -2856 \text{ kJ} \cdot \text{mol}^{-1}$
- 3.5 a) $\Delta H = +5712 \text{ kJ}$ b) $\Delta H = -1229 \text{ kJ}$
- 3.6 $\Delta H_A = +2586 \text{ kJ}$; $\Delta H_B = -1576 \text{ kJ}$; $\Delta H_C = -1430$
 $\Delta H_D = -150 \text{ kJ}$
- 3.7 a) $12\text{C(s)} + 11\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)}$
b) $2\text{Na(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{Na}_2\text{O(s)}$
c) $\frac{1}{2}\text{N}_2\text{(g)} + \frac{3}{2}\text{H}_2\text{(g)} \rightarrow \text{NH}_3\text{(g)}$
- 3.8 $\Delta H_{\text{comb}} = -2219.9 \text{ kJ} \cdot \text{mol}^{-1}$
- 3.9 $\Delta H_f = -147 \text{ kJ} \cdot \text{mol}^{-1}$
- 3.10 $D_{\text{C-H}} = 412 \text{ kJ} \cdot \text{mol}^{-1}$
- 3.11 $\Delta H_f = +8 \text{ kJ} \cdot \text{mol}^{-1}$
- 3.12 $\text{C}_7\text{H}_8\text{(l)} + 9\text{O}_2\text{(g)} \rightarrow 7\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(l)}$
 $\Delta E_{\text{comb}} = -3905 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta n_g RT = -4.96 \text{ kJ}$
 $\Delta H_{\text{comb}} = -3910 \text{ kJ} \cdot \text{mol}^{-1}$ $\Delta H_f = 12.3 \text{ kJ} \cdot \text{mol}^{-1}$

After studying the material presented in this chapter, you should be able to:

1. distinguish between a system, its surroundings, and the universe for a thermodynamic process (Section 3.1);
2. calculate the heat absorbed by a system given its heat capacity and temperature change (Section 3.2);
3. distinguish between heat capacity and specific heat (Section 3.2);
4. state the difference between the effects of work done *on* and work done *by* a system (Section 3.2);
5. use the expression, $\Delta E = q + w$, to determine how much of an energy flow is in the form of heat and how much is in the form of work (Section 3.3);
6. define a state function (Section 3.3);
7. calculate the amount of work associated with a change in the number of moles of gas in a reaction carried out at constant temperature and pressure (Section 3.3);
8. define the enthalpy of reaction and distinguish between it and the energy change of a reaction in terms of the heat absorbed at constant pressure or volume (Section 3.4);
9. calculate the enthalpy of reaction from the energy change of the reaction and *vice versa* (Section 3.4);
10. identify the standard state of a substance (Section 3.5);
11. apply Hess' law of heat summation to determine the enthalpy of reaction (Section 3.6);
12. determine the enthalpy of reaction given the heats of formation of the reactants and products (Section 3.7);
13. determine the enthalpy of formation of one of the reactants or products of a reaction given the ΔH of the reaction and the heats of formation of all other participants in the reaction (Section 3.7);
14. determine the enthalpy of atomization of a molecule and the average bond energy of its bonds when all of the bonds are between the same pair of atoms (Section 3.8);
15. use bond energies to estimate enthalpies of gas-phase reactions (Section 3.8); and
16. calculate the heat of a reaction from the temperature change it causes in a calorimeter with known heat capacity, and decide whether the heat is an enthalpy change or a change in the energy of the system (Section 3.9).

3.12 EXERCISES

THE FIRST LAW OF THERMODYNAMICS

- What state functions correspond to the heat absorbed at constant pressure and the heat absorbed at constant volume?
- Many devices are constructed to convert one type of energy to another. Give an example for each of the following energy conversions:
 - thermal \rightarrow mechanical
 - mechanical \rightarrow thermal
 - electrical \rightarrow light
 - chemical \rightarrow electrical
 - electrical \rightarrow thermal
 - chemical \rightarrow thermal
- Classify each of the following processes as endothermic or exothermic:
 - melting a solid
 - combustion of butane
 - condensing a liquid
 - photosynthesis
 - a battery reaction
- Can all of the potential energy of the object described in Figure 3.3 be transferred to the mechanical surroundings by its fall? Explain.
- What is the energy change of the system if the system:
 - absorbs 50. J of heat and does 50. J of work?
 - releases 20. J of heat and has 415 J of work done on it?
- What is the energy change of the system if the system:
 - absorbs no heat and does 125 J of work?
 - releases 180. J of heat and has 825 J of work done on it?
- What are ΔE , ΔE_{sur} and ΔE_{univ} for a gas that gives off 312 J of heat while being compressed 862 ml by a pressure of 1.64 atm?
- How much heat is required to heat 1.0×10^3 kg of aluminum from room temperature (25 °C) to its melting point (660. °C)? $s_{\text{Al}} = 0.90 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$
- Determine the mass of octane (C_8H_{18} , $\Delta H_{\text{comb}} = -5500. \text{ kJ}\cdot\text{mol}^{-1}$) must be combusted to yield the amount of energy equivalent to:
 - 3.1 kJ, the kinetic energy of a 220. lb linebacker running at a speed of 40. yd in 4.7 seconds.
 - 17 J, the potential energy of a 5 lb bag of sugar on top of a 30. inch high counter.
 - 320 kJ, the amount of heat required to raise the temperature of 1 quart of water from 25 °C to its boiling point, .
- How many joules of work must be done to inflate a balloon to a volume of 2.0 L if atmospheric pressure is 0.98 atm?
- $\Delta H_{\text{vap}} = 26.7 \text{ kJ}\cdot\text{mol}^{-1}$ for CS_2 at its normal boiling point (46 °C). What is ΔH for the condensation 41.2 g of CS_2 gas to liquid at 46 °C.
- How much heat must be supplied to 35 g of ice at -26 °C to convert it to steam at 148 °C? Specific heats: ice = $2.0 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$; water = $4.2 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$; steam = $2.0 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$. The molar heat of fusion of water at 273 K is $\Delta H_{273} = 6.01 \text{ kJ}\cdot\text{mol}^{-1}$, and the molar heat of vaporization of water at 373 K is $\Delta H_{373} = 40.7 \text{ kJ}\cdot\text{mol}^{-1}$.
- Use the information in the preceding exercise to answer the following:
 - What mass of ice can be melted at 0 °C by 35.0 kJ of heat?
 - What mass of water can be vaporized at 100 °C by 35.0 kJ of heat?
- Mercury has the following physical properties: melting point = -39 °C, boiling point = 357 °C, heat of fusion = $2.33 \text{ kJ}\cdot\text{mol}^{-1}$, heat of vaporization = $284 \text{ J}\cdot\text{g}^{-1}$, specific heat of liquid = $0.139 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$. Calculate ΔH for the conversion of 100. g of solid mercury at its freezing point to mercury vapor at its boiling point.
- Determine ΔH , q , w , and ΔE for the evaporation of 0.10 mol CCl_4 at 298 K and 1 atm pressure?
- Determine ΔH , q , w , and ΔE at 298 K and 1 atm pressure for the reaction of 9.184 g of $\text{NH}_3(\text{g})$ with excess $\text{HCl}(\text{g})$ to produce $\text{NH}_4\text{Cl}(\text{s})$.
- Indicate $\Delta H > \Delta E$, $\Delta H \sim \Delta E$, or $\Delta H < \Delta E$ for each of the following processes:
 - condensing steam
 - melting ice
 - heating a gas at constant pressure
 - a solid decomposes into two gases at constant volume
- The combustion of one cubic foot of natural gas produces 1000 kJ of heat. Assume 60% efficiency for the heat transfer and determine how many cubic feet of natural gas must be burned to raise the temperature of 40 gallons of water from 20.0 °C to 90.0 °C. Note: 1 gal = 3.79 L = 4 qt

19. How much work is done on (or by) the gases in each of the following at 298 K and 1 atm? Indicate whether the work is done on or by the gas.
- evaporation of 0.80 g of CH_3OH
 - decomposition of 3.2 g of $\text{CaCO}_3(\text{s})$ to $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$
 - reaction of 4.0 g of $\text{H}_2(\text{g})$ with excess $\text{N}_2(\text{g})$ to produce $\text{NH}_3(\text{g})$
 - reaction of 12 g of $\text{NH}_3(\text{g})$ with excess $\text{HCl}(\text{g})$ to produce $\text{NH}_4\text{Cl}(\text{s})$
20. How much work is done on (or by) the gases in each of the following at 298 K and 1 atm? Indicate whether the work is done on or by the gas.
- the condensation of 16.0 g of water
 - the reaction of 7.5 g $\text{Na}(\text{s})$ and 12.0 g $\text{Cl}_2(\text{g})$ to produce $\text{NaCl}(\text{s})$
 - the decomposition of 12.6 g KClO_3 into $\text{KCl}(\text{s})$ and $\text{O}_2(\text{g})$
 - 6.0 g of $\text{H}_2(\text{g})$ reacts with 4.0 g of $\text{CO}_2(\text{g})$ to form $\text{H}_2\text{O}(\text{g})$ and $\text{CO}(\text{g})$.

ENTHALPY AND ENTHALPIES OF FORMATION

21. Determine the enthalpy change for each of the processes in Exercise 19.
22. Determine the enthalpy change for each of the processes in Exercise 20.
23. Write the chemical equation for the reaction corresponding to the standard enthalpy of formation of $\text{N}_2\text{O}_5(\text{g})$, and determine its value from the following thermochemical data:
- $$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) \quad \Delta H^\circ = -114.1 \text{ kJ}$$
- $$4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}) \quad \Delta H^\circ = -110.2 \text{ kJ}$$
- $$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) \quad \Delta H^\circ = +180.5 \text{ kJ}$$
24. Given the following thermodynamic data:
- $$2\text{Fe}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) \quad \Delta H^\circ = -823 \text{ kJ}$$
- $$3\text{Fe}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) \quad \Delta H^\circ = -1120. \text{ kJ}$$
- Calculate the ΔH° for: $3\text{Fe}_2\text{O}_3(\text{s}) \rightarrow 2\text{Fe}_3\text{O}_4(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$
25. How are the heat of combustion of scandium and the heat of formation of Sc_2O_3 related?
26. Write the formation reaction for each of the following substances at 298 K. Refer to Appendix B to determine the standard states.
- $\text{NH}_4\text{NO}_3(\text{s})$
 - $\text{CH}_3\text{I}(\text{g})$
 - $\text{FeO}(\text{s})$
 - $\text{Hg}_2\text{Cl}_2(\text{s})$
27. Write the formation reaction for each of the following substances at 298 K. Refer to Appendix B to determine the standard states.
- $\text{B}_2\text{H}_6(\text{g})$
 - $\text{SO}_2(\text{g})$
 - $\text{PF}_3(\text{g})$
 - $\text{NaCl}(\text{s})$
28. Magnesium burns with a brilliant white light. How much heat is released when a 0.75 g magnesium ribbon is burned?
29. How much heat is liberated when a 1.00×10^3 kg of aluminum reacts with oxygen at 25 °C and 1 atm?
30. The heat of combustion of toluene, $\text{C}_7\text{H}_8(\text{l})$, is $-3910.3 \text{ kJ}\cdot\text{mol}^{-1}$. What is the enthalpy of formation of toluene?
31. The heat of formation of $\text{OF}_2(\text{g})$ is 24.7 kJ/mol, that of $\text{Cl}_2\text{O}(\text{g})$ is 80.3 kJ/mol, and that of $\text{ClF}_3(\text{l})$ is $-189.5 \text{ kJ}\cdot\text{mol}^{-1}$.
- Determine the heat of formation of $\text{ClF}(\text{g})$ given the following thermochemical equation:

$$2\text{ClF}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{g}) + \text{OF}_2(\text{g}) \quad \Delta H^\circ = 206 \text{ kJ}$$
 - Determine the standard enthalpy change for the following reaction.

$$2\text{ClF}_3(\text{l}) + 2\text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{g}) + 3\text{OF}_2(\text{g})$$
32. Use the data in Appendix B and the following thermochemical equation to determine the enthalpy of formation of $\text{MgCO}_3(\text{s})$.
- $$\text{MgCO}_3(\text{s}) + 2\text{HCl}(\text{g}) \rightarrow \text{MgCl}_2(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -24 \text{ kJ}$$
33. The reaction of quicklime (CaO) with water produces slaked lime [$\text{Ca}(\text{OH})_2$]. The reaction of quicklime with water is highly exothermic:
- $$\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{s}). \quad \Delta H = -350. \text{ kJ}$$
- What is the heat of reaction per gram of CaO ?
 - How much heat is released when 25.0 kg of slaked lime is produced?
34. C_2H_6 is ethane, a component of natural gas. All of the heat from the complete combustion of 8.506 mmol C_2H_6 gas at 298 K is transferred to 1.000 kg of water that is initially at 25.00 °C. Determine the final temperature of the water if the combustion is carried out at
- constant pressure
 - constant volume.
35. Use the data in Appendix B to determine ΔH° of the following reactions.
- $\text{Pb}^{2+}(\text{aq}) + 2\text{Br}^{-}(\text{aq}) \rightarrow \text{PbBr}_2(\text{s})$
 - $\text{NaCl}(\text{s}) \rightarrow \text{Na}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$
 - $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
 - $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

36. Use the data in Appendix B to determine ΔH° for each of the following reactions:

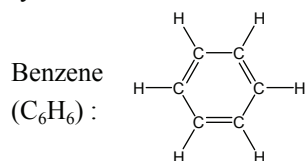
- a) $\text{Ag}_2\text{O}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{Ag}(\text{s}) + \text{H}_2\text{O}(\text{l})$
- b) $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$
- c) $2\text{Ag}^+(\text{aq}) + \text{Pb}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Pb}^{2+}(\text{aq})$
- d) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- e) $\text{CH}_3\text{COOH}(\text{l}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

37. Determine the heat liberated in the reaction of 5.0 g of Al and 20.0 g of Fe_2O_3 at 25 °C to produce Fe and Al_2O_3 . The reaction, which is known as the thermite reaction, is so exothermic that it was used to weld railroad ties because the iron is produced in the molten state.

BOND ENERGIES

Use the data in Appendix B in Exercises 38–44.

- 38. Determine the P-H and Si-H bond energies.
- 39. Determine the Ti-Cl and Na-Cl bond energies.
- 40. What is the average O-O bond energy in O_3 ? How does it compare to the O-O and O=O bond energies in Table 3.3?
- 41. What is the O-O bond energy in H_2O_2 . What can you conclude about the O-O bond order in H_2O_2 based on its bond energy?
- 42. Determine N-O bond energy in NOCl (O is central atom). Based on your answer and the tabulated bond energies in Table 3.2, what is the bond order of the N-O bond in NOCl?
- 43. What is the N-N bond energy in N_2O_4 , which is two NO_2 units bound through the N-N bond?
- 44. What is the C-H bond energy in HCN?
- 45. Use the data in Appendix B and the C-H bond energy in Table 3.3 to determine the average C-C bond energy in benzene (structure given below). How does this value compare to the average of a single bond and a double bond, the result expected from the Lewis structure? The difference is due to the fact that the pi system is delocalized that makes it more stable.



- 46. Use the bond energies given in Table 3.3 to estimate the enthalpy of combustion at 298 K for each of the following organic compounds. Remember that water is a liquid at 298 K.
 - a) $\text{H}_3\text{C}-\text{CH}_3(\text{g})$
 - b) $\text{H}_2\text{C}=\text{CH}_2(\text{g})$
 - c) $\text{HC}\equiv\text{CH}(\text{g})$
- 47. Use the data in Appendix B and the information given in Exercise 31 to determine values for the O-Cl and O-F bond energies.
- 48. Use bond energies to estimate the enthalpy change of each of the following gas-phase reactions:
 - a) $\text{H}_2\text{C}=\text{CH}_2(\text{g}) + \text{HC}\equiv\text{N}(\text{g}) \rightarrow \text{H}_3\text{C}-\text{CH}_2-\text{C}\equiv\text{N}(\text{g})$
 - b) $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$
 - c) $\text{CH}_3\text{F}(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HF}(\text{g})$
- 49. Use bond energies and the data in Appendix B to estimate the enthalpies of formation of the following substances:
 - a) $\text{NF}_3(\text{g})$
 - b) $\text{H}_2\text{N}-\text{NH}_2(\text{g})$
- 50. Use bond energies and the data in Appendix B to estimate the enthalpies of formation of the following substances. Note that the standard state of C is graphite not a gas.
 - a) $\text{F}_2\text{C}=\text{CH}_2(\text{g})$
 - b) $\text{CH}_3\text{Cl}(\text{g})$

CALORIMETRY

- 51. What is the final temperature of a mixture prepared by adding 12.4 g of Fe at 89.4 °C to 25.6 mL of water in an insulated container at 18.6 °C? The density of water is $1.00 \text{ g}\cdot\text{mL}^{-1}$ and $s_{\text{Fe}} = 0.44 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$.
- 52. What is the specific heat of tin if a mixture of 100.0 g of Cu at 10.0 °C and 200.0 g of Sn at 120.0 °C reach thermal equilibrium at a temperature of 69.0 °C? The specific heat of copper is $0.38 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$.
- 53. At what temperature would thermal equilibrium be reached in a mixture prepared by adding 1.00 g of N_2 at 0 °C to 1.00 g of Kr at 200 °C in an insulated container? See Table 3.1 for specific heats.
- 54. A 14.6-g sample of beryllium at 96.7 °C is placed into 35.0 mL of water at 20.2 °C in an insulated container. The temperature of the water at thermal equilibrium is 32.0 °C. What is the specific heat of beryllium? Assume a density of $1.00 \text{ g}\cdot\text{mL}^{-1}$ for water.

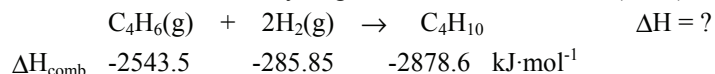
55. A 35.4-g metal bar at 97.6 °C is placed into an insulated flask containing 75.0 g of ice at 0 °C. What is the specific heat of the metal if cooling the bar to 0 °C melted 2.36 g of the ice? The heat of fusion of water at 0 °C is 6.01 kJ·mol⁻¹.
56. A 0.186-mole sample of NaX is dissolved in 275 mL of water in an insulated container at 23.7 °C. After the solid dissolves, the temperature of the water is 19.2 °C. What is the heat of solution of NaX? The solution process is NaX(s) → NaX(aq).
57. 25.0 mL of 0.12 M HX(aq) at 22.0 °C and 25.0 mL of 0.12 M NaOH(aq) at 22.0 °C are mixed. After reaction, the temperature of the mixture is 27.6 °C. What is the heat of neutralization; HX(aq) + NaOH(aq) → H₂O(l) + NaX(aq)? Assume a specific heat of 4.18 J·g⁻¹·°C⁻¹ and a density of 1.00 g·mL⁻¹ for all solutions.
58. What is the heat of combustion of the sugar D-sorbose (C₆H₁₂O₆) at 298 K if combustion of 0.0187 moles of the solid caused a 6.56 °C rise in temperature in a bomb calorimeter with a heat capacity of 7.97 kJ·°C⁻¹?
59. The combustion of 0.3268 g of oleic acid, C₁₈H₃₄O₂(l), resulted in a temperature rise of 3.462 °C in a constant pressure calorimeter with a heat capacity of 3.715 kJ·°C⁻¹.
- What is the standard enthalpy of combustion of oleic acid at 298 K?
 - What is the standard heat of formation of oleic acid at 298 K?
60. What is the heat capacity of a bomb calorimeter if the combustion of 2.360 mmol of salicylic acid (C₇H₆O₃(s), ΔH_{comb} = -3022 kJ·mol⁻¹) increases the temperature of the calorimeter by 2.612 °C?
61. Burning 117.7 mg of naphthalene, C₁₀H₈(s), the active ingredient in mothballs, results in a temperature rise of 3.275 °C in a bomb calorimeter with a heat capacity of 1.444 kJ·°C⁻¹.
- Write the balanced equation for the combustion at 25 °C.
 - What is ΔE_{comb} of C₁₀H₈(s) in kJ·mol⁻¹?
 - What is ΔH_{comb} of C₁₀H₈(s) at 298 K?
 - What is ΔH_f of C₁₀H₈(s) at 298 K?
62. When 1.020 g of ethanol was burned in oxygen in a bomb calorimeter containing 2400. g of water, the temperature of the water rose from 22.46 °C to 25.52 °C. What is the enthalpy change, ΔH, for the combustion of 1 mol of ethanol? C₂H₅OH(l) + 3O₂(g) → 2CO₂(g) + 3H₂O(l)
63. Combustion of 2.000 g of propane (C₃H₈) in a bomb calorimeter produces 105.0 kJ of heat at 25 °C. What is the heat of combustion of propane?
64. ΔE_{comb} = -8942.6 kJ·mol⁻¹ for chrysene, C₁₈H₁₂(s), at 25 °C. When any hydrocarbon (such as chrysene) is burned completely, the products are CO₂ and H₂O.
- Write and balance a chemical equation for the combustion of chrysene and determine the value of Δn_g for the combustion reaction.
 - Determine the value of ΔH per mole for the combustion of chrysene at 298 K.
 - When 1.1492 g of chrysene, C₁₈H₁₂(s) (M_m = 228.29 g·mol⁻¹), was burned in a bomb calorimeter, the temperature of the water rose from 23.00 °C to 27.72 °C. What is the heat capacity of this calorimeter.
65. When 0.8681 g of cetyl palmitate (C₃₂H₆₄O₂(s), (M_m = 464.86 g·mol⁻¹) was burned in a calorimeter having a heat capacity of 9.535 kJ·°C⁻¹, the temperature rose by 3.99 °C. Calculate the standard enthalpy change per mole, ΔH° at 298 K for the combustion of cetyl palmitate.

FOOD AS FUEL

66. The serving size listed on a bag of tortilla chips is 1 oz (28 g or ~ 6 chips), which contains 6 g of fat, 19 g of carbohydrates and 2 g of protein. What are the total number of dietary calories in one serving of chips?
67. A package of cookies from the vending machine has the following dietary information for a serving size of 6 cookies: 10. g of fat, 25 g of carbohydrates, and 6 g of protein. What are the total number of dietary calories in a serving?
68. The nutrition label on a jar of maple syrup indicates that a serving (60 mL) contains 200 Calories. Assume that all of the calories come from sugars (carbohydrates) and determine the number of grams of sugar that are in one serving of maple syrup.

MISCELLANEOUS PROBLEMS

69. Use Hess' law of heat summation and the heats of *combustion* given below to determine the heat of hydrogenation of 1,3-butadiene (C_4H_6)?



70. What are ΔE , q , w and ΔH for the evaporation of 10.0 g of $Br_2(l)$ at 298 K and 1 atm?
71. Bicycle riding at 13 mph consumes 2800 kJ per hour for a 150 lb. person. How many miles must this person ride to lose 1 lb. of body fat? Hint: body fat contains 39 kJ·g⁻¹ of stored energy?
72. Kerosene is a mixture of organic compounds that has a density of 0.749 g/mL and a heat of combustion of -88 kJ·g⁻¹. Note that 1 gal = 3.79 L = 4 qt.
- How much heat is liberated when 0.75 gal of kerosene is burned?
 - Assume that all of the heat of the combustion is transferred to the water and determine how many quarts of kerosene must be burned to take 1.0 gal of water from 25 °C to its boiling point. Give two reasons why the actual amount of heat required on a stove is much higher than the calculated value.
73. Use the following thermochemical equations:
- $MnO_2(s) + CO(g) \rightarrow MnO(s) + CO_2(g) \quad \Delta H^\circ = -151 \text{ kJ}$
 - $Mn_3O_4(s) + CO(g) \rightarrow 3MnO(s) + CO_2(g) \quad \Delta H^\circ = -54 \text{ kJ}$
 - $3Mn_2O_3(s) + CO(g) \rightarrow 2Mn_3O_4(s) + CO_2(g) \quad \Delta H^\circ = -142 \text{ kJ}$
- to determine ΔH° for each of the following reactions:
- $2MnO_2(s) + CO(g) \rightarrow 2Mn_2O_3(s) + CO_2(g)$
 - $Mn_2O_3(s) + CO(g) \rightarrow 2MnO(s) + CO_2(g)$
 - $MnO(s) + MnO_2(s) \rightarrow Mn_2O_3(s)$
 - $Mn_2O_3(s) + MnO(s) \rightarrow Mn_3O_4(s)$
74. Dissolving 8.65 g NH_4NO_3 in 50.0 mL water in an insulated container resulted in a temperature drop of 13.3 °C. What is the heat of solution of ammonium nitrate?
75. Ammonium nitrate is a common ingredient in fertilizers that can also be used to make explosives because it decomposes as follows:
- $$2NH_4NO_3(s) \rightarrow 2N_2(g) + O_2(g) + 4H_2O(g) \quad \Delta H = -236 \text{ kJ.}$$
- The following questions deal with the decomposition of 12.0 g of NH_4NO_3 .
- How much heat is liberated under standard conditions?
 - How much work would be done by the gases at 300. °C?
 - What volume of gas would be produced at 1.00 atm and 300. °C?
76. Benzoic acid ($HC_7H_5O_2$, $\Delta E_{\text{comb}} = -26.38 \text{ kJ} \cdot \text{g}^{-1}$) is a common standard used to determine the heat capacities of bomb calorimeters. The following combustion data were collected in an experiment.
- Combustion of 1.066 g of solid benzoic acid resulted in a rise of 2.860 °C in a bomb calorimeter.
 - Combustion of 0.7832 g of liquid toluene (C_7H_8) caused the temperature of the same bomb calorimeter to rise by 3.376 °C
- Use the above data and 25 °C as the temperature of the experiment to determine the heat of formation of liquid toluene at 298 K.

CHAPTER 4

Thermodynamics and Equilibrium

4.0 Introduction

4.1 Entropy

4.2 Second and Third Laws of Thermodynamics

4.3 Determining Entropy Changes

4.4 Free Energy

4.5 Determining Free Energy Changes

4.6 Standard Free Energy and Equilibrium

4.7 Temperature Dependence of ΔG , ΔG° and K

4.8 Coupled Reactions

4.9 Chapter Summary and Objectives

4.10 Exercises

4.0 INTRODUCTION

A spontaneous process is one that takes place without intervention. A ball rolls downhill spontaneously because doing so lowers its energy, but it does not move back up the hill spontaneously because an input of energy is required to do so. Thus, it would be tempting to conclude that processes should be spontaneous if they are exothermic. However, there are many examples of spontaneous endothermic processes, the most common being evaporation in which liquid molecules spontaneously break their intermolecular forces to pass into the gas phase. Thus, the enthalpy change is an important factor, but it is not the sole factor in determining spontaneity of a chemical process. Consequently, we require a more complete understanding of energy than is provided by the first law alone.

Related to the spontaneity of a reaction is the extent of reaction. Thus far, we have assumed that the limiting reactant is always consumed completely in a reaction, but this is not always the case; many reactions reach equilibrium well before the limiting reactant is fully consumed. In this chapter, we examine the thermodynamic basis of equilibrium and develop methods to predict both the spontaneity and extent of chemical reactions.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- define entropy;
- state the second law of thermodynamics;
- define the Gibbs free energy;
- discuss the third law of thermodynamics;
- explain how to use thermodynamic tables to calculate ΔG° and ΔS° ;
- describe equilibrium as a thermodynamic consequence;
- show how to calculate an equilibrium constant from thermodynamic data;
- quantify the temperature dependence of the equilibrium constant; and
- show how thermodynamically favorable reactions can be used to drive unfavorable reactions.

4.1 ENTROPY

The various ways in which a particle can move are called its **degrees of freedom**. The motion of an atom can be fully described by the x, y, and z components of the motion. Thus, each atom has three degrees of freedom, so a molecule with N atoms has 3N degrees of freedom, which can be classified as follows:

- **Translational** degrees of freedom involve straight line motions of the center of mass. They result when all of the atoms move in the same direction. All molecules have three translational degrees of freedom.
- **Rotational** degrees of freedom involve rotations of the molecule about an axis through its center of mass. All non-linear molecules have three rotational degrees of freedom, but linear molecules have only two.
- **Vibrational** degrees of freedom involve small changes in the bond lengths and/or angles, which oscillate about their equilibrium values. All degrees of freedom that are not rotations or translations are vibrations.

Figure 4.1 shows the six degrees of freedom of CO. The motions can be broken down into three translations in which both atoms move in the same direction, two rotations that result when the two atoms move perpendicular to the bond but in opposite directions, and one vibration when the two atoms move in opposite directions along the bond axis.

The energy of a degree of freedom is quantized just as the energy of an electron in an atom or molecule is quantized. There are translational, rotational, and vibrational quantum numbers and energy levels. The speed with which a molecule translates, the frequency with which it rotates, and the speed with which its atoms move relative to one another as it vibrates are all dictated by its translational, rotational, and vibrational quantum numbers. The energy of the m^{th} molecule (E_m) is the sum of the energies of each of its degrees of freedom*:

$$E_m = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} \quad \text{Eq. 4.1}$$

The total energy of a system of molecules (E_{tot}) is the sum of the molecular energies.

$$E_{\text{total}} = \sum_m E_m \quad \text{Eq. 4.2}$$

For example, if a molecule has $4 U^\dagger$ of translational energy, $2 U$ of rotational energy, and $0 U$ of vibrational energy, then Equation 4.1 allows us to determine that its total energy is $E_m = 4 + 2 + 0 = 6 U$. If a system contains three molecules with 6, 3, and 3 U of energy each, then Equation 4.2 can be used to determine that the total energy of the system is $E_{\text{total}} = 6 + 3 + 3 = 12 U$.

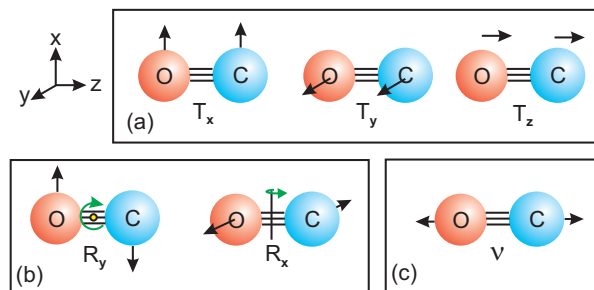


Figure 4.1 Degrees of Freedom in CO

- (a) three translational degrees along x, y, and z axes (T_x is used to designate a translation along the x axis.)
 (b) two rotational degrees about y and x axes (R_y is used to designate a rotation about the y axis.)
 (c) one vibrational degree of freedom (The Greek symbol ν (nu) is often used to designate vibrational motions like the one shown here.)

* Energy can also be distributed into electronic energy levels, but more energy than is available at common conditions is required to do so in most molecules.

[†] U is used to represent arbitrary units of energy in this section. Read "4 U of translational energy" as "4 units of translational energy."

We now examine the number of ways in which the total energy can be distributed into the molecular energies. For example, consider particle X that has energy levels at 0, 3, 6, 9... U as described in Figure 4.2. The energy of the particle in Figure 4.2 is 3 U as shown by the blue circle. A system of three X particles with a total energy of $E_{\text{total}} = E_1 + E_2 + E_3 = 6 \text{ U}$ is represented in Figure 4.3. There are only two combinations of allowed energies, called **energy configurations**, that produce 6 U: $E_{\text{total}} = 6 + 0 + 0$ and $E_{\text{total}} = 3 + 3 + 0$. As shown in Figure 4.3, there are three ways to arrive at each configuration, so there are a total of six ways in which to distribute 6 U of energy in this system. The actual distribution would vary as the molecules transfer energy to one another when they collide. However, as long as the temperature (total energy) remains the same, the molecules would always be in one of these six distributions. Recall that thermal energy is the average kinetic energy of the molecules; some have more energy and others have less.

We now present a method for determining the number of ways in which the particles can be distributed into a given configuration. We begin by rewriting Equation 4.2 in terms of the allowed molecular energies and the number of molecules with that energy.

$$E_{\text{total}} = \sum_{\text{allowed energies}} n_i E_i \quad \text{Eq. 4.3}$$

n_i is the number of molecules that have energy E_i . This is equivalent to rewriting $6 = 3 + 3 + 0$ as $6 = (2)3 + (1)0$. The number of arrangements of N particles in the E_i energy levels is given in Equation 4.4.

$$W = \frac{N!}{\prod_i (n_i!)} \quad \text{Eq. 4.4}$$

W is called the **weight** of the configuration; it is the number of ways in which the configuration can be achieved. n_i is the number of particles with energy E_i as defined in Equation 4.3. The "!" sign indicates a factorial, and Π represents the product. For example, $5!$ is read 'five factorial' and is equal to $5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 120$. Zero factorial, $0!$ is defined as 1. We now apply Equation 4.4 to Figure 4.3b to confirm that there are only three ways in which the energy can be distributed. There are three particles, so $N = 3$. One particle is in the first level ($n_1 = 1$), two are in the second level ($n_2 = 2$), and none are in the third ($n_3 = 0$), so

$$W = \frac{3!}{1!2!0!} = \frac{3 \cdot 2 \cdot 1}{(1)(2 \cdot 1)(1)} = 3$$

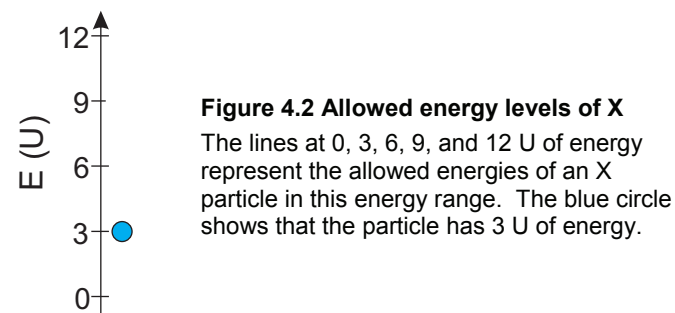


Figure 4.2 Allowed energy levels of X

The lines at 0, 3, 6, 9, and 12 U of energy represent the allowed energies of an X particle in this energy range. The blue circle shows that the particle has 3 U of energy.

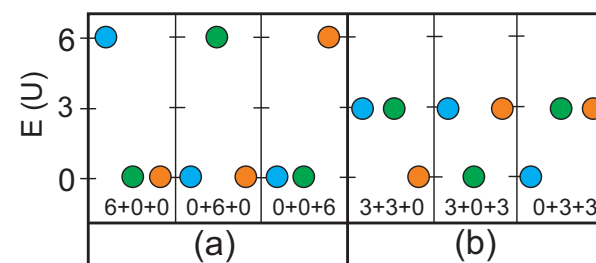


Figure 4.3 Distribution of six units of energy among three molecules that have energy levels at 0, 3, and 6 units

Figures a and b represent the two possible energy configurations. Each configuration has a weight of three ($W = 3$) as shown by the three different ways in which the configuration can be achieved.

- Each of the three particles can be the one with 6 U of energy.
 $E = 6+0+0 = 6$ $E = 0+6+0 = 6$ $E = 0+0+6 = 6$
 $E = (1)6 + 2(0) = 6$ and $W_a = 3!/(1!2!) = 3$
- Each of the three particles can be the one with no energy.
 $E = 3+3+0 = 6$ $E = 3+0+3 = 6$ $E = 0+3+3 = 6$
 $E = (2)3 + 1(0) = 6$ and $W_b = 3!/(2!1!) = 3$

Example 4.1

What is the total energy of the system shown in the figure? What is the weight of the configuration?

Three particles (3) have 6 U of energy, four particles (4) have 3 U, and five particles (5) have no energy, so there are $3 + 4 + 5 = 12$ particles, and the total energy in the form given in Equation 4.3 is

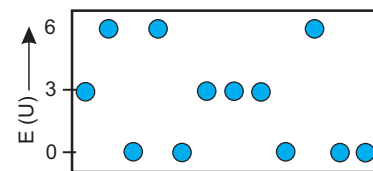
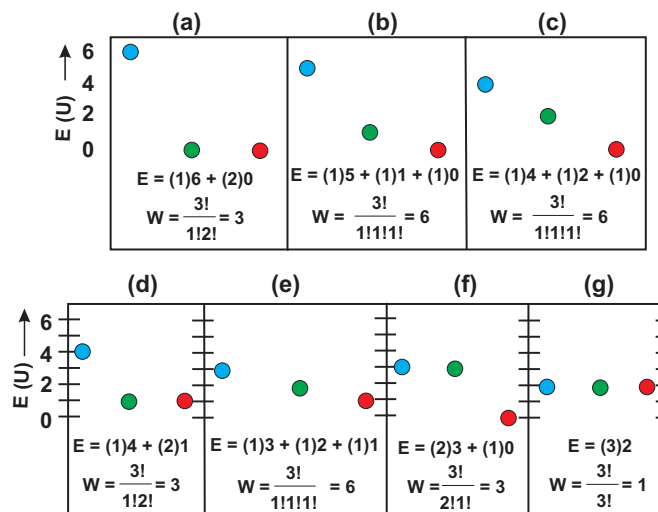
$$E_{\text{total}} = (3 \text{ particles})(6 \text{ U}) + (4 \text{ particles})(3 \text{ U}) + (5 \text{ particles})(0 \text{ U}) = 30 \text{ U}$$

Applying Equation 4.4, we obtain

$$W = \frac{12!}{3!4!5!} = \frac{12 \cdot 11 \cdot 10 \cdot 9 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1}{(3 \cdot 2 \cdot 1) \cdot (4 \cdot 3 \cdot 2 \cdot 1) \cdot (5 \cdot 4 \cdot 3 \cdot 2 \cdot 1)} = 27,720$$

There are 27,720 ways in which this configuration can be achieved; i.e., there are 27,720 ways in which 3 particles have 6 U, 4 particles have 3 U, and 5 particles have no energy.

Equation 4.4 shows that W increases when the number of particles (N) increases or the number of particles in each energy level (each n_i) decreases. The number of particles in any one level (n_i) decreases as the number of available levels increases. We now demonstrate this affect by again considering a system of three molecules with a total energy of 6 U. However, this time the system is composed of Y molecules with energy levels that are separated by only one energy unit. The energy levels available to each Y molecule in a system with a total energy of 6 U are 0, 1, 2, 3, 4, 5, or 6 U. The fact that each Y molecule has more levels available to it in this energy range than does each X molecule means that there are more ways to distribute the energy in the Y molecules. Indeed, Figure 4.4 shows that there seven possible energy configurations that produce a total of 28 ways to distribute the energy in this system; i.e., there are 28 states of Y molecules with total energy of 6 U, while there were only six states of X molecules. The number of states available in this energy range is greater for Y molecules, so we say that Y has a greater **density of states**. The density of states is greater for Y molecules because the energy separation between allowed levels in individual Y molecules is smaller; i.e., there are more energy levels available.

**Example 4.1****Figure 4.4 Seven configurations that produce 6 U of energy**

The weight of each configuration is determined in the bottom of its box. The total number of ways in which the system can achieve a total of 6 U of energy is the sum of the weights: $3+6+6+3+6+3+1 = 28$. There are a total of 28 ways for this system to distribute its energy.

Example 4.2

How many ways can a system of three X molecules distribute 9 U of energy?

$E_{\text{total}} = E_1 + E_2 + E_3 = 9$ and E_1 , E_2 , and E_3 must each be 0, 3, or 6, so only configurations of (9,0,0), (6,3,0), and (3,3,3) are allowed. Using Equation 4.4, we obtain the following weights for each configuration:

a) $E_{\text{total}} = (1)9 + (2)0$, so $W_a = 3!/1!2! = 3$

9 0 0 0 9 0 0 0 9

b) $E_{\text{total}} = (1)6 + (1)3 + (1)0$, so $W_b = 3!/1!1!1! = 6$

6 3 0 6 0 3 3 6 0

0 6 3 0 3 6 3 0 6

c) $E_{\text{total}} = (3)3$, so $W_c = 3!/3! = 1$

3 3 3

The total number of ways in which 9U of energy can be distributed equals $W_a + W_b + W_c = 3 + 6 + 1 = 10$. The ten distributions are shown in Figure 4.5. Note that the number of ways in which energy can be distributed is greater for 9 U than for 6 U. We conclude that the number of ways in which the energy of a system can be distributed increases with its energy.

Consider the process $3X \rightarrow 3Y$ at a temperature where the total energy is 6 U. We showed in Figure 4.4 that there are 28 states over which three Y molecules can distribute this energy but only 6 states over which three X molecules can distribute it. If enthalpy effects can be ignored ($\Delta H = 0$), then energy is more likely to be found on Y molecules than on X molecules. For this purely statistical reason, the number of Y molecules at equilibrium will be greater than the number of X molecules, i.e., *the reaction is extensive because the products can distribute energy in more ways than can the reactants*. The number of ways in which a system can distribute its energy is such an important property that a thermodynamic property, entropy, is defined to measure it. The **entropy (S)** of a system is related to the number of ways in which it can distribute its energy (W) by the Boltzmann formula given in Equation 4.5.

$$S = k \ln W^*$$

Eq. 4.5

k is the Boltzmann constant, which equals the ideal gas constant divided by Avogadro's number: $k = R/N_A = 8.314/6.023 \times 10^{23} = 1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$.

Systems with high entropies are favored over those with low entropies because they can distribute energy over more states. For example, the entropy of Y (S_Y) is greater than

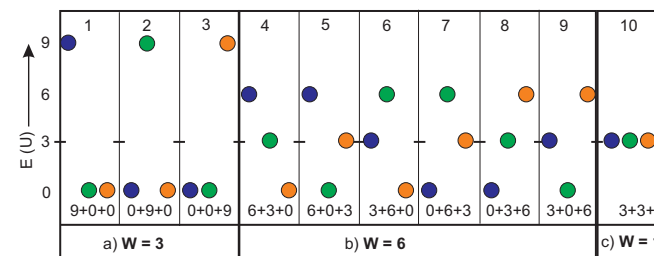


Figure 4.5 Ten ways for three molecules to distribute 9 U of energy in energy level spaced by 3 U

PRACTICE EXAMPLE 4.1

How many ways can 8U of energy be distributed among three particles each with energy levels at 0, 2, 4, 6, and 8U?

The allowed combinations of energy

Answer: _____

How does the entropy of this system compare to that in Example 4.2?

* When the number of particles is very large, as it is in a molecular system, one configuration dominates over the others. W in the Boltzmann formula is the weight of the dominant configuration.

that of X (S_X) because Y can distribute energy in more ways than X. The entropy change for $X \rightarrow Y$ is $\Delta S = S_Y - S_X$, so $\Delta S > 0$. The process is extensive if $\Delta H \sim 0$ because the product can disperse energy better than can the reactant. We conclude that the two driving forces behind a process are:

1. the tendency of systems to minimize their potential energy (enthalpy), and
2. the tendency of systems to maximize the dispersion of their energy (entropy).

As we shall see, these two driving forces can act either in concert or in opposition.

Figure 4.6 shows the effect that *constraints* (confinements or restrictions) on the degrees of freedom have on the density of states. The particles in Figure 4.6a are not constrained, so their energy is not constrained, which is shown by the complete shading. These particles are unbound and can have any energy in the range; *i.e.*, there are no quantized energy levels. Figure 4.6b shows a slightly constrained system, such as a rotating or translating molecule. The low constraints on the motion result in only slight constraints on the rotational energies, so their energy separations are small. Figure 4.6c shows the energy levels of a more constrained system, such as two vibrating atoms. The bonds constrain the motion to very small regions of space, so the separation between vibrational energy levels is greater than for translational or rotational levels. We conclude that increasing the constraints on molecular motion increases the constraints on the allowed energies; *i.e.*, highly constrained systems have low densities of states.

Now let's compare the entropies of a substance in the gas and solid states. The major constraints on vibrational motion are due to the bonds, which are not substantially different in the solid and gas phase, so vibrations have little impact on entropy differences between the two states. Thus, it is differences in the translational and rotational degrees of freedom that result in large entropy differences. Translations in a gas are confined to the relatively large volume of a flask, so they are not very constrained. However, these same motions in the solid are constrained to oscillations about the molecule's equilibrium position in the lattice. Similarly, rotation in a gas is free, but it is constrained to a back-and-forth oscillation in the lattice. The increased constraints on movement in the solid result in energy levels that are much farther apart. Motion in a liquid is much more constrained than in a gas, but it is slightly less than in a solid. Consequently, the density of states increases in the order gas \gg liquid $>$ solid, so the relative entropies of a substance in the three states of matter are given by the following:

$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$$

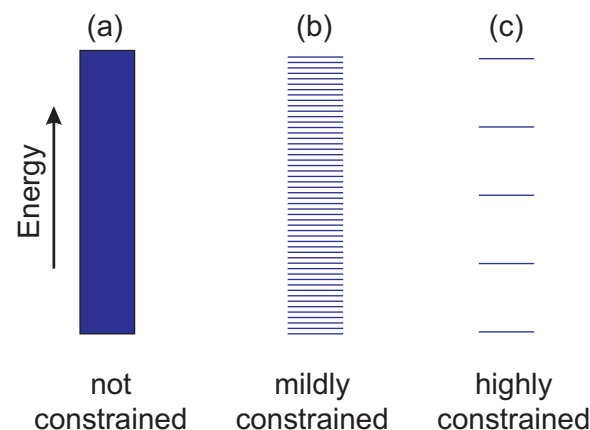


Figure 4.6 Energy levels move apart as systems become more constrained.

(a) Free particles with no constraints can have any energy.
 (b) Translational and rotational motions in a gas are only slightly constrained, so the energy separation is small. Thus, many but not all energies in the range are available.
 (c) Vibrations are highly constrained by the bonds, so the energy levels are relatively far apart and only a few vibrational energies are available.

Based on the preceding entropy inequalities, we conclude that processes that increase the number of molecules in the gas phase increase the entropy of the system, while processes that decrease the number of molecules in the gas phase decrease the entropy of the system. Entropy changes in processes that do not change the number of moles of gas are usually much smaller than those that do.

We have now shown that the entropy of a system decreases as the constraints on the particles in the system are increased and increasing the constraints on a system ordinarily introduces order into the system. For example, constraining gas-phase molecules sufficiently moves them from a very disordered collection of molecules undergoing random motion into a very ordered collection of molecules in the solid state that undergo organized motion. Although entropy is a measure of the number of ways in which the energy of a system can be distributed, it is often loosely defined as a measure of the amount of disorder in a system. However, disorder is simply a good indicator of entropy because disordered systems, such as the gas phase, have higher densities of states and higher entropies than do ordered ones. Consequently, *the relative disorder in two systems is frequently used as an indicator of their relative entropies*.

As shown in Example 4.2, the number of ways in which the energy of a system can be distributed increases as its energy increases. The energy of a system increases with its temperature, so we conclude that *the entropy of a system always increases with temperature*. One way to increase the energy of a system is to add heat. However, the addition of a fixed amount of heat to a system has a much greater impact on the system when its entropy is low because increasing the number of accessible states has more impact when there are only a few states to start with. The system entropy is low when its temperature is low, so we can say that the effect of heating is reduced as the temperature at which the system is heated is raised. For example, adding 1 J of heat at 5 K (low entropy) has a much more dramatic effect on the entropy than adding 1 J at 500 K (high entropy). The relationship between the change in entropy and the heat added (q) to produce it at some temperature (T), which was derived rigorously in the 19th century, is given in Equation 4.6.

$$\Delta S = \frac{\text{heat added reversibly}^*}{\text{temperature at which heat is added}} = \frac{q_{\text{rev}}}{T} \quad \text{Eq. 4.6}$$

Note that, consistent with Equation 4.6, the units of entropy are $\text{J}\cdot\text{K}^{-1}$.

* Heat added reversibly means that thermal equilibrium is maintained as the heat is added. In order to maintain thermal equilibrium, heat must be added very slowly.

4.2 SECOND AND THIRD LAWS OF THERMODYNAMICS

You may be asking “If the dispersal of energy is so important, why isn’t $\Delta S > 0$ sufficient to drive all processes?” The answer is that systems interact with their surroundings, and, as stated in the second law of thermodynamics, it is energy dispersal in both that is important.

Second Law of Thermodynamics: the entropy of the universe increases ($\Delta S_{\text{univ}} > 0$) in all spontaneous processes.

The thermodynamically favorable direction of any process is the one for which $\Delta S_{\text{univ}} > 0$.

Example 4.3

A piece of tin at 50 °C is placed into water that is in an insulated container and at 100 °C. Can 1 J of heat flow spontaneously from the tin to the water?

We use the second law to determine the spontaneity. No heat can leave the (water + tin) mixture because the container is insulated, so it constitutes our thermodynamic universe. Thus, the entropy change in the universe caused by the heat flow is

$$\Delta S_{\text{univ}} = \Delta S_{\text{tin}} + \Delta S_{\text{water}}$$

Use Equation 4.6 to determine ΔS_{tin} and ΔS_{water} for the transfer of 1 J of heat from the water to the tin.

$$\Delta S_{\text{water}} = +\frac{1 \text{ J}}{373 \text{ K}} = +2.68 \times 10^{-3} \text{ J} \cdot \text{K}^{-1} \quad \Delta S_{\text{tin}} = -\frac{1 \text{ J}}{323 \text{ K}} = -3.10 \times 10^{-3} \text{ J} \cdot \text{K}^{-1}$$

The signs of the above entropy changes reflect the requested direction of heat flow, which is out of the tin (negative) and into the water (positive). ΔS_{univ} for the process is then

$$\Delta S_{\text{univ}} = -3.10 \times 10^{-3} + 2.68 \times 10^{-3} = -4.2 \times 10^{-4} \text{ J} \cdot \text{K}^{-1}$$

ΔS_{univ} is negative, so the process is not spontaneous in the specified direction. However, reversing the direction of the process changes the sign of ΔS_{univ} , so we can conclude that heat flows spontaneously from the water at 100 °C to the tin at 50 °C. This is an example of the common rule that **heat always flows spontaneously from hot to cold**.

Thermodynamic tables give values for ΔH_f° rather than simply H because only relative enthalpies (ΔH 's) can be determined.* However, tabulated values of S° are known because there is a known reference point for entropy. This reference point is established by the third law of thermodynamics. To establish the third law, we define a *perfect crystal* as one in which all lattice sites are occupied by the correct particles, which differs from a real crystal in which some sites may not be occupied or may be occupied by impurities.† We

* The same is true of kinetic and potential energy. In both, a reference is implied. When the kinetic energy of a moving object is given, it is usually relative to that of the earth. Thus, the kinetic energy of an object usually ignores all of the motion of the earth. Similarly, potential energies are given for one position relative to another.

† Unoccupied sites and sites with impurities reduce the constraints on the crystal, which increases the number of ways in which energy can be distributed.

must also recognize that all molecules at 0 K are in their lowest energy levels. Thus, there is just one way in which the energy of a perfect crystal at 0 K can be distributed; *i.e.*, $W = 1$ for a perfect crystal at 0 K. Applying Equation 4.5 we obtain $S = k \ln(1) = 0$. This conclusion is stated in the third law of thermodynamics.

Third Law of Thermodynamics: the entropy of a perfect crystal at 0 K is zero.

The third law gives us a reference point for entropy; $S = 0$ at $T = 0$ K, which is why the tabulated entropies in Appendix B are values of S , not ΔS . Lacking a reference for absolute enthalpies, we tabulate values of heats of formation, which are heats of reactions, not absolute enthalpies. By definition, the heat of formation of an element in its standard state must be zero. However, all substances, even elements, have non-zero entropies at 298 K. The standard entropy of formation of an element (ΔS_f°) is zero, but its absolute entropy is not.

The factors that influence the entropy of a substance are its state of matter, its temperature, and the number and nature of its bonds (degrees of freedom). We have already seen that the entropy of a substance increases with its temperature and that its entropy increases in going from solid to liquid to gas ($S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$). For example, the absolute entropy of liquid water at 298 K is $69.91 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, while that of water vapor at 298 K is $188.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The entropy of a substance also increases as the number of atoms it contains increases because additional atoms provide more degrees of freedom. For example, the entropy at 298 K of O atoms is $160.95 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, while that of O_2 molecules is $205.03 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and that of O_3 molecules is $237.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Example 4.4

Indicate the substance with the greater entropy in each case.

a) CO(g) or $\text{CO}_2\text{(g)}$ at 300 K

Both compounds are gases, and they are at the same temperature. However, CO has six degrees of freedom - (2 atoms)(3 degrees/atom), while CO_2 has nine degrees. The added degrees of freedom give CO_2 more ways to distribute its energy, so it has the higher entropy. $S^\circ(\text{CO}) = 198 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and $S^\circ(\text{CO}_2) = 214 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

b) CO(g) at 50 °C or CO(g) at 150 °C

Molecules at the higher temperature have more energy available, which increases the number of ways in which the energy can be distributed. Therefore, CO(g) has the higher entropy at 150 °C.

c) CO(g) or CH₃OH(l) at 298 K

There are two affects working in opposite directions in this example. CO is a gas while CH₃OH is a liquid, and the gas is expected to have the higher entropy. However, CO has only two atoms and 6 degrees of freedom while CH₃OH has six atoms and 18 degrees of freedom. Such differences cannot be predicted with confidence. In this example, CO has the higher entropy because it is a gas.

4.3 DETERMINING ENTROPY CHANGES

Tabulated values of entropy are normally the standard state values and represented as S° . Everything we have discussed to this point applies to either standard or nonstandard conditions, so the superscript was unnecessary. However, tabulated values of absolute entropies are always the standard state values, so any entropy change that is calculated with them is a standard entropy of reaction; *i.e.*, it is ΔS° that is determined. The entropy change accompanying a process is the entropy of the final state minus the entropy of the initial state: $\Delta S = S_f - S_i$. In a chemical reaction, the final entropy is the entropy of the products, and the initial entropy is that of the reactants. Consequently, the following expression can be used to determine ΔS° from tabulated values of standard state entropies:

$$\Delta S^\circ = \sum c(\text{product}) \times S^\circ(\text{product}) - \sum c(\text{reactant}) \times S^\circ(\text{reactant}) \quad \text{Eq. 4.7}$$

$c(\text{product})$ is the coefficient in the balanced chemical equation of the product whose standard entropy is $S^\circ(\text{product})$. Thus, if the standard entropies of all of the products and reactants are known, the standard entropy of reaction can be determined.

Example 4.5

Determine the entropy change of each process at 298 K and 1 atm.

a) The vaporization of water

Write the process and the absolute entropies from Appendix B under each substance.

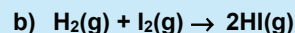


Use Equation 4.7 to obtain ΔS° .

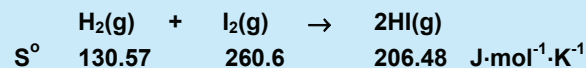
$$\Delta S^\circ = 1S^\circ(\text{product}) - 1S^\circ(\text{reactant}) = 1S^\circ(\text{gas}) - 1S^\circ(\text{liquid})$$

$$\Delta S^\circ = (1 \text{ mol})(188.7 \text{ J·mol}^{-1}\cdot\text{K}^{-1}) - (1 \text{ mol})(69.91 \text{ J·mol}^{-1}\cdot\text{K}^{-1}) = +118.8 \text{ J·K}^{-1} *$$

* Absolute entropy has units of J·mol⁻¹·K⁻¹, which is multiplied by the number of moles of the substance in the balanced equation to yield units of J·K⁻¹ for ΔS . As with enthalpies, the "per mole" is included when referring to the entropy of a named process without the reaction. Thus, the entropy of vaporization of water at 298 K is 118.8 J·mol⁻¹·K⁻¹.



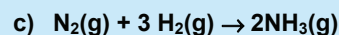
The process and relevant entropies from Appendix B:



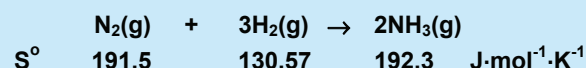
Note the nonzero entries for the elements in their standard state. Next, apply Equation 4.7 to determine ΔS° .

$$\Delta S^\circ = 2S^\circ(\text{HI}) - 1S^\circ(\text{H}_2) - 1S^\circ(\text{I}_2) = 2(206.48) - 130.57 - 260.6 = +21.8 \text{ J}\cdot\text{K}^{-1}$$

Note that the reaction involves gases, but ΔS is not very large because $\Delta n_g = 0$.



$\Delta n_g = 2 - 4 = -2$, so we expect ΔS to be large and negative.



$$\Delta S^\circ = 2S^\circ(\text{NH}_3) - 3S^\circ(\text{H}_2) - S^\circ(\text{N}_2) = 2(192.3) - 3(130.57) - 191.5 = -198.6 \text{ J}\cdot\text{K}^{-1}$$

The chemical equation in this example is for the production of two moles of ammonia from its elements in their standard state. Therefore, the calculated ΔS° is twice the standard entropy of formation of NH_3 ; i.e., $\Delta S_f^\circ(\text{NH}_3) = \frac{1}{2}(-198.6) = -99.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Entropies of formation such as this could be tabulated and used in the same way that heats of formation are used. However, absolute entropies are used instead.

4.4 FREE ENERGY

The spontaneity of a process depends upon both the entropy and the enthalpy change of the system, but the effects of these two thermodynamic properties are combined into one, the entropy of the universe, in the second law. To separate the effects of ΔH and ΔS explicitly and to make the predictive power of the second law more manageable, we require an expression for ΔS_{univ} in terms of *system* variables. We begin by dividing the thermodynamic universe into a system and its surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sur}} + \Delta S$$

Entropy changes in the surroundings result from changes in the thermal surroundings, which are caused by the transfer of heat between the surroundings and the system. At constant pressure and temperature, the heat flowing from the system into the surroundings is $-\Delta H$. Setting $q_{\text{rev}} = -\Delta H$ in Equation 4.6, we obtain

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

Thus, exothermic reactions are favored because they add heat to the surroundings, which increases the entropy of the surroundings. Substitution of this expression for ΔS_{sur} into the expression for ΔS_{univ} yields

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

Multiplying the above equation by $-T$, we obtain

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

The right side of the above expression depends only on system quantities, so it is also a property of the system. This new thermodynamic property is known as the **Gibb's free energy** and given the symbol ΔG .*

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

Eq. 4.8

According to the second law, a spontaneous process is one in which $\Delta S_{\text{univ}} > 0$ or $-T\Delta S_{\text{univ}} < 0$. Consequently, a spontaneous process at constant temperature and pressure is one in which $\Delta G < 0$; *i.e.*, reactions proceed in the forward direction (\rightarrow) when $\Delta G < 0$, in the reverse direction (\leftarrow) when $\Delta G > 0$, and they are at equilibrium (\rightleftharpoons) when $\Delta G = 0$.

The second law can also be stated as follows:

$\Delta G < 0$ for all spontaneous processes at constant temperature and pressure; *i.e.*, the sign of ΔG indicates the spontaneous direction.

Equation 4.8 shows that the free energy results from the interplay of two energy terms: ΔH and $T\Delta S$. ΔH is the *potential* energy difference between the reactants and the products. It arises from differences in bond energies and intermolecular interactions. $\Delta H < 0$ when the energy of the reactants is greater than that of the products (Figure 4.7a). The decrease in enthalpy results in the release of energy, which decreases the free energy of the system. However, reactions in which the products are at higher energy (Figure 4.7b) require energy, which increases the free energy of the system.

$T\Delta S$ is the free energy change resulting from entropy differences in the reactants and products. If $T\Delta S > 0$ (Figure 4.8a), then the entropy of the products is greater than that of the reactants and the reaction releases $T\Delta S$ joules of energy, which decreases the free energy. When $T\Delta S$ is negative (Figure 4.8b), the reaction produces a system that has less entropy, which requires an input of $-T\Delta S$ joules and increases the free energy.

ΔG is called the 'free energy' because it is the energy that is free to do work at constant temperature and pressure.

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

Eq. 4.9

* The Gibb's free energy, ΔG , is the free energy only for processes carried out at constant T and P . However, these are the only conditions considered in this text, so ΔG will be referred to as simply the "free energy."

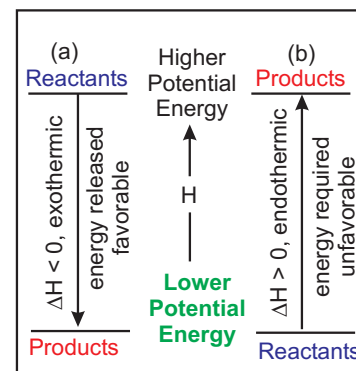


Figure 4.7 Enthalpy change

Systems seek to lower their potential energy, so $\Delta H < 0$ is favorable.

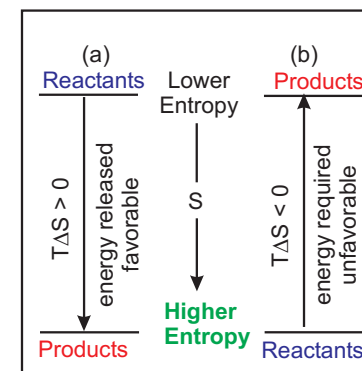


Figure 4.8 Entropy change

Systems seek to increase their entropy, so $\Delta S > 0$ is favorable.

$-w_{\max}$ is the maximum amount of work* that can be done by a system during a process at constant T and P. If ΔG is negative, free energy is released and the process can do work, but, if it is positive, ΔG joules must be supplied to force the process uphill in free energy. For example, consider a process in which $\Delta H = -100$ J and $T\Delta S = -90$ J. The ΔH term is favorable as 100 J of energy are given off by the change in bonds and other interactions. However, the $T\Delta S$ term is unfavorable because $\Delta S < 0$. At the temperature of the process, 90 J of energy is required to decrease the entropy, and it must come from the ΔH term if the process is to be spontaneous. Thus, $\Delta G = -100 - (-90) = -10$ J. $\Delta G < 0$, so the process is spontaneous, but only 10 J of energy are free to do work.

Most of our calculations will be for the standard state, so we apply Equation 4.8 to the standard state to obtain the standard free energy of reaction

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

Eq. 4.10

ΔG° is the free energy of a reaction when all reactants and products are in their standard state, so its sign indicates the spontaneous direction under these specific set of conditions. Consider the reaction $A(g) \rightarrow B(g)$. ΔG° is the value of ΔG when both A and B are in their standard states, which is a partial pressure of 1 atm for each gas. If $\Delta G^\circ < 0$, the spontaneous direction is $A \rightarrow B$. If A is consumed and B is formed when they are at equal pressures, then B will be present in the greater amount when the reaction is complete; *i.e.*, the reaction is extensive because there is more product than reactant at completion. If $\Delta G^\circ > 0$, the spontaneous process is $A \leftarrow B$ when they are at equal pressures, so more A than B will be present at completion and the reaction is not extensive. We conclude that

The sign of ΔG° indicates the side of the reaction that is favored at equilibrium. If $\Delta G^\circ > 0$, the reactants are favored, but if $\Delta G^\circ < 0$, the products are favored.

Thus, ΔG and ΔG° have very different meanings, but they are often confused. For example, $\Delta G_{\text{vap}}^\circ = +8.6 \text{ kJ}\cdot\text{mol}^{-1}$ for water at 25 °C, which is often misinterpreted to mean that the evaporation of water is not spontaneous at 25 °C. However, $\Delta G^\circ > 0$ means that the water cannot evaporate spontaneously *at standard conditions*. Consistent with $\Delta G^\circ > 0$, water vapor would spontaneously condense if its pressure were 1 atm at 25 °C. The fact that $\Delta G^\circ > 0$ simply means that the equilibrium pressure of water vapor is less than 1 atm. In fact, the equilibrium pressure of water vapor at 25 °C is only 0.031 atm.

* It is the maximum amount of work because some of the energy change in real processes is lost, usually through heat.

PRACTICE EXAMPLE 4.2

Determine the standard entropies of formation of the following:

a) $\text{SO}_3(g)$

formation reaction (Hint: The standard state of S is the state that has a zero heat of formation):

$$\Delta S_f^\circ = \text{_____} \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

b) $\text{NH}_4\text{Cl}(g)$

formation reaction:

$$\Delta S_f^\circ = \text{_____} \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

c) $\text{O}_2(g)$

formation reaction:

$$\Delta S_f^\circ = \text{_____} \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

4.5 DETERMINING FREE ENERGY CHANGES

The absolute free energy of a substance cannot be determined, but relative values can. Consequently, standard free energies of formation (ΔG_f°), not absolute standard free energies (G°), are tabulated in Appendix B. We again employ Hess's law of heat summation along with the free energies of formation to obtain free energies of reactions:

$$\Delta G^\circ = \sum c(\text{product}) \times \Delta G_f^\circ(\text{product}) - \sum c(\text{reactant}) \times \Delta G_f^\circ(\text{reactant}) \quad \text{Eq. 4.11}$$

$c(\text{product})$ is the coefficient in the balanced chemical equation of the product whose free energy of formation is $\Delta G_f^\circ(\text{product})$. The result obtained using Equation 4.11 is the same as that obtained by determining the ΔH° and ΔS° and then applying Equation 4.10.

As with enthalpies, the units of free energies of formation are $\text{kJ}\cdot\text{mol}^{-1}$ (named reaction) but multiplication by the number of moles of each substance in the balanced equation produces units of kJ for free energy changes in thermochemical equations.

Example 4.6

Determine ΔG° at 298 K for each process described in Example 4.5 from free energies of formation, and from enthalpies of formation and absolute entropies.

Proceed as in Example 4.5 by writing the expression describing the process and then writing the pertinent thermodynamic data directly under each reactant and product.

a) The vaporization of water

	$\text{H}_2\text{O}(\text{l})$	\rightarrow	$\text{H}_2\text{O}(\text{g})$	
ΔG_f°	-237.2		-228.59	$\text{kJ}\cdot\text{mol}^{-1}$
ΔH_f°	-285.83		-241.82	$\text{kJ}\cdot\text{mol}^{-1}$
S°	69.91		188.7	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

The free energy of vaporization of water can be determined directly from the standard free energies of formation and Equation 4.11

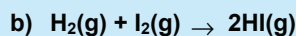
$$\Delta G^\circ = 1(-228.59) - 1(-237.2) = 8.6 \text{ kJ}$$

or from the standard enthalpy and entropy of vaporization and Equation 4.10.

$$\Delta H^\circ = -241.82 - (-285.83) = 44.01 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S^\circ = 188.7 - 69.91 = 118.8 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 44.01 \text{ kJ} - (298 \text{ K})(0.1188 \text{ kJ}\cdot\text{K}^{-1}) = 8.61 \text{ kJ}$$



	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightarrow	$2\text{HI}(\text{g})$	
ΔG_f°	0		19.36		1.71	$\text{kJ}\cdot\text{mol}^{-1}$
ΔH_f°	0		62.438		26.5	$\text{kJ}\cdot\text{mol}^{-1}$
S°	130.57		260.6		206.48	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

The standard free energy from standard free energies of formation is

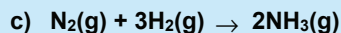
$$\Delta G^\circ = 2(1.71) - 19.36 - 0 = -15.94 \text{ kJ}$$

The standard free energy from the standard enthalpy and entropy of reaction is

$$\Delta H^\circ = 2(26.5) - 0 - 62.438 = -9.4 \text{ kJ}$$

$$\Delta S^\circ = 2(206.48) - 130.57 - 260.6 = 21.79 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -9.4 - 298(0.02179) = -15.9 \text{ kJ}$$



	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightarrow	$2\text{NH}_3(\text{g})$	
ΔG_f°	0		0		-16.5	$\text{kJ}\cdot\text{mol}^{-1}$
ΔH_f°	0		0		-46.11	$\text{kJ}\cdot\text{mol}^{-1}$
S°	191.5		130.57		192.3	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

Using the free energies of formation, we obtain

$$\Delta G^\circ = 2(-16.5) - 0 - 0 = -33.0 \text{ kJ}$$

Using the standard enthalpy and entropy, we obtain the following:

$$\Delta H^\circ = 2(-46.11) - 0 - 0 = -92.22 \text{ kJ}$$

$$\Delta S^\circ = 2(192.3) - 3(130.57) - 191.5 = -198.6 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92.22 - 298(-0.1986) = -33.04 \text{ kJ}$$

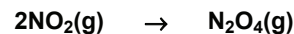
The following properties apply to all thermodynamic quantities:

1. They change sign when the direction of the reaction is reversed.
2. They are multiplied by the same number by which a chemical equation is multiplied.

For example, consider the thermochemical equations in Table 4.1. Reaction A is the reaction considered in Example 4.4c. In Reaction B, the reaction has been multiplied by $1/2$ as have all of the thermodynamic quantities. Reaction C is the reverse of Reaction A, and the signs of the thermodynamic quantities have all been changed.

PRACTICE EXAMPLE 4.3

Determine the standard free energy for the following reaction at 298 K from tabulated data:



$$\Delta G_f^\circ \quad \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta H_f^\circ \quad \text{kJ}\cdot\text{mol}^{-1}$$

$$S^\circ \quad \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

ΔG° from standard free energies of formation

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

ΔG° from standard enthalpies and entropies

$$\Delta H^\circ = \text{_____ kJ}$$

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

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

Table 4.1 Thermodynamic properties as a function of how the reaction is written

Reaction	ΔH° $\text{kJ}\cdot\text{mol}^{-1}$	ΔG° $\text{kJ}\cdot\text{mol}^{-1}$	ΔS° $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
A. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	-92.2	-33.0	-198.6
B. $1/2\text{N}_2(\text{g}) + 3/2\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$	-46.1	-16.5	-99.3
C. $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	+92.2	+33.0	+198.6

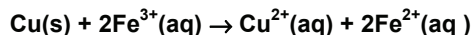
4.6 STANDARD FREE ENERGY AND EQUILIBRIUM

We concluded Section 4.4 with a statement that the sign of ΔG° indicated the side of the reaction that is favored at equilibrium. In this section, we quantify that conclusion. We begin by examining the free energy of reaction in more detail. The free energy of a substance deviates from its standard free energy by the following relationship: *

$$G = G^\circ + RT \ln a \quad \text{Eq. 4.12}$$

a is a *unitless* quantity known as the *activity*. The **activity** of a substance indicates the extent to which the state of the substance deviates from its standard state. It is defined as the ratio of the concentration of the species to its concentration in its *standard state*. The activity of a substance as a function of its state of matter is shown in Table 4.2. The concentrations of pure solids and liquids at constant temperature and pressure are constant, so the ratio of the concentration of a solid or liquid to its concentration in its standard state is unity, *i.e.*, the activities of pure solids and liquids are unity. The standard state of a gas is 1 atm and for a solute in a liquid solution it is a concentration of 1 M. Thus, the activity of solute A in a liquid solution is $a_A = [A]/1 \text{ M}$, which is unitless but numerically equal to the molarity of A. For example, the activity of chloride ion in a 0.2 M solution is $^{0.2 \text{ M}}/1 \text{ M} = 0.2$. Similarly, the activity of gas B is $a_B = P_B/1 \text{ atm}$, which is also unitless but numerically equal to its partial pressure in *atmospheres*. Consequently, we will represent the activities of solutes and gases by their molar concentrations and partial pressures in atmospheres, respectively, but remember that activities are unitless.

Equation 4.12 can be used to determine ΔG for a reaction in terms of the standard free energy change and the activities (pressures or concentrations) of the reactants and products. For example, consider the following aqueous reaction:



The free energy change is the free energy of the products minus that of the reactants

$$\Delta G = \{G_{\text{Cu}^{2+}} + 2G_{\text{Fe}^{2+}}\} - \{G_{\text{Cu}} + 2G_{\text{Fe}^{3+}}\}$$

Applying Equation 4.12 to the above, we get

$$\Delta G = \{G_{\text{Cu}^{2+}}^\circ + RT \ln(a_{\text{Cu}^{2+}})\} + 2\{G_{\text{Fe}^{2+}}^\circ + RT \ln(a_{\text{Fe}^{2+}})\} - \{G_{\text{Cu}}^\circ + RT \ln(a_{\text{Cu}})\} - 2\{G_{\text{Fe}^{3+}}^\circ + RT \ln(a_{\text{Fe}^{3+}})\}$$

Using the relationship $n \ln x = \ln x^n$ and gathering terms, we obtain the following:

$$\Delta G = G_{\text{Cu}^{2+}}^\circ + 2G_{\text{Fe}^{2+}}^\circ - G_{\text{Cu}}^\circ - 2G_{\text{Fe}^{3+}}^\circ + RT \ln(a_{\text{Cu}^{2+}}) + 2RT \ln(a_{\text{Fe}^{2+}})^2 - RT \ln(a_{\text{Cu}}) - 2RT \ln(a_{\text{Fe}^{3+}})^2$$

Equate the first four terms to ΔG° and combine the last four terms by using the following property of logarithms: $\ln w + \ln x - \ln y - \ln z = \ln (wx/yz)$ to obtain

* As was the case with enthalpies, we cannot determine absolute free energies because we have no reference energy. G° in Equation 4.11 is the unknown reference energy and the reason we do not know the value of G .

Table 4.2 Activities as a function of the state of a substance

Substance	Activity	Numerically equal to
pure solid	1	1
pure liquid	1	1
solute A	$[A]/1 \text{ M}$	$[A]$ as molarity
gas B	$P_B/1 \text{ atm}$	P_B in atm

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{(a_{\text{Cu}^{2+}})(a_{\text{Fe}^{2+}})^2}{(a_{\text{Cu}})(a_{\text{Fe}^{3+}})^2} \right)$$

Metallic Cu is a solid, so $a_{\text{Cu}} = 1$, and the other substances are all solutes in aqueous solution with activities equal to their molar concentrations, so we can express the free energy as follows:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{[\text{Cu}^{2+}][\text{Fe}^{2+}]^2}{(1)[\text{Fe}^{3+}]^2} \right)$$

The term in parenthesis is called the **reaction quotient** and given the symbol Q . It is equal to the product of the activities of the substances on the right side of the chemical equation divided by the product of the activities of the substances on the left side of the equation. Each activity is raised to an exponent equal to the coefficient of the substance in the balanced chemical equation. The reaction quotient can have any non-negative value. Unit activities are not usually included in the expression of Q , so Q for the reaction between Cu and Fe^{3+} would be written as

$$Q = \frac{[\text{Cu}^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

Substituting Q for the reaction quotient, we obtain Equation 4.13.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{Eq. 4.13}$$

The activities of the products are very small at the beginning of a reaction, so $Q \sim 0$. Thus, $\ln Q$ is a very large, negative number early in the reaction. The large, negative number for $\ln Q$ in Equation 4.13 is usually sufficient to make $\Delta G < 0$ and the reaction spontaneous at the start of reaction even if ΔG° is large and positive. However, as the reaction proceeds, the activities of the products increase and those of the reactants decrease, so Q increases and $\ln Q$ gets less negative, which makes ΔG less negative. Eventually, Q reaches a value such that $\Delta G = 0$, at which point the system has reached equilibrium. The value of Q at that point is called the **equilibrium constant**, K , for the reaction. Q and K are identical except that the activities used to determine K are equilibrium activities, while those used to determine Q are not. Q is a variable that changes as the reaction proceeds, and K is the constant that Q becomes at equilibrium. K is a function of only the reaction and the temperature.

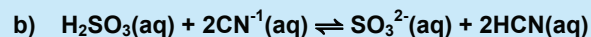
Example 4.7

Write the reaction quotient expression for each of the following.



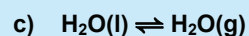
All substances are gases, so each enters as its partial pressure in atmospheres. The coefficient of HI means that its partial pressure must be squared.

$$Q = \frac{P_{\text{H}_2} P_{\text{I}_2}}{(P_{\text{HI}})^2}$$



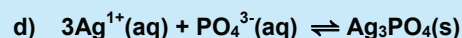
All substances are solutes in aqueous solution, so each enters as its molar concentration. The CN^{-1} and HCN concentrations are squared because their coefficients are two.

$$Q = \frac{[\text{SO}_3^{2-}][\text{HCN}]^2}{[\text{H}_2\text{SO}_3][\text{CN}^{-1}]^2}$$



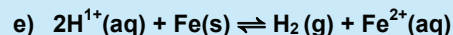
Pure liquids enter as unity (1) and gases as their partial pressures in atmospheres.

$$Q = \frac{P_{\text{H}_2\text{O}}}{1} = P_{\text{H}_2\text{O}}$$



Ag^{1+} and PO_4^{3-} are solutes, so they enter as their molar concentrations. Ag_3PO_4 is a solid, so it is entered as unity (1). The Ag^{1+} concentration must be cubed.

$$Q = \frac{1}{[\text{Ag}^{1+}]^3 [\text{PO}_4^{3-}]}$$



H^{1+} and Fe^{2+} are aqueous solutes and enter as molar concentrations. Fe is a solid, so its activity is unity. H_2 is a gas, so its activity is expressed by its partial pressure in atmospheres.

$$Q = \frac{P_{\text{H}_2} [\text{Fe}^{2+}]}{[\text{H}^{1+}]^2}$$

Substitution of $\Delta G = 0$ and $Q = K$ into Equation 4.13 produces Equation 4.14, which relates the equilibrium constant to the value of ΔG° .

$$\Delta G^\circ = -RT \ln K$$

Eq. 4.14

or, solving for K, we obtain Equation 4.15:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = e^{-\frac{\Delta G^\circ}{RT}}$$

Eq. 4.15

ΔG° dictates the value of K and the extent of reaction, and Table 4.3 shows how the magnitude of K varies with the sign of ΔG° . Reactions become more extensive as their standard free energies become more negative.

Table 4.3 The relationship between ΔG° and K

ΔG°	K	extent of reaction
> 0	< 1	not extensive
< 0	> 1	extensive
$= 0$	$= 1$	comparable amounts of both reactants and products

Substitution of $\Delta G^\circ = -RT \ln K$ into Equation 4.13 yields,

$$\Delta G = -RT \ln K + RT \ln Q$$

Application of the identity, $\ln x - \ln y = \ln (x/y)$, to the preceding yields Equation 4.16.

$$\Delta G = RT \ln \left(\frac{Q}{K} \right) \quad \text{Eq. 4.16}$$

Thus, the sign of ΔG is dictated by the relative magnitudes of Q and K . If $Q < K$, then $Q/K < 1$, $\ln (Q/K) < 0$, $\Delta G < 0$, and the reaction is spontaneous in the direction that it is written.

Table 4.4 summarizes the relationship between Q , K , and ΔG .

Figure 4.9 shows the variation of the free energy of the reaction $A(g) \rightarrow B(g)$ at 300 K as a function of the partial pressures of A (bottom axis) and B (top axis).

- ΔG° and K are constants for this reaction at this temperature. Equilibrium lies at the minimum in the curve (Point 4), so the equilibrium pressures are $P_A = 0.80$ atm (top scale) and $P_B = 0.20$ atm (bottom scale). The equilibrium constant is

$$K = P_B/P_A = 0.80/0.20 = 4.0$$

$\Delta G^\circ = G_B^\circ - G_A^\circ$ can be determined from the value of K with Equation 4.14.

$$\Delta G^\circ = -RT \ln K = -(0.0083)(300) \ln(4.0) = -3.5 \text{ kJ} \cdot \text{mol}^{-1}$$

- ΔG and Q vary as the reaction proceeds. The sphere on the curve represents reaction progress as it spontaneously moves toward the minimum. As it moves, the pressures of A and B change, which causes $Q = P_B/P_A$ to change. Changes in Q are reflected in changes in ΔG as given by Equation 4.16. Note that ΔG is related to the slope of the tangent at each point. At Point 1, the slope of the tangent is negative, so $\Delta G < 0$ and the reaction is spontaneous.

$$Q_1 = \frac{P_B}{P_A} = \frac{0.20}{0.80} = 0.25 \quad \Delta G_1 = RT \ln \left(\frac{Q}{K} \right) = (0.0083)(300) \ln \left(\frac{0.25}{4.0} \right) = -6.9 \text{ kJ} \cdot \text{mol}^{-1}$$

As the reaction continues, Q gets closer to K and ΔG closer to zero (the slope of the red tangent line becomes less negative). At Points 2 and 3,

$$Q_2 = \frac{0.30}{0.70} = 0.43 \quad \Delta G_2 = (0.0083)(300) \ln \left(\frac{0.43}{4.0} \right) = -5.6 \text{ kJ} \cdot \text{mol}^{-1}$$

$$Q_3 = \frac{0.50}{0.50} = 1.0 \quad \Delta G_3 = (0.0083)(300) \ln \left(\frac{1.0}{4.0} \right) = -3.5 \text{ kJ} \cdot \text{mol}^{-1}$$

At Point 4, the slope of the tangent line is zero, so $\Delta G = 0$ as the reaction has reached the minimum in free energy.

$$Q_4 = \frac{0.80}{0.20} = 4.0 = K \quad \Delta G_4 = (0.0083)(300) \ln \left(\frac{4.0}{4.0} \right) = 0$$

Movement in either direction at this point requires energy, so the reaction proceeds no further as equilibrium is established.

Table 4.4 The spontaneous direction of reaction as a function of the relative magnitudes of Q and K

	ΔG	Direction of reaction
$Q < K$	< 0	\rightarrow spontaneous to the right
$Q > K$	> 0	\leftarrow spontaneous to the left
$Q = K$	0	\rightleftharpoons system at equilibrium

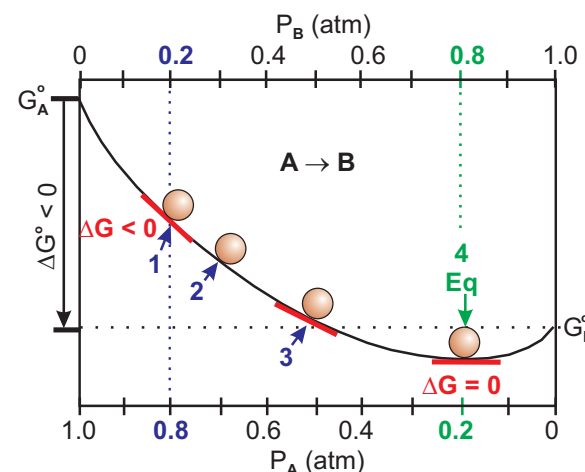


Figure 4.9 Free energy diagram for $A \rightarrow B$

The red lines at points 1, 3, and 4 represent the tangents to the curve at those points.

Example 4.8

Use the free energy diagram for the reaction $W(g) \rightarrow X(g)$ at 500 K shown in the margin to answer the following questions.

- a) What is the sign of ΔG° ?

$$\Delta G^\circ = G_X^\circ - G_W^\circ, \text{ and } G_X^\circ > G_W^\circ, \text{ so } \Delta G^\circ > 0.$$

- b) What is the value of K ?

$K = P_X/P_W$ and equilibrium occurs at the minimum in the curve, so the equilibrium pressures are $P_X = 0.40$ atm and $P_W = 0.60$ atm. Consequently, $K = 0.40/0.60 = 0.67$

- c) What is the value of ΔG° ?

$$\text{Use Equation 4.14 and } T = 500, \quad \Delta G^\circ = -(0.0083)(500) \ln (0.67) = +1.7 \text{ kJ}\cdot\text{mol}^{-1}.$$

- d) Is the reaction consuming or producing X at Points 1 and 2?

The reaction proceeds toward the minimum, which is the direction of increasing X at Point 1 but decreasing X at Point 2. Alternatively, $P_X = 0.1$ atm at Point 1, but it must reach 0.4 atm at equilibrium, so X must be produced at Point 1. $P_X = 0.8$ atm at Point 2, so X must be consumed at Point 2 to lower its pressure to its equilibrium value.

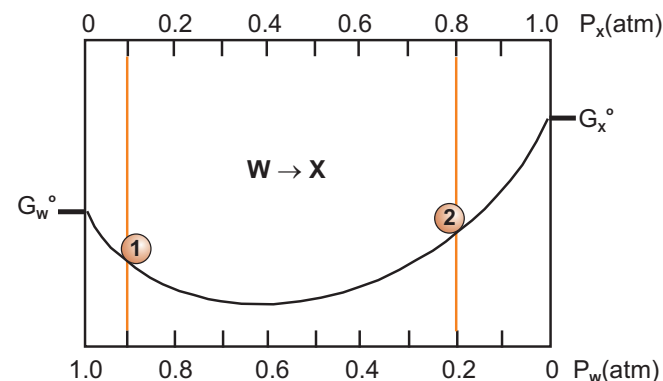
- e) What are the values of Q and ΔG at Points 1 and 2?

$$Q_1 = 0.10/0.90 = 0.11; \Delta G_1 = (0.0083)(500) \ln (0.11/0.67) = -7.5 \text{ kJ}\cdot\text{mol}^{-1}$$

The negative sign of ΔG indicates that the reaction is proceeding in the direction written, so X is produced.

$$Q_2 = 0.80/0.20 = 4.0; \Delta G_2 = (0.0083)(500) \ln (4.0/0.67) = +7.4 \text{ kJ}\cdot\text{mol}^{-1}$$

The positive sign of ΔG indicates that the reaction is proceeding in the direction opposite to that shown; *i.e.*, X is being consumed.



Example 4.8

PRACTICE EXAMPLE 4.4

The vapor pressure of CH_3OH (methanol or wood alcohol) is 132 torr at 25 °C. What is its standard free energy of vaporization?

Chemical equation for the process:

Equilibrium activities:

$$a_{\text{liquid}} = \underline{\hspace{2cm}} \quad a_{\text{vapor}} = \underline{\hspace{2cm}}$$

The value of the equilibrium constant:

$$K = \underline{\hspace{2cm}}$$

The standard free energy of vaporization at 298 K:

$$\Delta G^\circ = \underline{\hspace{2cm}} \text{ kJ}$$

Example 4.9

- a) The vapor pressure of water at 25 °C is 23.8 torr, but the instantaneous pressure of water in an experiment at 25 °C was found to be 35.6 torr. What are Q , K , ΔG° , and ΔG for the process $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ at the instant the pressure was measured?

The activity of the liquid is unity, and the activity of the vapor is numerically equal to the pressure in atmospheres, so we first convert the two pressures from torr to atmospheres:

$$P_{\text{H}_2\text{O}} = 35.6 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.0468 \text{ atm} \quad \& \quad P_{\text{H}_2\text{O}}^\circ = 23.8 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.0313 \text{ atm}$$

Q and K are both unitless but numerically equal to the instantaneous pressure and vapor pressure expressed in atmospheres, respectively.

$$Q = \frac{0.0468 \text{ atm}}{1 \text{ atm}} = 0.0468 \quad \& \quad K = \frac{0.0313 \text{ atm}}{1 \text{ atm}} = 0.0313$$

Use Equation 4.14 and the value of K to determine ΔG° .

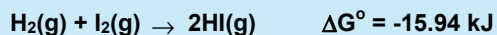
$$\Delta G^\circ = -RT \ln K = -(8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) \ln(0.0313) = 8.58 \text{ kJ} \cdot \text{mol}^{-1}$$

Finally, use Equation 4.16 to determine the value of ΔG .

$$\Delta G = RT \ln \left(\frac{Q}{K} \right) = (8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) \ln \left(\frac{0.0468}{0.0313} \right) = 0.997 \text{ kJ} \cdot \text{mol}^{-1}$$

$Q > K$, and $\Delta G > 0$, so the process is spontaneous in the reverse direction; *i.e.*, the water vapor condenses. As it condenses, the pressure of the vapor drops and Q gets smaller until $Q = 0.0313$, and the system reaches equilibrium.

- b) Given the following partial pressures: $P_{\text{I}_2} = P_{\text{H}_2} = 0.0332 \text{ atm}$ and $P_{\text{HI}} = 0.827 \text{ atm}$, determine Q , K , and ΔG for the following at 298 K:



All species are gases, so the expression for the reaction quotient is

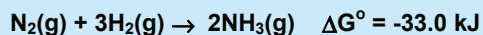
$$Q = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{0.827^2}{(0.0332)(0.0332)} = 620.$$

We use Equation 4.15 and the given value of ΔG° to obtain K .

$$K = \exp \left(-\frac{\Delta G^\circ}{RT} \right) = \exp \left(-\frac{-15,940 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} \right) = e^{+6.430} = 620$$

$Q = K$, so the system is at equilibrium and $\Delta G = 0$.

- c) Given the following partial pressures: $P_{\text{N}_2} = 0.361 \text{ atm}$, $P_{\text{H}_2} = 0.224 \text{ atm}$, and $P_{\text{NH}_3} = 0.424 \text{ atm}$, determine Q , K , and ΔG for the following at 298 K.



$$Q = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3(P_{\text{N}_2})} = \frac{0.424^2}{(0.224)^3(0.361)} = 44.3$$

$\Delta G^\circ = -33.0 \text{ kJ} \cdot \text{mol}^{-1}$, so we expect a large value for K .

$$K = \exp \left(-\frac{\Delta G^\circ}{RT} \right) = \exp \left(-\frac{-33,000 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} \right) = e^{+13.3} = 6.05 \times 10^5$$

$Q \ll K$, so $\Delta G < 0$ and the reaction is proceeding as written. Use Equation 4.16 to determine the value of ΔG .

$$\Delta G = RT \ln \left(\frac{Q}{K} \right) = (8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) \ln \left(\frac{44.3}{6.1 \times 10^5} \right) = -23.6 \text{ kJ} \cdot \text{mol}^{-1}$$

PRACTICE EXAMPLE 4.5

$K = 4.3 \times 10^9$ for the following aqueous redox reaction at 298 K
 $3\text{Fe}^{2+} + \text{NO}_3^{1-} + 4\text{H}^{1+} \rightarrow 3\text{Fe}^{3+} + \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

where all of the ions are in solution.

Determine the reaction quotient at the following conditions:

$[\text{Fe}^{2+}] = 0.0685 \text{ M}$; $[\text{NO}_3^{1-}] = 0.106 \text{ M}$; $[\text{H}^{1+}] = 0.242 \text{ M}$

$[\text{Fe}^{3+}] = 0.0211 \text{ M}$; $P_{\text{NO}} = 622 \text{ torr}$

$$Q = \underline{\hspace{2cm}}$$

What are ΔG (Eq. 4.12) and ΔG° (Eq. 4.10) for the reaction?

$$\Delta G = \underline{\hspace{2cm}} \text{ kJ}$$

$$\Delta G^\circ = \underline{\hspace{2cm}} \text{ kJ}$$

PRACTICE EXAMPLE 4.6

$K = 4.3 \times 10^9$ for the following aqueous redox reaction at 298 K:
 $3\text{Fe}^{2+}(\text{aq}) + \text{NO}_3^{1-}(\text{aq}) + 4\text{H}^{1+}(\text{aq}) \rightarrow 3\text{Fe}^{3+}(\text{aq}) + \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

Determine the reaction quotient at the following conditions:

$[\text{Fe}^{2+}] = 0.0685 \text{ M}$; $[\text{NO}_3^{1-}] = 0.106 \text{ M}$; $[\text{H}^{1+}] = 0.242 \text{ M}$

$[\text{Fe}^{3+}] = 0.0211 \text{ M}$; $P_{\text{NO}} = 622 \text{ torr}$

$$Q = \underline{\hspace{2cm}}$$

What are ΔG and ΔG° for the reaction?

$$\Delta G = \underline{\hspace{2cm}} \text{ kJ}$$

$$\Delta G^\circ = \underline{\hspace{2cm}} \text{ kJ}$$

4.7 TEMPERATURE DEPENDENCE OF ΔG , ΔG° , AND K

The variation of ΔG with temperature can be seen by rewriting Equations 4.7 in the form of a linear equation ($y = mx + b$).

$$\Delta G = (-\Delta S)T + \Delta H$$

Thus, a plot of ΔG versus T is a straight line with a slope of $-\Delta S$ and an intercept of ΔH .* $\Delta G = 0 = \Delta H - T\Delta S$ where the two driving forces are equal and opposed; *i.e.*, where $\Delta H = T\Delta S$. The temperature where they are equal is obtained by solving for T .

$$T = \frac{\Delta H}{\Delta S} \quad \text{Eq. 4.17}$$

Figure 4.10 and Table 4.5 describe the linear relationship between ΔG and T . The signs of ΔH and ΔS are determined from the intercepts and slopes in Figure 4.10, respectively.

Line A: $\Delta H > 0$, $\Delta S > 0$: A positive intercept means that $\Delta G > 0$ at low temperature, but the negative slope means that it becomes less positive with increasing temperature. Thus, the process is not spontaneous at low temperature because there is not enough $T\Delta S$ energy released to overcome the positive ΔH . However, at high temperature, sufficient $T\Delta S$ energy is produced and the process is spontaneous. For example, consider a process in which $\Delta H = 10 \text{ kJ}$ and $\Delta S = 20 \text{ J}\cdot\text{K}^{-1}$. At $T = 0 \text{ K}$, $\Delta G = \Delta H = +10 \text{ kJ}$ and the process is not spontaneous. Using Equation 4.17, we can determine the T at which $\Delta G = 0$.

$$T = \frac{10 \text{ kJ}}{0.020 \text{ kJ}\cdot\text{K}^{-1}} = 500 \text{ K}$$

At temperatures above 500 K, $\Delta G < 0$ and the process is spontaneous as written.

Line B: $\Delta H > 0$, $\Delta S < 0$: Both driving forces are unfavorable ($\Delta H > 0$ and $\Delta S < 0$), so both require energy. In the absence of energy from an outside source, this process cannot occur; *i.e.*, the process is not spontaneous at any temperature.

Line C: $\Delta H < 0$, $\Delta S < 0$: At low T , there is sufficient energy liberated by the ΔH term to drive the unfavorable $T\Delta S$ term. However, as the temperature increases, the $T\Delta S$ term becomes more important. Eventually, $-T\Delta S > \Delta H$ and the reaction is no longer spontaneous. The temperature at which the $T\Delta S$ and ΔH terms are the same can be found with Equation 4.17. If $\Delta H = -15 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S = -50 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, then $\Delta G = 0$ at

$$T = \frac{-15 \text{ kJ}\cdot\text{mol}^{-1}}{-0.050 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}} = 300 \text{ K}$$

The process is spontaneous at $T < 300 \text{ K}$, but not above.

Line D: $\Delta H < 0$, $\Delta S > 0$: Both terms are favorable, so this process is spontaneous at all T .

Line E: $\Delta H < 0$, $\Delta S \sim 0$: It is often the case that $\Delta S \sim 0$ compared to ΔH . When that occurs, the spontaneity is dictated solely by ΔH . In line E, $\Delta S \sim 0$, while $\Delta H < 0$, so this process is always spontaneous.

* The linear behavior assumes that ΔH° and ΔS° are each temperature independent. While the absolute entropies (S) and enthalpies (H) are temperature dependent, the assumption that their changes (ΔH° and ΔS°) are temperature independent is usually valid over small temperature ranges because the absolute values vary in the same direction for both the reactants and products.

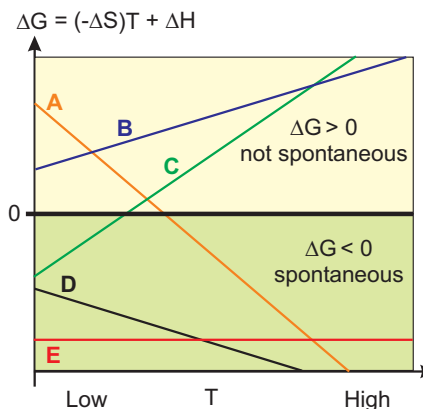


Figure 4.10 Temperature variation of the free energy

Table 4.5 Temperature and Spontaneity of Reaction

Line	ΔH	$-\Delta S$	Spontaneity
A	+	+	Unfavorable ΔH makes process not spontaneous at low T , but favorable ΔS can drive reaction at high T .
B	+	-	Both ΔH and ΔS are unfavorable, so process is never spontaneous.
C	-	-	Favorable ΔH makes process spontaneous at low T , but unfavorable ΔS can make it not spontaneous at high T .
D	-	+	Both ΔH and ΔS are favorable, so process is always spontaneous.
E	-	~ 0	The spontaneity of a process in which $\Delta S \sim 0$ is dictated solely by ΔH .

The variation of ΔG° with temperature is obtained by modifying Equation 4.10:

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

Thus, a plot of ΔG° versus T is a straight line with a slope of $-\Delta S^\circ$ and an intercept of ΔH° . Such a plot is shown in Figure 4.11, which is identical to Figure 4.10 except that superscripts have been added to all thermodynamic quantities and 'spontaneous' has been replaced with 'extensive' to reflect the difference between ΔG and ΔG° . The same changes were made to Table 4.5 to arrive at Table 4.6.

Example 4.10

Estimate ΔG° and K for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ at the given temperatures

a) 435 K

Use the ΔH° and ΔS° values from Example 4.6c in Equation 4.10 to obtain ΔG° .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92.22 \text{ kJ} - (435 \text{ K})(-0.1986 \text{ kJ}\cdot\text{K}^{-1}) = -5.83 \text{ kJ}$$

Use the value of ΔG° determined above in Equation 4.15 to determine K .

$$K = \exp\left\{-\frac{\Delta G^\circ}{RT}\right\} = \exp\left\{-\frac{-5830 \text{ J}}{(8.314)(435) \text{ J}}\right\} = e^{+1.61} = 5.0$$

b) 635 K

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92.22 \text{ kJ} - (635 \text{ K})(-0.1986 \text{ kJ}\cdot\text{K}^{-1}) = +33.9 \text{ kJ}$$

$$K = \exp\left\{-\frac{\Delta G^\circ}{RT}\right\} = \exp\left\{-\frac{33,900 \text{ J}}{(8.314)(635) \text{ J}}\right\} = e^{-6.42} = 1.6 \times 10^{-3}$$

Note that K increases as T decreases for this reaction. As we shall see, this is because the reaction is exothermic.

The normal boiling point is the temperature at which the pressure of the vapor in equilibrium with its liquid is 1 atm. Thus, the boiling point is the temperature at which a process is at equilibrium and the reactants (pure liquid) and products (vapor at 1 atm) are all in their standard states. The equilibrium condition is therefore defined by $\Delta G^\circ = 0$. Consequently, Equation 4.17 can be used with ΔH° and ΔS° for the vaporization process to determine the normal boiling point.

$$T_{\text{bp}} = \frac{\Delta H_{\text{vap}}^\circ}{\Delta S_{\text{vap}}^\circ}$$

Eq. 4.18

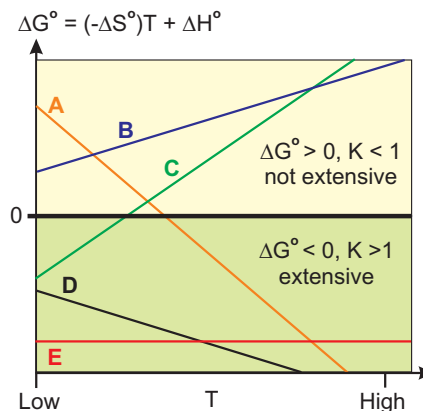


Figure 4.11 Temperature Variation of the Standard Free Energy

Table 4.6 Temperature and Extent of Reaction

Line	ΔH°	$-\Delta S^\circ$	Extent
A	+	+	Unfavorable ΔH° makes process not extensive at low T , but favorable ΔS° makes it extensive at high T .
B	+	-	Both ΔH° and ΔS° are unfavorable, so process is never extensive.
C	-	-	Favorable ΔH° makes it extensive at low T , but unfavorable ΔS° can make it not extensive at high T .
D	-	+	Both ΔH° and ΔS° are favorable, so process is always extensive.
E	-	~ 0	The extent of a process in which $\Delta S^\circ \sim 0$ is dictated solely by ΔH° .

Example 4.11**Estimate the normal boiling point of water.**

Use the values given in Example 4.3a in Equation 4.18.

$$T = \frac{\Delta H_{\text{vap}}^{\circ}}{\Delta S_{\text{vap}}^{\circ}} = \frac{44,010 \text{ J} \cdot \text{mol}^{-1}}{118.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} = 370.4 \text{ K or } 97.3^{\circ} \text{C}$$

Our estimated boiling point is 2.7 °C lower than the actual boiling point because we used thermodynamic data at 298 K to approximate the data at 373 K.

We have seen how to determine the value of the equilibrium constant from values of ΔH° and ΔS° , and we now turn that process around to show how ΔH° and ΔS° can be determined from equilibrium constant data. There are two unknowns, so values of K are required at two different temperatures. As shown in Example 4.12, the process requires that each equilibrium constant be converted into a ΔG° . The two values of ΔG° are then used in Equation 4.10 to generate two equations with two unknowns.

Example 4.12**The vapor pressure of CS₂ is 40.3 torr at 250. K and 372 torr at 300. K. What are the standard heat and entropy of vaporization of CS₂?**

1) The activity of a liquid is unity, so the unitless equilibrium constant for vaporization is numerically equal to the vapor pressure expressed in atmospheres.

$$T_1 = 250. \text{ K}; K_1 = \frac{40.3}{760} = 0.0530 \quad \& \quad T_2 = 300. \text{ K}; K_2 = \frac{372}{760} = 0.489$$

2) Use Equation 4.14 to convert the equilibrium constants into standard free energies.

$$\Delta G_1^{\circ} = -RT_1 \ln K_1 = -(8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(250. \text{ K}) \ln (0.0530) = 6.10 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G_2^{\circ} = -RT_2 \ln K_2 = -(8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(300. \text{ K}) \ln (0.489) = 1.78 \text{ kJ} \cdot \text{mol}^{-1}$$

3) Put the two standard free energies and their temperatures into Equation 4.10.

$$1) 6.10 = \Delta H^{\circ} - 250 \Delta S^{\circ}$$

$$2) 1.78 = \Delta H^{\circ} - 300 \Delta S^{\circ}$$

4) Solve the two equations in two unknowns by first subtracting the second equation from the first to eliminate the ΔH° term.

$$(6.10 - 1.78) = (1 - 1) \Delta H^{\circ} - (250 + 300) \Delta S^{\circ} \quad \text{or} \quad 4.32 = 50 \Delta S^{\circ}$$

Multiply the left side by 1000 to convert from kJ to J and then solve for ΔS° .

PRACTICE EXAMPLE 4.7**Determine the following for the vaporization of CH₃OH.****Vaporization Process:** _____**Standard enthalpy and entropy of vaporization.**

$$\Delta H^{\circ} = \text{_____ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^{\circ} = \text{_____ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Normal boiling point of CH₃OH

$$t_{\text{bp}} = \text{_____}^{\circ} \text{C}$$

Vapor pressure of CH₃OH in torr at 40 °C

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

$$P^{\circ} = \text{_____ torr}$$

Vapor pressure of CH₃OH in torr at 10 °C

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

$$P^{\circ} = \text{_____ torr}$$

$$\Delta S_{\text{vap}}^{\circ} = \frac{4.32 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{50 \text{ K}} = 86.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Finally, use the value of ΔS° determined above in either equation derived in Step 3 to determine ΔH° . We use the first equation here,

$$\Delta H_{\text{vap}}^{\circ} = \Delta G_1^{\circ} + T_1 \Delta S_1^{\circ} = 6.10 \text{ kJ} + (250. \text{ K})(0.0864 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 27.7 \text{ kJ} \cdot \text{mol}^{-1}$$

If more than two equilibrium constants are given, the standard enthalpy and entropy should be determined graphically. To do so, we obtain the temperature dependence of the equilibrium constant by combining Equations 4.9 and 4.13.

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

Dividing both sides by $-T$ leads to Equation 4.19.

$$R \ln K = \Delta S^{\circ} - \Delta H^{\circ} \left(\frac{1}{T} \right) \quad \text{Eq. 4.19}$$

The temperature dependence is in the enthalpy term of Equation 4.19, so the effect of temperature on the equilibrium constant depends upon the sign of ΔH° . *Increasing the temperature increases the equilibrium constants of endothermic ($\Delta H^{\circ} > 0$) reactions but decreases the value of K for exothermic ($\Delta H^{\circ} < 0$) reactions.*

Example 4.13

Estimate the equilibrium constant for $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 635 K given that $\Delta H^{\circ} = -92.22 \text{ kJ}$ and $K = 6.1 \times 10^5$ at 298 K.

Use the given data in Equation 4.19 to determine the standard entropy of reaction.

$$(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \ln(6.1 \times 10^5) = \Delta S^{\circ} + 92.22 \times 10^3 \left(\frac{1}{298} \right)$$

$$110.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = \Delta S^{\circ} + 309.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\Delta S^{\circ} = 110.8 - 309.3 = -198.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Use the ΔS° above with the given ΔH° and the designated temperature to get $\ln K$ and K .

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} = \frac{-198.5}{8.314} - \frac{-92.22 \times 10^3}{(8.314)(635)} = -6.41$$

$$K = e^{-6.41} = 1.6 \times 10^{-3}$$

The reaction is exothermic, so K decreases when the temperature is raised. Note that this is the same result obtained in Example 4.10.

PRACTICE EXAMPLE 4.8

Use the following 298K data for $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ to estimate ΔG° at 0 °C then use Equations 4.11 and 4.14 to estimate K_{273} .

$$\Delta H_{298}^{\circ} = -58.02 \text{ kJ} \quad \text{and} \quad \Delta S_{298}^{\circ} = -0.1766 \text{ kJ} \cdot \text{K}^{-1}$$

$$\Delta G_{273}^{\circ} \sim \text{_____ kJ}$$

K_{273} using Equation 4.14

$$K_{273} = \text{_____}$$

K_{273} using Equation 4.18

$$K_{273} = \text{_____}$$

Using Equation 4.19 at two different temperatures and then subtracting the two equations to eliminate ΔS° yields the following equation that allows ΔH° to be determined directly from two equilibrium constants at two temperatures.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Eq. 4.20}$$

While Equation 4.20 is useful if only two data points are available, it is always preferable to use more data than the minimum required to determine any parameter. Thus, values of ΔH° and ΔS° are normally determined graphically from a plot of $R \ln K$ versus $1/T$, which is a straight line with an intercept of ΔS° and a slope of $-\Delta H^\circ$.

Example 4.14

- a) The autoionization reaction of water: $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^{1+}(\text{aq}) + \text{OH}^{1-}(\text{aq})$ is very important in aqueous chemistry. The equilibrium constant for the reaction is called the ionization constant for water, K_w . Determine ΔS° and ΔH° for the autoionization reaction from the following data:

T (°C)	0	25	50	75	100
K_w	1.15×10^{-15}	1.00×10^{-14}	5.25×10^{-14}	1.95×10^{-13}	5.50×10^{-13}
1/T	0.003663	0.003356	0.003096	0.002874	0.002681
$R \ln K_w$	-285.993	-268.012	-254.225	-243.316	-234.695

Convert the given temperatures to the Kelvin scale and determine $1/T$ in K^{-1} . Then calculate $R \ln K_w$ in $\text{J} \cdot \text{K}^{-1}$ to obtain

1/T	0.003663	0.003356	0.003096	0.002874	0.002681
$R \ln K_w$	-285.993	-268.012	-254.225	-243.316	-234.695

A plot of the above $R \ln K_w$ versus $1/T$ data is shown in the margin. Linear regression yields an intercept of $-93.4 \text{ J} \cdot \text{K}^{-1}$ and a slope of $-5.23 \times 10^4 \text{ J}$ for the best-fit line. Thus,

$$\Delta S^\circ = \text{intercept} = -93.4 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta H^\circ = -\text{slope} = 52.3 \text{ kJ}$$

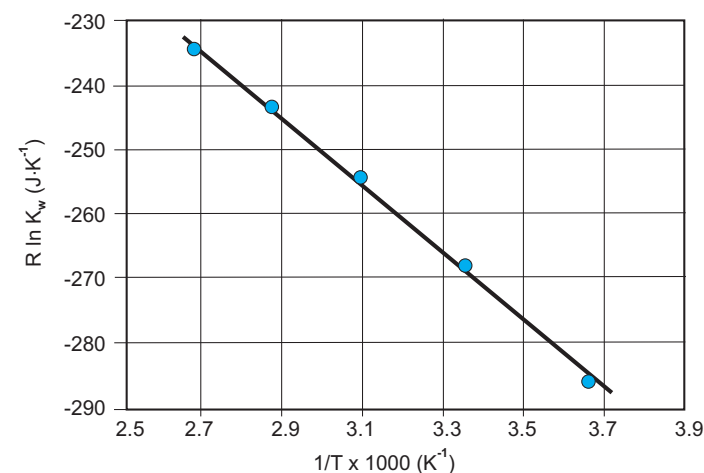
Using Equation 4.20 with the $t_1 = 75^\circ\text{C}$ and $t_2 = 100^\circ\text{C}$ points, we obtain

$$\ln\left(\frac{5.50 \times 10^{-13}}{1.95 \times 10^{-13}}\right) = \frac{\Delta H^\circ}{8.314} \left(\frac{1}{348} - \frac{1}{373} \right) \text{ or } \Delta H^\circ = 4.48 \times 10^4 \text{ J} = 44.8 \text{ kJ}$$

The 14% difference between this value of ΔH° and the one determined graphically arises because the line defined by the two points chosen for Equation 4.20 has a different slope than the best straight line used for the graphical determination.

- b) What is the value of K_w at 37°C , the temperature of the human body?

Use the ΔH° and ΔS° determined above and Equation 4.19. $T = 37 + 273 = 310 \text{ K}$



Example 4.14

Data points are shown as blue circles, and the straight line is the best fit of the data.

$$R \ln K_w = \Delta S^\circ - \Delta H^\circ \left(\frac{1}{T} \right) = -93.4 - 52,283 \left(\frac{1}{310} \right) = -262 \text{ J} \cdot \text{K}^{-1}$$

Divide $R \ln K_w$ by R to obtain $\ln K_w$, then determine K_w from the exponential

$$\ln K_w = \frac{R \ln K_w}{R} = \frac{-262}{8.314} = -31.5 \Rightarrow K_w = e^{-31.5} = 2.1 \times 10^{-14} \text{ at } 37^\circ \text{C}$$

The experimental value is $K_w = 2.4 \times 10^{-14}$, so the number above is off by 14%. The high error arises because the value taken from the graph ($R \ln K_w$) is used in an exponential to get the final answer. The experimental $R \ln K_w$ is $-261 \text{ J} \cdot \text{K}^{-1}$, which differs from the value above by only 0.4%.

4.8 COUPLED REACTIONS

A thermodynamically unfavorable reaction can be driven by a thermodynamically favorable reaction that is *coupled* to it. We consider two important examples: the smelting of iron ore and the use of adenosine triphosphate (ATP) in biological systems.

The largest source of iron is the ore hematite (Fe_2O_3), but to get the iron from direct decomposition is thermodynamically unfavorable by a substantial amount (Reaction 4.1).



In order to drive Reaction 4.1 in the unfavorable direction shown, we must input energy from another source. Carbon monoxide is used to supply the energy in a blast furnace because the oxidation of carbon monoxide liberates free energy as shown in Reaction 4.2.



Reactions 4.1 and 4.2 are *coupled* in a blast furnace. Hess's law of heat summation can be used to determine ΔG° of the overall reaction. In order to cancel the $\frac{3}{2}\text{O}_2$ formed in Reaction 4.1, we multiply Reaction 4.2 by 3. The two coupled reactions are



Summing the two reactions yields the net thermochemical reaction in Reaction 4.3.



The free energy of the reaction is the sum of the free energies of the two coupled reactions.

$$\Delta G^\circ = 742.2 - 771.6 = -29.4 \text{ kJ}$$

The negative value of ΔG° means that the reaction is extensive at 298 K.

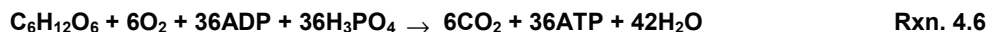
The combustion of glucose (Reaction 4.4) is the primary source of energy in all oxygen-using organisms and another important example of coupled reactions.



The release of such a large amount of energy in an uncontrolled reaction would be wasteful and destroy cells. Consequently, the body extracts the energy in sequential chemical reactions that allow it to harvest the energy a little at a time. Part of the energy is released in the form of heat, which helps maintain the body temperature. However, much of the energy is used to produce high-energy molecules that undergo exothermic reactions that can be coupled with thermodynamically unfavorable reactions to produce favorable ones. The most important of these energy containing molecules is *adenosine triphosphate* (Figure 4.12), which exists in the body as a 4- ion that is abbreviated as ATP^{4-} or simply ATP. The repulsion of the three negatively charged phosphate groups makes the P-O-P bonds very weak, which makes ATP an energy-rich ion. As shown in Reaction 4.5 and Figure 4.13, the terminal phosphate group is readily removed by water to form *adenosine diphosphate* (ADP^{3-} or ADP).



All living organisms use the free energy supplied by Reaction 4.5 to drive reactions that are not extensive. The overall reaction for the combustion of glucose in the body is

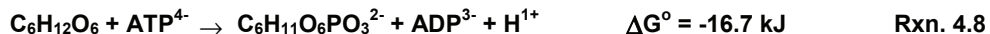


Much of the energy of Reaction 4.6 is stored in the 36 molecules of ATP that are produced.

As an example of the use of ATP in the body, consider the first step of the glucose oxidation, which involves placing a phosphate on glucose. The process (Reaction 4.7 and Figure 4.14a) is not extensive in the absence of ATP due to the strength of the P-O bond that must be broken.



However, placing a phosphate on glucose can be made extensive by coupling Reactions 4.5 and 4.7 to produce Reaction 4.8, which is also shown in Figure 4.14b.



Note that H_2O and HPO_4^{2-} cancel in the addition of Reactions 4.5 and 4.7. Reaction 4.8 is far more extensive than Reaction 4.7 because the P-O bond that is broken is much weaker in the highly energetic ATP ion than in the HPO_4^{2-} ion.

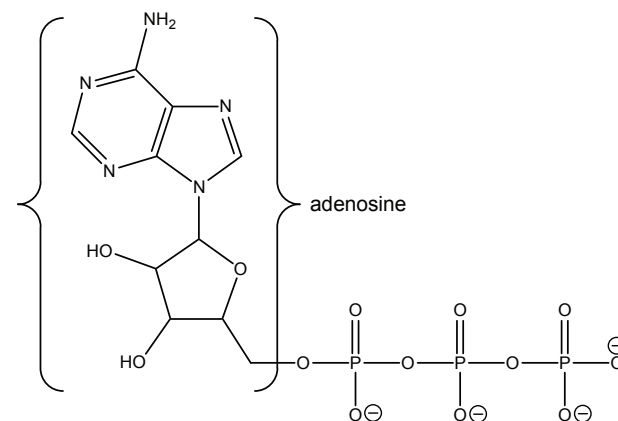


Figure 4.12 Adenosine triphosphate or ATP

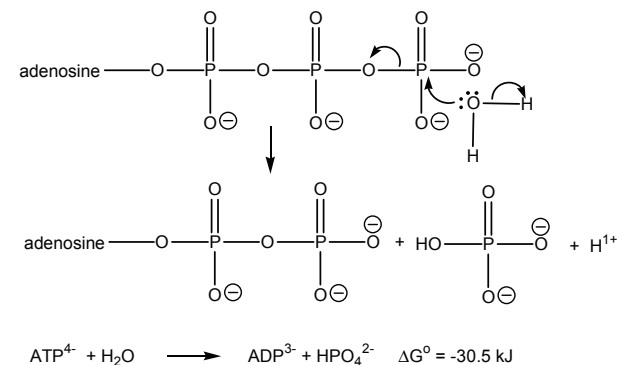


Figure 4.13 Conversion of ATP to ADP

The free energy that is released in this reaction is used to drive other reactions.

Most of the remaining steps in the glucose oxidation are down hill in free energy, and much of the energy is used to convert ADP back into ATP. ATP is a short-lived species in the cell as it is usually consumed within a minute of being formed. During strenuous activity, ATP can be used at a rate of up to 0.5 kg/min.

4.9 CHAPTER SUMMARY AND OBJECTIVES

Entropy is a measure of the number of ways in which a system can distribute its energy among its energy levels. Systems that are less constrained can distribute their energy in more ways and have higher entropies than systems that are more constrained. Adding constraints usually increases the order of a system, so disorder is often used as an indicator of entropy; highly disordered systems have high entropies. The second law of thermodynamics states that the entropy of the universe must increase in a spontaneous process. The entropy change of the universe caused by a process carried out at constant temperature and pressure is related to the change in the Gibbs free energy for the processes ($\Delta G = \Delta H - T\Delta S$). The second law can then be restated as $\Delta G < 0$ for all spontaneous processes carried out at constant temperature and pressure.

The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero, so absolute entropies, not entropies of formation, are tabulated. Standard entropies and free energies of reaction at 25 °C can be determined from tabulated values of absolute entropies and free energies of formation in the same manner that enthalpies of reaction were determined in Chapter 3. In order to estimate the standard free energy of a reaction at a different temperature, we use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and assume that ΔH° and ΔS° do not vary with temperature. The maximum work that can be derived from a reaction at constant temperature and pressure is $-\Delta G$.

Processes seek the minimum in free energy, which is the equilibrium condition. The free energy is related to the reaction quotient, Q , which is the product of the activities of the substances on the right side of the equation (products) divided by the activities of the substances on the left side of the equation (reactants), where the activity of each reactant and product is raised to a power equal to its coefficient in the balanced equation. The activities of solids and liquids are unity; the activities of gases are their partial pressures in atmospheres; and the activities of solutes are their molar concentrations. If the activities are equilibrium activities, the reaction quotient becomes the equilibrium constant. The two expressions, $\Delta G^\circ = -RT \ln K$ and $\Delta G = -RT \ln(Q/K)$, show the significance of ΔG and

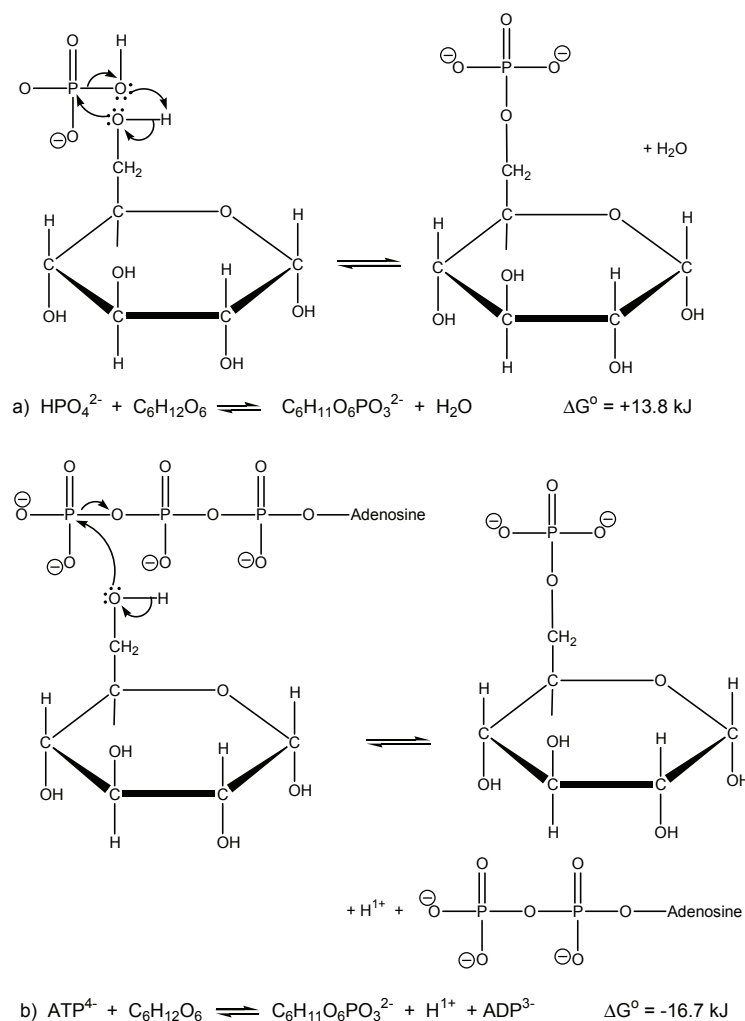


Figure 4.14 Formation of glucose phosphate from glucose

(a) The reaction of glucose and hydrogen phosphate ion is not extensive. (b) The reaction is extensive when coupled with the ATP \rightarrow ADP reaction.

ΔG° . ΔG° indicates the extent of the reaction (K), while ΔG indicates the spontaneous direction of the reaction. For example, $K > 1$ for an extensive reaction, which means that ΔG° must be negative. If $Q < K$, then ΔG is negative and the reaction proceeds from left to right. The effect of temperature on the equilibrium constant is dictated by the sign of ΔH . If ΔH is positive, then K increases with temperature.

A thermodynamically unfavorable process can be driven by a favorable one if the two processes are coupled. Extracting iron from its oxides is uphill in free energy, but when the process is coupled to the oxidation of CO, it becomes thermodynamically favorable. ATP is used by biological systems to supply free energy to drive thermodynamically unfavorable reactions.

After studying the material presented in this chapter, you should be able to:

1. explain how the constraints on a system affect its entropy (Section 4.1);
2. determine which of several systems has the greater entropy given the number of particles, spacing between energy levels, and the total energy of the system (Section 4.1);
3. state the second and third laws of thermodynamics (Section 4.2);
4. calculate the entropy change of a reaction from tabulated values of the absolute entropies of the reactants and products (Section 4.3);
5. predict whether a reaction is spontaneous from ΔH and ΔS values (Section 4.4);
6. define the free energy and explain why it is "free energy" (Section 4.4);
7. determine free energy of a reaction from tabulated free energies of formation (Section 4.5);
8. calculate the reaction quotient of a reaction given the activities of the reactants and the products (Section 4.6);
9. calculate the equilibrium constant of a reaction from the standard free energy of the reaction and vice versa (Section 4.6);
10. indicate the direction of a reaction from the relative values of Q and K (Section 4.6);
11. predict the temperature dependence of the extent or spontaneity of a reaction (Section 4.7);
12. estimate the value of ΔG° at temperatures other than 298 K from ΔH° and ΔS° values (Section 4.7);
13. estimate the boiling point of a liquid from thermodynamic data (Section 4.7);
14. determine the equilibrium constant at one temperature given the equilibrium constant at another temperature and the enthalpy of reaction (Section 4.7);
15. determine ΔH° and ΔS° given K at several temperatures (Section 4.7); and
16. calculate the free energy of reaction from the free energies of two reactions that can be coupled to produce the desired reaction (Section 4.8).

ANSWERS TO PRACTICE EXAMPLES

4.1 (8,0,0); (6,2,0); (4,4,0); (4,2,2)

The energy can be distributed in 15 ways.

This system has the higher entropy because there are more ways in which the energy can be distributed.

4.2 a) $-82.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

b) $-469.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

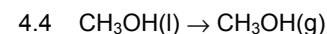
c) 0

4.3 $\Delta G^\circ = -5.4 \text{ kJ}$

$\Delta H^\circ = -58.02 \text{ kJ}$

$\Delta S^\circ = -0.1766 \text{ kJ}\cdot\text{K}^{-1}$

$\Delta G^\circ = -5.39 \text{ kJ}$



$a_{\text{liquid}} = 1$ $a_{\text{vapor}} = 0.174$ (the pressure in atm)

$K = 0.174$

$\Delta G^\circ = 4.34 \text{ kJ}\cdot\text{mol}^{-1}$

4.5 $Q = 1.40$; $K = 8.81$; $\Delta G = -4.56 \text{ kJ}$

4.6 $Q = 65.8$; $\Delta G = -44.6 \text{ kJ}$; $\Delta G^\circ = -55.0 \text{ kJ}$

4.7 $\Delta H^\circ = 36.4 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta S^\circ = 0.1108 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

$t_{\text{bp}} = 55.4^\circ\text{C}$

at 40°C , $\Delta G^\circ = 1.7 \text{ kJ}$; $P^\circ = 392 \text{ torr}$

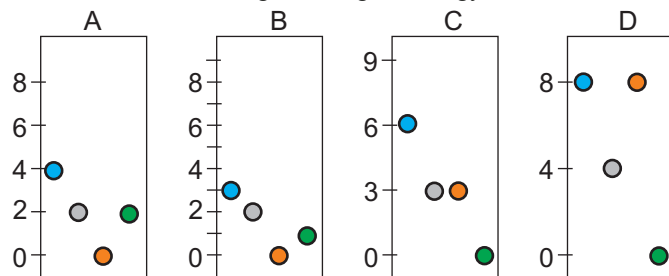
at 10°C , $\Delta G^\circ = 5.0 \text{ kJ}$; $P^\circ = 89 \text{ torr}$

4.8 $K_{273} = 75$ (either method)

4.10 EXERCISES

ENTHALPY, ENTROPY AND FREE ENERGY CHANGES

Refer to the following figures for Exercises 1-6. The lines on the vertical axis represent the allowed energies. Assume constant spacing between levels to determine the energies of higher energy levels.



Use the letter 'U' for the energy unit.

- What are the energies of systems A and B? Which system is at the higher temperature?
 - What are the energies of systems C and D? Which system is at the higher temperature?
 - In how many ways can the energies of systems A and B be distributed? Which system has the greater entropy?
 - In how many ways can the energies of systems C and D be distributed? Which system has the greater entropy?
 - List the systems in order of increasing entropy at a temperature where they all had 12 U of energy.
 - How many ways are there to distribute the energy of system B at 0 K? What is its entropy?
-
- State the second law of thermodynamics.
 - Explain why the second law of thermodynamics is frequently stated as 'spontaneous processes increase the disorder of the universe'.
 - What effect does the enthalpy change of a process have on the entropy of the universe in processes carried out at constant T and P?
 - What is ΔS_{sur} in a process that liberates 20 kJ of heat at 1 atm and 300 K?
 - Consider the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ $\Delta G^\circ = 2.6 \text{ kJ}$ at 298 K. Criticize and correct the following statement: $\Delta G^\circ > 0$, so the reaction is not spontaneous and HI cannot be made from this reaction at 298 K.
 - A large collection of cells is far more 'ordered' in an animal than as individual one-cell organisms. Does this mean that evolution is a violation of the second law? Explain.
 - Explain why dissolving sugar in water always results in a homogeneous solution.
 - Indicate which member of each pair has the higher entropy and indicate the reason:
 - pure silicon wafer or one that has small amounts of germanium present
 - water vapor at 25 °C or liquid water at 25 °C
 - liquid water at 25 °C or liquid water at 50 °C
 - $\text{H}_2\text{O}(\text{l})$ or $\text{H}_2\text{O}_2(\text{l})$ at the same temperature
 - Indicate which member of each pair has the higher entropy and indicate the reason:
 - $\text{PF}_3(\text{g})$ or $\text{PF}_5(\text{g})$ at 75 °C
 - $\text{I}_2(\text{s})$ or $\text{I}_2(\text{g})$ at 300 K
 - $\text{He}(\text{g})$ at 400 K or $\text{He}(\text{g})$ at 600 K
 - A piece of tin or a piece of 60:40 solder (a solid solution that is 60% Pb and 40% Sn)
 - What is a *spontaneous process*? What thermodynamic property of the system indicates spontaneity at constant temperature and pressure?
 - What is an *extensive process*? What thermodynamic property of the system indicates the extent of a reaction at constant temperature and pressure?
 - What can be said about ΔS_{sur} if the entropy change of the system caused by a spontaneous process is $-50 \text{ J}\cdot\text{K}^{-1}$?
 - Indicate whether each of the following statements must be, can be, or cannot be true for a spontaneous endothermic reaction at constant pressure and temperature:

a) $\Delta H^\circ > 0$	b) $\Delta S_{\text{univ}} = 0$	c) $\Delta G^\circ < 0$
d) $\Delta G < 0$	e) $\Delta S > 0$	f) $\Delta E_{\text{univ}} = 0$

20. Indicate whether each of the following statements must be true, can be true or false, or cannot be true for a reaction at *equilibrium*:
- a) $\Delta H^\circ = 0$ b) $\Delta S_{\text{univ}} = 0$ c) $\Delta G^\circ = 0$
 d) $\Delta G < 0$ e) $\Delta S = 0$ f) $\Delta E_{\text{univ}} = 0$
21. Indicate the sign of the entropy change for each of the following processes:
- a) Increasing the temperature of a pot of water from 18 °C to 23 °C.
 b) Condensing a liquid
 c) Clearing a field and planting rows of corn
 d) $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{N}_2\text{O}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
22. Use the data in Appendix B to calculate ΔH° , ΔS° and ΔG° at 298 K for the following reactions:
- a) $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightarrow 2\text{HBr}(\text{g})$
 b) $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$
 c) $2\text{CH}_3\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
 d) $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
23. Use data in Appendix B to calculate the standard entropy change for
- a) the rusting of iron: $4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$
 b) the decomposition reaction: $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
24. Consider the extraction of copper from the ore Cu_2S from the decomposition
- $$\text{Cu}_2\text{S}(\text{s}) \rightarrow 2\text{Cu}(\text{s}) + \text{S}(\text{s}) \quad (\text{Rxn 1})$$
- a) Calculate ΔH° , ΔS° and ΔG° at 298 K.
 b) Is the extraction of copper from Cu_2S extensive?
 c) Given the reaction
- $$\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) \quad (\text{Rxn 2})$$
- Calculate ΔH° , ΔS° and ΔG° at 298 K.
 d) Adding Rxn 1 and Rxn 2 yields the equation for the overall reaction
- $$\text{Cu}_2\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Cu}(\text{s}) + \text{SO}_2(\text{g}) \quad (\text{Rxn 3})$$
- Calculate ΔH° and ΔG° for the reaction above at 298 K.
 e) Is the overall process in Rxn 3 extensive?
25. Gasohol is a mixture of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and gasoline. Write the chemical equation for the combustion of ethanol and determine the maximum amount of work that can be obtained from the combustion of 1 gal of ethanol at 298 K and standard conditions. The density of ethanol is $0.789 \text{ g}\cdot\text{mL}^{-1}$, and 1 gal is 3.79 L.
26. The standard entropy of formation of stannane (SnH_4) is $-84.64 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 298 K. What is the absolute entropy of stannane at 298 K?
27. Determine the standard entropy of formation for each of the following substances at 298 K:
- a) $\text{H}_2(\text{g})$ b) $\text{H}_2\text{O}(\text{g})$ c) $\text{NH}_3(\text{g})$
28. The free energies of formation of $\text{SO}_2(\text{g})$, $\text{H}_2\text{S}(\text{g})$, and $\text{NO}_2(\text{g})$ are -300.2 , -33.6 , and $+51.8 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. Which of these gases has the greatest tendency to decompose to its elements at 298 K?
29. Which of the following is the most stable under standard conditions: $\text{Al}_2\text{O}_3(\text{s})$, $\text{NO}(\text{g})$ or $\text{FeO}(\text{s})$?

FREE ENERGY AND EQUILIBRIUM

30. Draw diagrams that indicate the relative positions of the free energy minima for reactions with the following ΔG° values. Refer to Figure 4.9.
- a) large and positive b) small and positive
31. Draw diagrams that indicate the relative positions of the free energy minima for reactions with the following ΔG° values. Refer to Figure 4.9.
- a) small and negative b) large and negative
32. Calculate the equilibrium constant at 298 K for the reaction
- $$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$$
33. Gaseous ozone, O_3 , is formed from O_2 by the following reaction:
- $$\frac{3}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{O}_3(\text{g})$$
- What is the equilibrium constant of this reaction at 298 K?
34. Write the expression for the reaction quotient for each of the following:
- a) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 b) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 c) $\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^{-1}(\text{aq})$
 d) $2\text{Al}(\text{s}) + 6\text{H}^{1+}(\text{aq}) \rightleftharpoons 2\text{Al}^{3+}(\text{aq}) + 3\text{H}_2(\text{g})$
 e) $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$

35. Write the expression for the reaction quotient and use the data in Appendix B to determine the value of the equilibrium constant at 298 K for each of the following reactions:

- $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightarrow 2\text{HBr}(\text{g})$
- $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$
- $2\text{CH}_3\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
- $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$

36. Write the equilibrium constant expression and use the data in Appendix B to determine the value of ΔG° at 298 K for each of the following equilibria to be discussed in upcoming chapters.

- $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^{1+}(\text{aq}) + \text{Cl}^{1-}(\text{aq})$ $K = 1.8 \times 10^{-10}$
- $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^{1+}(\text{aq}) + \text{OH}^{1-}(\text{aq})$ $K = 1.8 \times 10^{-5}$
- $\text{NH}_4^{1+}(\text{aq}) + \text{CN}^{1-}(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{HCN}(\text{aq})$ $K = 1.4$
- $\text{Pb}^{2+}(\text{aq}) + \text{Sn}(\text{s}) \rightleftharpoons \text{Pb}(\text{s}) + \text{Sn}^{2+}(\text{aq})$ $K = 2$

37. Indicate the activity of each of the following:

- NH_3 gas at 0.024 atm
- Cl^{1-} ion in a 0.11 M solution of NaCl
- A crystal of AgCl sitting in liquid water
- H_2 gas at 321 torr

38. Indicate the activity of each of the following:

- Liquid ammonia at -50°C
- He gas that is 0.0376 M at 325 K
- NO_3^{1-} ion in a solution of 0.206 M $\text{Mg}(\text{NO}_3)_2$
- Ar gas at 388 torr

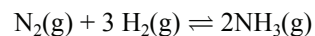
39. What are the units of K_p for each of the following the reactions?

- $2\text{ClF}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Cl}_2\text{O}(\text{g}) + \text{OF}_2(\text{g})$
- $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- $\text{NH}_4\text{NO}_3(\text{s}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$

40. What are the units of K_c for each of the following the reactions?

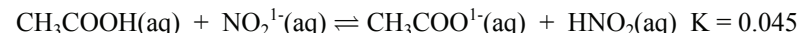
- $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^{1+}(\text{aq}) + \text{Cl}^{1-}(\text{aq})$
- $\text{Al}(\text{s}) + 3\text{Ag}^{1+}(\text{aq}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3\text{Ag}(\text{s})$
- $\text{HNO}_2(\text{aq}) + \text{F}^{1-}(\text{aq}) \rightleftharpoons \text{HF}(\text{aq}) + \text{NO}_2^{1-}(\text{aq})$

41. Consider the following gas phase equilibrium at 298 K:



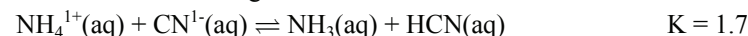
- Use standard free energies of formation, calculate value of K at 298 K.
- Calculate ΔG when a reaction mixture consists of 10 atm N_2 , 10 atm H_2 , and 1 atm NH_3 .

42. Consider the following acid-base equilibrium at 25°C :



- What would be the sign of ΔG immediately after the addition of NO_2^{1-} to an equilibrium mixture? How would the reaction mixture respond?
- What effect would the addition of $\text{CH}_3\text{COO}^{1-}$ to an equilibrium mixture have on the sign of ΔG ? How would the reaction mixture respond?
- State a general rule that summarizes what happens when you add a reactant or product to an equilibrium mixture. This effect is known as Le Châtelier's principle.

43. Consider the following acid-base reaction at 25°C :

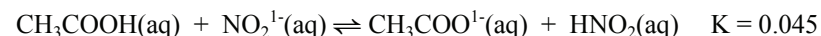


- What is the value of ΔG° ?

What are the values of Q and ΔG at 298 K under the following conditions, and in which direction (\rightarrow , \leftarrow , or \rightleftharpoons) is the reaction proceeding?

	$[\text{NH}_4^{1+}]$	$[\text{CN}^{1-}]$	$[\text{NH}_3]$	$[\text{HCN}]$
b)	0.10 M	0.10 M	0.10 M	0.10 M
c)	0.12 M	0.10 M	0.17 M	0.12 M
d)	0.18 M	0.18 M	0.10 M	0.10 M

44. Consider the acid-base reaction at 25°C



- What is the value of ΔG° at 298 K?

What are the values of Q and ΔG at 298 K under the following conditions, and in which direction (\rightarrow , \leftarrow , or \rightleftharpoons) is the reaction proceeding?

	$[\text{CH}_3\text{COOH}]$	$[\text{NO}_2^{1-}]$	$[\text{CH}_3\text{COO}^{1-}]$	$[\text{HNO}_2]$
b)	0.10 M	0.10 M	3.0 M	0
c)	0.010 M	0.10 M	1.0 M	0.50 M
d)	0.088 M	0.10 M	0.021 M	0.019 M
e)	0.12 M	0.12 M	0.15 M	0.15 M

45. The process of dissolving a gas in a liquid is exothermic due to solvent-solute interactions. Consider the process of making carbonated water,
 $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq}) \quad \Delta H^\circ = -19.4 \text{ kJ}$
- Write the equilibrium constant expression for the carbonation process and solve it for the equilibrium concentration of CO_2 in solution in terms of the partial pressure of the gas in equilibrium with it. This expression is known as Henry's Law.
 - Use Equation 4.19 and the expression for the equilibrium constant for the carbonation process to explain why a carbonated drink gets *flat* when it is allowed to warm.
 - Explain why a carbonated drink gets *flat* when allowed to sit in an open container.
46. CO_2 is pumped into a container at -70°C until its pressure is 1800 torr. If the vapor pressure of CO_2 is 1486 torr at -70°C , what are the signs of ΔG and ΔG° for $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$ under these conditions?
47. The pressure of water vapor in a closed container is 0.3 atm. If the vapor pressure of water at this temperature is 1.5 atm, what are the signs of ΔG and ΔG° for $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$?
53. The enthalpy of vaporization of H_2S at 212.8 K is $18.67 \text{ kJ}\cdot\text{mol}^{-1}$. What is the molar entropy of vaporization of 2.50 moles of H_2S at this temperature?
54. The equilibrium constant of a reaction is 6.0 at 326 K and 9.0 at 412 K. What are ΔH° and ΔS° for the reaction?
55. The equilibrium constant of a reaction is 3.2×10^3 at 358 K and 1.7×10^2 at 456 K. What are ΔH° and ΔS° for the reaction?
56. Iodine sublimes, and a closed jar of iodine at room conditions consists of both the solid and the vapor.
- What is the pressure of iodine gas in equilibrium with the solid at 25°C and 1 atm?
 - At what temperature is the pressure of the gas at 1 atm?
57. The vapor pressure of solid CO_2 (dry ice) is 280. torr at $-90.^\circ\text{C}$ and 105 torr at $-100.^\circ\text{C}$.
- What is ΔG° for the reaction $\text{CO}_2(\text{s}) \rightleftharpoons \text{CO}_2(\text{g})$ at each temperature?
 - What are ΔH° and ΔS° for the reaction $\text{CO}_2(\text{s}) \rightleftharpoons \text{CO}_2(\text{g})$ at these temperatures? Assume that ΔH° and ΔS° are constant over this temperature range.
 - A *dry ice bath* is used routinely in the laboratory to keep things cold. It is made by making a powder of the dry ice and then mixing the powder with a solvent to make a slurry. Estimate the temperature of a *dry ice bath* by determining the temperature at which the vapor pressure of CO_2 is 1 atm.

TEMPERATURE DEPENDENCE OF ΔG° AND K

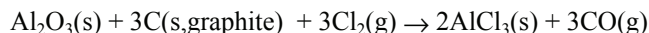
48. The amount of product in an equilibrium mixture increases when the temperature is raised. Is the reaction exothermic or endothermic? Explain.
49. Use the data in Appendix B to estimate the vapor pressure of water at $50.^\circ\text{C}$. Express your answer in torr.
50. The standard enthalpy of vaporization of methanol is $36.4 \text{ kJ}\cdot\text{mol}^{-1}$ and the standard entropy of vaporization is $110.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. What is the normal boiling point of methanol in degrees Celsius?
51. The heat of vaporization of SiCl_4 at 300. K is $29.7 \text{ kJ}\cdot\text{mol}^{-1}$ and its vapor pressure is 34.0 torr.
- What are ΔG° and ΔS° of vaporization of SiCl_4 at 300. K?
 - Assume ΔH° and ΔS° are temperature independent and estimate the boiling point of SiCl_4 .
52. What are the vapor pressure at 298 K in torr and the normal boiling point in degree Celsius of CS_2 ?

COUPLED REACTIONS

58. Write the reaction that would result when the oxidation of CO is coupled to each of the following reactions. Calculate ΔG° at 298 K for each coupled reaction and indicate whether it is extensive.
- $\text{Al}_2\text{O}_3(\text{s}) \rightarrow 2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$
 - $2\text{PbO}(\text{s}) \rightarrow 2\text{Pb}(\text{s}) + \text{O}_2(\text{g})$
 - $\text{Ag}_2\text{O}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$
59. Write the reaction that would result when the oxidation of S to SO_2 is coupled to each of the following reactions. Calculate ΔG° at 298 K for each coupled reaction and indicate whether it is extensive.
- $\text{Cr}_2\text{O}_3(\text{s}) \rightarrow 2\text{Cr}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$
 - $\text{SiO}_2(\text{s}) \rightarrow \text{Si}(\text{s}) + \text{O}_2(\text{g})$
60. How many moles of ATP ions must be converted to ADP to drive a biochemical reaction in which $\Delta G^\circ = 350 \text{ kJ}$?

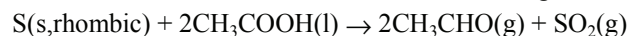
MISCELLANEOUS PROBLEMS

61. Calculate ΔH° , ΔS° , and ΔG° at 298 K for the following reaction:



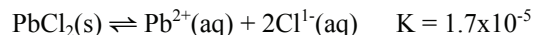
- Is the reaction extensive at standard conditions and 298 K?
- Write the expression for K and calculate its value at 298 K.
- Estimate the value of K at 600 K.

62. Calculate ΔH° , ΔS° and ΔG° at 298 K for the following reaction:



- Is the reaction extensive at standard conditions and 298 K?
- What are the equilibrium constant expression and value at 298 K?
- Estimate the equilibrium constant at 600. K.

63. Consider the following equilibrium, which defines the solubility of lead chloride in water at 25 °C:



- What is the value of ΔG° for the reaction at 25 °C?

Determine Q and ΔG for the above reaction given the solutions described in Parts b and c and indicate whether more solid could dissolve or more solid would precipitate.

- $[\text{Pb}^{2+}] = 1.2 \text{ mM}$ and $[\text{Cl}^{-}] = 15.2 \text{ mM}$
- $[\text{Pb}^{2+}] = 0.075 \text{ M}$ and $[\text{Cl}^{-}] = 0.040 \text{ M}$

64. Indicate whether each of the following must be true, must be false, or can be either true or false for an *exothermic* process that is *extensive* but *not spontaneous*.

- $\Delta H^\circ > 0$
- $\Delta S_{\text{univ}} = 0$
- $\Delta G^\circ < 0$
- $\Delta G < 0$
- $\Delta S > 0$
- $\Delta E_{\text{univ}} = 0$

65. Indicate whether ΔG increases, decreases, or remains the same as the partial pressure of CO_2 is increased in each of the following:

- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$
- $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$

66. Use the data in Appendix B to determine the value of the equilibrium constant for the following reaction at 298 K: $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
Estimate the value of the equilibrium constant at 500 K.

67. When both driving forces in a reaction are favorable ($\Delta H^\circ < 0$ and $\Delta S^\circ > 0$) the reaction is extensive ($K > 1$) at all temperatures, and when both are unfavorable, the reaction is never extensive ($K < 1$). However, when one driving force is favorable and the other is not, the reaction can be either extensive or not depending upon the temperature. Determine the temperature at which $K \sim 1$ for each of the following reactions and discuss the conditions at which the reaction is likely to be extensive.

- $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
- $\text{SO}_3(\text{g}) \rightleftharpoons \frac{1}{2}\text{O}_2(\text{g}) + \text{SO}_2(\text{g})$
- $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s})$
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

68. What are the values of ΔS° and ΔH° for the reaction $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ if $K_{600} = 381$ and $K_{700} = 2.69 \times 10^3$. What would be the value of the equilibrium constant at 400 K? Assume that enthalpy and entropy are temperature independent.

69. Determine ΔS° and ΔH° from the following equilibrium constant/temperature data. Note the use of the Celsius scale for temperature.

T (°C)	200	225	230	250	260
K	19.6	10.9	11.6	7.8	5.6

70. Determine ΔS° and ΔH° from the following equilibrium constant/temperature data..

T (°C)	20	60	90	110	125
K	2.31×10^4	8.97×10^4	2.09×10^5	3.92×10^5	5.03×10^5

71. Use the following equilibrium constant-temperature data to determine ΔH° and ΔS° for the reaction.

T (K)	300	350	375	400	460
K	2000.0	87.7	33.2	7.0	1.8

CHAPTER 5

Chemical Equilibrium

5.0	<i>Introduction</i>
5.1	<i>The Equilibrium Constant</i>
5.2	<i>Le Châtelier's Principle</i>
5.3	<i>Using the Equilibrium Constant</i>
5.4	<i>Chapter Summary and Objectives</i>
5.5	<i>Exercises</i>

5.0 INTRODUCTION

The equilibrium constant was defined in Chapter 4, and calculations were done to establish the relationship between it and the standard free energy change for a reaction. However, the equilibrium constant is most valuable because it lets us predict the composition of an equilibrium mixture and to determine how the reactant concentrations should be adjusted so as to obtain an equilibrium mixture with a desired composition. These calculations are so important that they form the basis of this chapter and much of Chapters 6-9, where the principles established in this chapter are applied to proton transfer, solubility, and electron transfer processes.

IN THIS CHAPTER YOU LEARN HOW TO:

- convert between the K_c and K_p for a gas-phase reaction;
- manipulate the equilibrium constants of reactions to obtain equilibrium constants for related reactions;
- use Le Châtelier's principle to predict the effect of changing an equilibrium; and
- treat equilibrium problems quantitatively.

5.1 THE EQUILIBRIUM CONSTANT

K_p VERSUS K_c

The thermodynamic equilibrium constant (K)* discussed in Chapter 4 is unitless because it is defined in terms of unitless activities. However, equilibrium constants can be defined in terms of partial pressures or molar concentrations. These equilibrium constants typically, but not always, have units. The equilibrium constant of a gas-phase reaction is called K_p if it is expressed in partial pressures, and K_c if it is expressed in molar concentrations. For a reaction that involves only gases, K_p equals K when the partial pressures are in atmospheres because the activity of a gas is numerically equal to its partial pressure in atmospheres. For a reaction that involves only solutes in a liquid solution, K_c equals K because the activity of a solute is numerically equal to its molar concentration.

There are times when it is more convenient to consider gas-phase equilibria in terms of molar concentrations rather than partial pressures. However, K_c is not equal to the thermodynamic K for a gas-phase reaction. Consequently, the K (or K_p) must be converted to a K_c . This is done by converting the partial pressures of the gases into molar concentrations. The conversion is made with the ideal gas law,

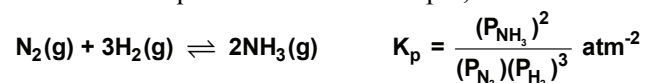
$$P_A = \frac{n_A RT}{V} = \frac{n_A}{V} \times RT$$

where P_A is the partial pressure of A, n_A is the number of moles of gas A. n_A/V is the number of moles of A per liter of gas, which is $[A]$ the molar concentration of A. Substitution of $n_A/V = [A]$ into the above equation yields Equation 5.1, which relates the pressure and concentration of a gas.

$$P_A = [A]RT$$

Eq. 5.1

To convert a K_p into a K_c , we convert each partial pressure in the K_p expression into a concentration with Equation 5.1. For example, consider the following equilibrium:



Using Equation 5.1 to convert each pressure to a concentration, we obtain

$$K_p = \frac{[NH_3]^2 (RT)^2}{[N_2] (RT) \times [H_2]^3 (RT)^3} = \frac{[NH_3]^2}{[N_2][H_2]^3} \times (RT)^{2-(1+3)} = K_c (RT)^{-2}$$

The exponent of RT in the final expression is Δn_g which is also the exponent of the units of K_p . The ratio preceding the $(RT)^{\Delta n_g}$ term is K_c , so K_p and K_c are related as follows:

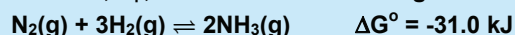
$$K_p = K_c \times (RT)^{\Delta n_g} \quad \text{or} \quad K_c = K_p \times (RT)^{-\Delta n_g} \quad \text{Eq. 5.2}$$

* The thermodynamic K is defined by $\Delta G^\circ = -RT \ln K$. Thus, K is an equilibrium constant derived from thermodynamic properties. Any quantity whose logarithm is required must be unitless.

$R = 0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. A $K_p \leftrightarrow K_c$ conversion is an $\text{atm}^{\Delta n_g} \leftrightarrow \text{M}^{\Delta n_g}$ unit conversion. The units of R can be made more useful for this type of conversion by recognizing that $\text{L}\cdot\text{mol}^{-1} = \text{M}^{-1}$, the reciprocal of the molar concentration of the gas. Thus, $R = 0.08206 \text{ atm}\cdot\text{K}^{-1}\cdot\text{M}^{-1}$ and the units of RT are $\text{atm}\cdot\text{M}^{-1}$ in $K_p \leftrightarrow K_c$ conversions. Finally, note that when $\Delta n_g = 0$, $K_c = K_p = K$. Thus, using either molarities or partial pressures in the equilibrium constant expression yields the same value of K , which is unitless and numerically equal to the thermodynamic equilibrium constant.

Example 5.1

What are K , K_p , and K_c for the following at 298 K?



Use Equation 4.14 to determine K .

$$K = \frac{(a_{\text{NH}_3})^2}{(a_{\text{N}_2})(a_{\text{H}_2})^3} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{-31,000}{(8.314)(298)}\right) = e^{12.5} = 2.7 \times 10^5$$

K is unitless because it is defined in terms of activities. This is a gas-phase reaction, so $K_p = K$ except that it has units of $\text{atm}^{\Delta n_g}$. $\Delta n_g = 2 - 4 = -2$ for the given reaction, so

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = 2.7 \times 10^5 \text{ atm}^{-2}$$

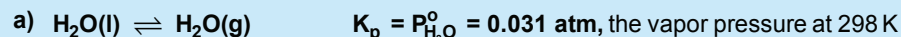
Use Equation 5.2 and $RT = (0.0821 \text{ atm}\cdot\text{K}^{-1}\cdot\text{M}^{-1})(298 \text{ K}) = 24.5 \text{ atm}\cdot\text{M}^{-1}$ to convert K_p to K_c .

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = K_p \times (RT)^{-\Delta n_g} = 2.7 \times 10^5 \text{ atm}^{-2} \times \left(\frac{24.5 \text{ atm}}{\text{M}}\right)^2 = 1.6 \times 10^8 \text{ M}^{-2}$$

Example 5.2

Convert the following K_p 's to K_c 's at 298 K.

All equilibrium constants in this example are at 298 K, so we first determine the value of RT to be $(0.0821 \text{ atm}\cdot\text{K}^{-1}\cdot\text{M}^{-1})(298 \text{ K}) = 24.5 \text{ atm}\cdot\text{M}^{-1}$.



$$\Delta n_g = 1, \text{ so } K_c = K_p(RT)^{-1} = 0.031 \text{ atm} \times \left(\frac{\text{M}}{24.5 \text{ atm}}\right) = 1.3 \times 10^{-3} \text{ M}$$

PRACTICE EXAMPLE 5.1

Consider the following equilibrium at 350 K: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$

Use the data in Appendix B and assume that ΔH° and ΔS° are independent of temperature to determine ΔG° at 350 K.

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

What is the value of the equilibrium constant at 350 K for the reaction?

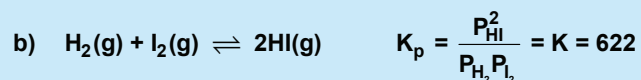
$$K = \text{_____}$$

What is the value of K_p at 350 K?

$$K_p = \text{_____ atm}^{-1}$$

What is the value of K_c at 350 K?

$$K_c = \text{_____ M}^{-1}$$



$\Delta n_g = 0$ for this reaction, and that makes it an important special case. When $\Delta n_g = 0$, the units of the numerator and denominator cancel, making both K_p and K_c unitless. In this special case, $K = K_p = K_c$, which is 622 in this example.

PROPERTIES OF THE EQUILIBRIUM CONSTANT

We examine three properties of the equilibrium constant by considering two equilibria:

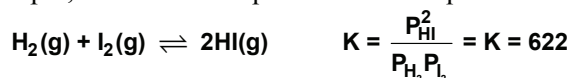


Each of the following properties is demonstrated in the margin.

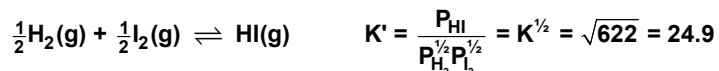
- 1) The equilibrium constant of a chemical equation that is obtained by multiplying another equation by a number n equals the original K raised to the n^{th} power: $K' = K^n$.
- 2) The equilibrium constant of a chemical equation that is obtained by reversing the direction of another equation equals the reciprocal of the original: $K' = 1/K = K^{-1}$.
- 3) The equilibrium constant of a chemical equation that is obtained from the addition of two other equations equals the product of the original K 's: $K' = K_a K_b$.

Note that B cancels in the addition of Equilibria a and b shown in the margin and then in the product of their equilibrium constants.

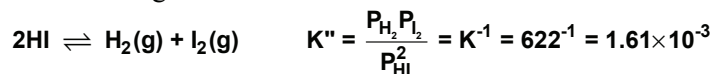
For example, consider the equilibrium and equilibrium constant given below.



According to the first property, the equilibrium constant of the reaction in which all of the coefficients have been multiplied by $\frac{1}{2}$ is the square root of the original constant.



The second property indicates that the equilibrium constant for the reverse reaction is the reciprocal of the original constant.

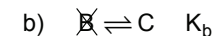


Properties of Equilibrium Constants

$$1) \text{ Multiply Equilibrium a by } n: \quad n\text{A} \rightleftharpoons n\text{B} \quad K' = \frac{[\text{B}]^n}{[\text{A}]^n} = \left(\frac{[\text{B}]}{[\text{A}]}\right)^n = (K_a)^n$$

$$2) \text{ Reverse Equilibrium a: } \quad \text{B} \rightleftharpoons \text{A} \quad K' = \frac{[\text{A}]}{[\text{B}]} = \left(\frac{[\text{B}]}{[\text{A}]}\right)^{-1} = (K_a)^{-1} = \frac{1}{K_a}$$

$$3) \text{ Add Equilibria a and b: } \quad \text{a) } \text{A} \rightleftharpoons \text{B} \quad K_a$$



$$\text{a + b) } \quad \text{A} \rightleftharpoons \text{C} \quad K' = \frac{[\text{C}]}{[\text{A}]} = K_a K_b = \frac{[\text{C}]}{[\text{A}]} \times \frac{[\text{B}]}{[\text{B}]}$$

PRACTICE EXAMPLE 5.2

Consider the following equilibrium at 350 K: $\frac{1}{2}\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons \text{NO}_2(\text{g})$.

Use the ΔG° determined in Practice Example 5.1 to determine ΔG° for this reaction?

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

What is the value of K as determined from the above ΔG° ?

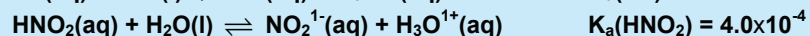
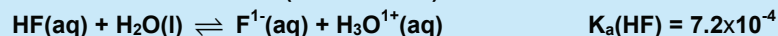
$$K = \text{_____}$$

Use the K determined in Practice Example 5.1 and the properties of K given in the text to determine K for the chemical equation in this example.

$$K = \text{_____}$$

Example 5.3

Write the equilibrium constant expression for the acid dissociation reactions for hydrofluoric and nitrous acids (K_a reactions).

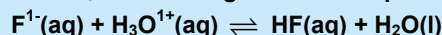


The activity of liquid water is unity, so the equilibrium constant expressions are

$$K_a(\text{HF}) = \frac{[\text{F}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HF}]} = 7.2 \times 10^{-4} \quad \text{and} \quad K_a(\text{HNO}_2) = \frac{[\text{NO}_2^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HNO}_2]} = 4.0 \times 10^{-4}$$

Example 5.4

Write the equilibrium constant expression for the following acid-base reaction and use the K_a constants given in Example 5.3 to evaluate its equilibrium constant.

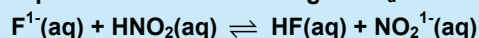


This reaction is the reverse of the K_a reaction for HF, so the value of K is the reciprocal of K_{HF} . Writing products over reactants, we obtain

$$\frac{[\text{HF}]}{[\text{F}^{1-}][\text{H}_3\text{O}^{1+}]} = \frac{1}{K_a(\text{HF})} = (7.2 \times 10^{-4})^{-1} = 1.4 \times 10^3$$

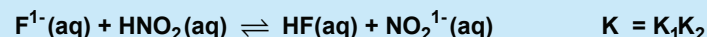
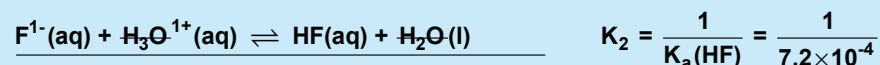
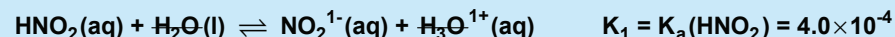
Example 5.5

Write the equilibrium constant expression for the following reaction and evaluate its equilibrium constant using the K_a values in Example 5.2.



$$\text{The equilibrium constant is } K = \frac{[\text{HF}][\text{NO}_2^{1-}]}{[\text{F}^{1-}][\text{HNO}_2]}$$

The reaction is the sum of the K_a of HNO_2 and the reverse of the K_a of HF.

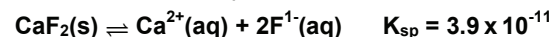


The reaction is the sum of two reactions, so K is the product of the two K 's.

$$K = K_1 K_2 = K_a(\text{HNO}_2) \times \frac{1}{K_a(\text{HF})} = \frac{K_a(\text{HNO}_2)}{K_a(\text{HF})} = \frac{4.0 \times 10^{-4}}{7.2 \times 10^{-4}} = 0.56$$

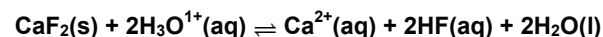
PRACTICE EXAMPLE 5.3

Write the equilibrium constant expression for the following reaction. This type of equilibrium constant is known as the solubility product, K_{sp} (Chapter 8).



$$K_{\text{sp}} =$$

Calcium fluoride dissolves in acid by the reaction shown below. Write the equilibrium constant expression for the reaction.



$$K =$$

Use the solubility product of calcium fluoride given above and the K_a of HF given in Example 5.3 to evaluate the above equilibrium constant.

Multiply the K_{sp} reaction by ____ to get CaF_2 into the final reaction with the correct coefficient.

I.

Reverse the K_a reaction of HF and multiply it by ____ to get HF into the final reaction with the correct coefficient.

II.

Summing reactions I and II yields:

The equilibrium constant for the above reaction is:

5.2 LE CHÂTELIER'S PRINCIPLE

In Chapter 4, the spontaneous direction of a reaction was predicted from known concentrations by using the fact that a reaction proceeds from left to right when $Q < K$ and from right to left when $Q > K$. We also saw that a temperature rise causes the equilibrium constants of endothermic reactions to increase and the equilibrium constants of exothermic reactions to decrease. However, the behavior of equilibria and equilibrium constants was known before their thermodynamic basis was discovered, and they were summarized in **Le Châtelier's principle**:

If a system at equilibrium is disturbed, then the system reacts so as to counteract the disturbance.

Le Châtelier's principle can be used to predict the direction of the shift in equilibrium caused by a disturbance without determining Q . We consider three types of disturbances: changing the amount of one of the components of the equilibrium, changing the volume, and change the temperature.

We begin by using Le Châtelier's principle to predict the effects of adding and removing material from the equilibrium mixture $A + B \rightleftharpoons C + D$ as shown in Figure 5.1a.

- **Adding B** (Figure 5.1b): The system counteracts the addition of B (shown by green arrow on the initial side) by reacting it with A, which produces C + D. Therefore, adding B decreases the concentration of A and increases the concentrations of C and D.
- **Removing C** (Figure 5.1c). When C is removed, the mixture reacts so as to replace some of the C, which can only be done by reacting A + B. Reaction of A + B also produces D, so removing C decreases the concentrations of A and B and increases that of D.

We conclude that

Adding a substance increases the concentrations of the substances on the opposite side of the chemical equation and decreases the concentrations of those on the same side.
Removing a substance increases the concentrations of the substances on the same side of the chemical equation and decreases the concentrations of those on the opposite side.

Le Châtelier's principle allows us to make quick conclusions about the direction of the concentration changes resulting from a disturbance to an equilibrium system. However, it does not tell us by how much the equilibrium position changes, which is the topic of the remainder of this chapter. We introduce those quantitative concepts now by showing how to use Q and K to make the same predictions as above. The initial equilibrium in Figure 5.1a is established with $[A] = [B] = 0.40$ M and $[C] = [D] = 0.80$ M, so we begin with

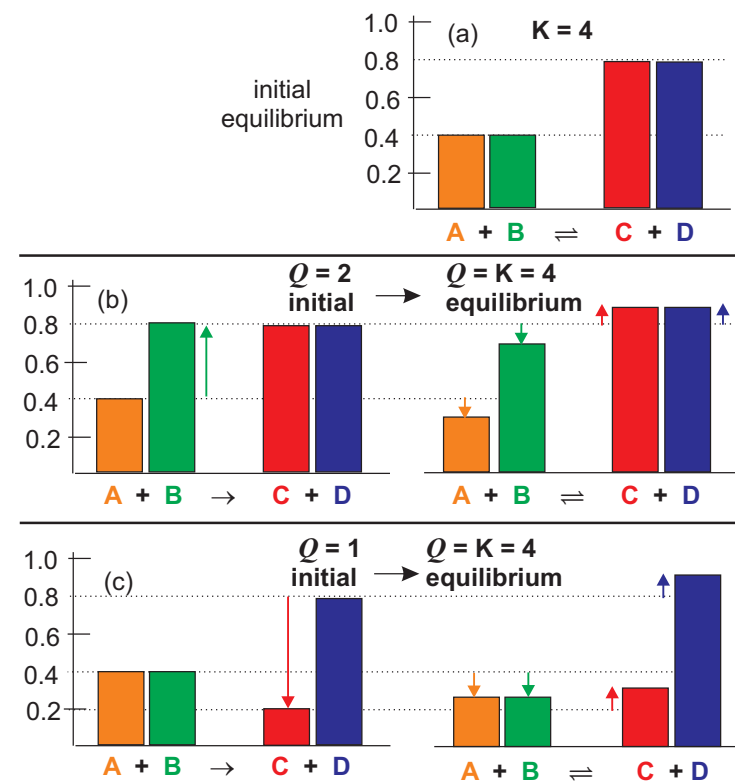


Figure 5.1 Le Châtelier's Principle

The concentrations of A, B, C, and D are represented by the heights of the rectangles as given on the axis. The colored arrows on the initial side indicate the disturbance to the equilibrium, and those on the equilibrium side show how the system counteracts the disturbance; *i.e.*, they are the Δ (change) for the process.

- The initial equilibrium mixture is $[A] = [B] = 0.40$ M and $[C] = [D] = 0.80$ M, so $K = 0.8^2/0.4^2 = 2^2 = 4$.
- Increasing the concentration of B from 0.40 M to 0.80 M causes the concentrations of C and D to increase and that of A to decrease.
- Removing C causes the concentrations of A and B to decrease and that of D to increase.

$$K = \frac{[C][D]}{[A][B]} = \frac{(0.80)(0.80)}{(0.40)(0.40)} = 4.0$$

- Adding B: Figure 5.1b shows the effect of increasing the concentration of B to 0.80 M, which lowers the value of Q .

$$Q = \frac{[C][D]}{[A][B]} = \frac{(0.80)(0.80)}{(0.40)(0.80)} = 2.0$$

$Q < K$, so the reaction proceeds as written ($A + B \rightarrow C + D$). As the reaction proceeds, Q increases as reactants disappear and products form. After reaction of $0.105 \text{ mol}\cdot\text{L}^{-1}$

$$Q = K = \frac{[C][D]}{[A][B]} = \frac{(0.905)(0.905)}{(0.295)(0.695)} = 4.0^\dagger$$

$Q = K$, so the system has established a new equilibrium in which the concentrations of C and D have increased and that of A has decreased.

Removing B would make $Q > K$ causing the reverse reaction to occur. The new equilibrium would be established by decreasing the concentrations of C and D and increasing that of A.

[†] Extra significant digits are retained in the concentrations to better reproduce the value of K .

- Removing C: Figure 5.1c shows the effect of removing C until $[C] = 0.20 \text{ M}$, which results in the following Q .

$$Q = \frac{[C][D]}{[A][B]} = \frac{(0.20)(0.80)}{(0.40)(0.40)} = 1.0$$

$Q < K$, so A and B react to produce C and D. After reaction of $0.125 \text{ mol}\cdot\text{L}^{-1}$,

$$Q = K = \frac{[C][D]}{[A][B]} = \frac{(0.325)(0.925)}{(0.275)(0.275)} = 4.0^\dagger$$

$Q = K$ and a new equilibrium is established in which the concentrations of A and B have been decreased and that of D has been increased.

Note that, irrespective of the substance whose amount was changed or whether it was added or removed, reaction always occurred after the change so as to attain concentrations that satisfied the equilibrium requirement; *i.e.*, irrespective of the initial Q , the final concentrations always satisfied the K for the reaction.

Changing the volume of a gas-phase reaction changes the pressures of the gases, and Le Châtelier's principle states that the equilibrium reacts to counteract that change. At constant temperature, the only way to counter a pressure/volume change is to change the number of moles of gas. We conclude that

A volume increase causes an equilibrium to shift toward the side with the greater number of moles of gas in the balanced chemical equation, while a volume decrease results in a shift toward the side with the fewer number of moles of gas. Reactions in which $\Delta n_g = 0$ are unaffected by volume changes.

Consider the $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium. The balanced chemical equation shows two

moles of gas on the left side but only one on the right. Thus, Le Châtelier's principle predicts that a volume increase should produce NO_2 and a volume decrease should produce N_2O_4 . We now use a comparison of Q and K to draw the same conclusion by examining the effects of doubling and then halving the volume of an equilibrium in which the concentrations are $[\text{NO}_2] = 0.200 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.400 \text{ M}$. The equilibrium constant determined from these concentrations is

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.400}{(0.200)^2} = 10.0 \text{ M}^{-1}$$

- Doubling the volume halves the concentrations, so the concentrations instantaneously drop to $[\text{NO}_2] = 0.100 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.200 \text{ M}$. However, the new concentrations are not equilibrium concentrations. To determine the effect of the volume increase on the equilibrium, we must determine Q_c with the new concentrations.

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.200}{(0.100)^2} = 20.0 \text{ M}^{-1} > K_c$$

$Q_c > K_c$, so the reaction proceeds from right to left ($2\text{NO}_2 \leftarrow 1\text{N}_2\text{O}_4$). Thus, an increase in volume causes the equilibrium to shift toward the side with the greater number of moles of gas, which is the same direction predicted with Le Châtelier's principle.*

- Halving the volume doubles the concentrations to $[\text{NO}_2] = 0.400 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.800 \text{ M}$, which are not equilibrium concentrations. Q_c is determined to be

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.800}{(0.400)^2} = 5.00 \text{ M}^{-1} < K_c$$

$Q_c < K_c$, so the reaction proceeds from left to right ($2\text{NO}_2 \rightarrow 1\text{N}_2\text{O}_4$). Thus, a decrease in volume causes the equilibrium to shift to the side with the lesser number of moles of gas. Again, this prediction is consistent with that of Le Châtelier's principle.

Changing the temperature at constant pressure changes K not Q , but Le Châtelier's principle predicts the effect that temperature has on the equilibrium constant by viewing heat as a product of an exothermic reaction and as a reactant in an endothermic reaction. Heating an exothermic reaction is the same as adding a substance to the right (product) side, which shifts the reaction toward the left (reactant) side (\leftarrow). The shift increases the concentrations of the substances on the left and decreases those on the right, which decreases K in agreement with the conclusion reached using Equation 4.18.

* The new equilibrium concentrations are determined in Example 5.14.

Example 5.6

Apply Le Châtelier's principle and considerations of Q and K to predict the effect that each of the following has on the following equilibrium.



Adding $\text{H}_2(\text{g})$

The system shifts to the right (\rightarrow) to remove some of the added H_2 . As a result, the number of moles of N_2 decreases and the number of moles of NH_3 increases.

Alternatively, adding H_2 increases P_{H_2} , which increases the denominator and makes Q smaller than K . $Q < K$, so the reaction proceeds to the right.

Removing NH_3

The system shifts to the right as H_2 and N_2 react to replace some of the lost NH_3 .

Removing NH_3 decreases the numerator of Q , which makes Q smaller than K . $Q < K$, so the reaction proceeds to the right.

Increasing the volume

Increasing the volume shifts the equilibrium to the side with the greater number of moles of gas to counteract the decrease in pressure. The balanced equation shows four moles of gas on the left side for every two moles on the right. Consequently, the equilibrium shifts to the left to produce H_2 and N_2 and consume NH_3 .

The Q_c expression in terms of moles and volumes* contains a $V^{-\Delta n_g}$ in the numerator. $\Delta n_g < 0$ for this reaction, so increasing the volume increases Q for this reaction. $Q > K$, so the reaction proceeds to the left (\leftarrow).

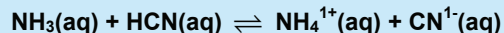
Increasing the temperature

The reaction is exothermic, so $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3 + \text{heat}$. Increasing the temperature or heating the reaction drives the reaction to the left to produce H_2 and N_2 and consume NH_3 . Decreasing the numerator and increasing the denominator decreases the value of K .

$$* Q_c = \frac{\left(\frac{n_{\text{NH}_3}}{V}\right)^2}{\left(\frac{n_{\text{H}_2}}{V}\right)^3 \left(\frac{n_{\text{N}_2}}{V}\right)} = \frac{n_{\text{NH}_3}^2}{n_{\text{H}_2}^3 n_{\text{N}_2}} \times V^2$$

Example 5.7

Predict the effect of dissolving NH_4Cl in the following equilibrium mixture.

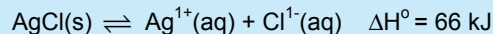


Dissolving NH_4Cl adds NH_4^{1+} and Cl^{1-} ions to the solution. Cl^{1-} is a spectator ion and has no effect. NH_4^{1+} lies on the right of the equilibrium, so adding more shifts the equilibrium to the left to produce NH_3 and HCN .

$Q = \frac{[\text{NH}_4^{1+}][\text{CN}^{1-}]}{[\text{NH}_3][\text{HCN}]}$, so adding NH_4^{1+} ions increases Q , which makes $Q > K$. The reaction proceeds to the left.

Example 5.8

Predict the effect of each of the following on the equilibrium mixture.

**a) Dissolving solid AgNO₃ in the solution**

Dissolving AgNO₃ adds Ag¹⁺ and NO₃¹⁻ ions to the solution, but NO₃¹⁻ ion is a spectator ion and has no effect. The reaction shifts to the left (\leftarrow) to consume some of the additional Ag¹⁺. The activity of a solid is unity, so $Q = [\text{Ag}^{1+}][\text{Cl}^{1-}]$. Adding AgNO₃ increases [Ag¹⁺], so Q becomes larger than K , and the reaction proceeds to the left.

b) Adding solid AgCl to the solution

It is tempting to predict that the additional solid AgCl should react to form more Ag¹⁺ and Cl¹⁻, but the fact that AgCl is already in equilibrium means that the solution is already saturated with AgCl, so no more can dissolve. Thus, adding the solid reactant has no effect. Note that the solid in Part a is treated differently because it is not directly involved in the equilibrium; it simply dissolves to produce an ion that is present in the equilibrium.

The result is more apparent when you consider the effect on Q . The activity of a solid is unity and does not change, so adding a solid reactant or product does not change Q . Q remains equal to K , so there is no shift in the equilibrium – there is simply more solid AgCl at the bottom of the flask. We conclude that the addition of a solid reactant or product to an equilibrium does not shift the equilibrium.

c) Increasing the temperature

The reaction is endothermic ($\Delta H > 0$), so heat enters the reaction and is, therefore, considered to be a reactant. Increasing the temperature is equivalent to adding heat (a reactant), which means that the reaction occurs so as to shift away from the added heat. Consequently, the solid dissolves, and the concentrations of Ag¹⁺ and Cl¹⁻ increase, which means that the equilibrium constant increases as expected for an endothermic reaction.

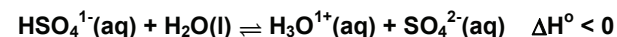
d) Adding water

Adding water to an aqueous reaction is analogous to a volume increase for gaseous reactions and shifts the equilibrium toward the side with the greater number of ions. The water decreases the concentrations of the ions, and the equilibrium shifts so as to counteract the decrease. In this example, that means that the reaction proceeds to the right, which increases the concentrations of the ions. Alternatively, diluting the concentrations of the ions reduces Q , so $Q < K$ and the reaction proceeds to the right.

Examples 5.7 and 5.8 demonstrate what is called the ‘common ion effect’ that will be discussed in Chapters 7 and 8. The common ion effect simply states that if an ion that participates in an equilibrium is added to the solution, the equilibrium is shifted away from the common ion. However, this effect is a direct consequence of the considerations of Chapter 4 and Le Châtelier’s principle.

PRACTICE EXAMPLE 5.4

Apply Le Châtelier’s principle to the following reaction and predict the effect (increase, decrease, unchanged) that each of the changes has on the hydrogen sulfate ion concentration and the equilibrium constant.

**a) adding Pb(NO₃)₂(aq), which causes PbSO₄ to precipitate**

effect on [HSO₄¹⁻] _____

effect on K _____

b) adding hydrochloric acid

effect on [HSO₄¹⁻] _____

effect on K _____

c) warming the solution

effect on [HSO₄¹⁻] _____

effect on K _____

5.3 USING THE EQUILIBRIUM CONSTANT

In the stoichiometry problems in Chapter 1, the amount of product produced in a reaction was determined from the amount of only one substance, the limiting reactant. However, that process assumes an extensive reaction, *i.e.*, one in which $K \gg 1$. When a reaction is not extensive, the concentration of a product in an equilibrium mixture depends upon the equilibrium constant and the concentrations of all other substances present in the equilibrium. Reactions that are not extensive are common in chemistry, and they are an important part of the next several chapters. Therefore, we devote the remainder of this chapter to the methods that will be used again and again in future chapters to solve equilibrium problems. Example 5.9 is an example of the easiest type of problem, one in which the equilibrium concentration of one species is determined from the other equilibrium concentrations and the value of K .

METHOD:

1. Solve the equilibrium expression for the unknown concentration.
2. Determine the unknown by substitution of the known quantities into the expression developed in Step 1.

Example 5.9

Use the K_a of acetic acid to determine the acetate ion concentration in a solution in which the concentration of acetic acid is 0.10 M and that of H_3O^{1+} is 1.0×10^{-5} M.



Writing the equilibrium constant expression, we obtain

$$K_a = \frac{[\text{CH}_3\text{COO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

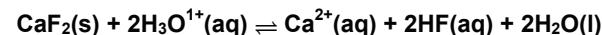
Solving for the acetate ion concentration yields

$$[\text{CH}_3\text{COO}^{1-}] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^{1+}]} = \frac{(1.8 \times 10^{-5})(0.10)}{1.0 \times 10^{-5}} = 0.18 \text{ M}$$

All other types of equilibrium problems involve the construction of a reaction table similar to the ones developed in Chapter 1. Recall that the three lines of a reaction table were labeled: *initial*, Δ , and *final*. This was an easy way to track all of the relevant quantities in a stoichiometry problem. We can use the same table when solving

PRACTICE EXAMPLE 5.5

What is the calcium ion concentration in equilibrium with $[\text{H}_3\text{O}^{1+}] = 0.10 \text{ M}$ and $[\text{HF}] = 0.20 \text{ M}$?



Equilibrium constant expression:

$$K = \quad \quad \quad = 7.5 \times 10^{-5}$$

Solve for the calcium ion concentration:

$$[\text{Ca}^{2+}] =$$

Substitute known quantities into the above to obtain the concentration

$$[\text{Ca}^{2+}] = \quad \quad \quad \text{M}$$

equilibrium problems. However, the label of the last line is changed from *final* to *eq* to emphasize that equilibrium is established, which means that none of the entries on this line can be zero.* In an equilibrium problem, the Δ line represents the amount of each substance that must form or react in order to change from *initial* to *equilibrium* conditions. If the initial system must shift to the right (\rightarrow , $Q < K$), the activities of *everything* on the right of the reaction increase ($\Delta > 0$) while those of *everything* on the left side of the reaction decrease ($\Delta < 0$). Similarly, if the shift is to the left (\leftarrow , $Q > K$), the activities of *everything* on the left side increase ($\Delta > 0$), while those of *everything* on the right side decrease ($\Delta < 0$).

An important point to remember as you do equilibrium problems is that **all of the equilibrium problems presented in this text involve one and only one unknown**. There are only three types of equilibrium problems that require a reaction table, and they differ in the location of that unknown:

1. **K is unknown:** If K is the unknown, all of the entries in the reaction table must be known.
2. **The amounts that react are unknown:** If K and the initial conditions are known, then the unknown is in the Δ line.
3. **An initial amount is unknown:** If the amount to be added or removed is asked, then the unknown is in the initial line.

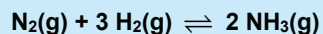
DETERMINING K FROM THE INITIAL CONDITIONS AND ONE EQUILIBRIUM CONCENTRATION

1. Enter the given concentrations and the one final concentration into the reaction table.
2. Determine the entry on the Δ line of the substance whose final concentration is given. The entry equals the initial concentration minus the equilibrium concentration.
3. Apply stoichiometry to the Δ line entry determined in Step 2 to determine the other entries in the Δ line.
4. Determine the other equilibrium concentrations by adding the initial and Δ lines.
5. Substitute the equilibrium concentrations into the equilibrium constant expression to determine K.

* Although the equilibrium concentration of the limiting reactant can be very small, it cannot be zero and satisfy a finite value for K. If the equilibrium concentration of the limiting reactant in an extensive reaction is not requested, it may be given as ~ 0 in the reaction table to indicate that very little remains at equilibrium.

Example 5.10

At some temperature, 6.0 moles of hydrogen and 4.0 moles of nitrogen are added to a 10.0-L flask and allowed to react. At equilibrium, there is 1.0 mole of hydrogen remaining. What is the value of K_c for the following reaction at this temperature?



1. Enter the given concentrations and the one final concentration into the reaction table. Concentrations are used to evaluate K_c , so the number of moles must be divided by the volume.

	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightleftharpoons	$2 \text{NH}_3(\text{g})$	
initial	0.40		0.60		0	M
Δ						
eq	0.10					M

2. Determine the entry on the Δ line of the substance whose final concentration is given. The entry equals the initial concentration minus the equilibrium concentration. The concentration of H_2 was 0.60 M initially, but it is only 0.10 M at equilibrium, so $\Delta = -0.50$ M for H_2 .

	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightleftharpoons	$2\text{NH}_3(\text{g})$	
initial	0.40		0.60		0	M
Δ			-0.50			
eq			0.10			M

3. Apply stoichiometry to the Δ line entry in Step 2 to obtain the rest of the Δ line.

$$0.50 \text{ M H}_2 \text{ react} \times \frac{1 \text{ mol N}_2 \text{ react}}{3 \text{ mol H}_2 \text{ react}} = 0.17 \text{ M N}_2 \text{ react} \Rightarrow \Delta[\text{N}_2] = -0.17 \text{ M}$$

$$0.50 \text{ M H}_2 \text{ react} \times \frac{2 \text{ mol NH}_3 \text{ form}}{3 \text{ mol H}_2 \text{ react}} = 0.33 \text{ M NH}_3 \text{ form} \Rightarrow \Delta[\text{NH}_3] = +0.33 \text{ M}$$

	$\text{N}_2(\text{g})$	+	$3 \text{H}_2(\text{g})$	\rightleftharpoons	$2\text{NH}_3(\text{g})$	
initial	0.40		0.60		0	M
Δ	-0.17		-0.50		+0.33	M
eq			0.10			M

4. Determine the other equilibrium concentrations by adding the initial and Δ lines.

	$\text{N}_2(\text{g})$	+	$3 \text{H}_2(\text{g})$	\rightleftharpoons	$2 \text{NH}_3(\text{g})$	
initial	0.40		0.60		0	M
Δ	-0.17		-0.50		+0.33	M
eq	0.23		0.10		0.33	M

5. Substitute the equilibrium concentrations into the equilibrium constant expression.*

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.33)^2}{(0.23)(0.10)^3} = 4.7 \times 10^2 \text{ M}^{-2}$$

* K_c is not equal to the thermodynamic equilibrium constant for this reaction because concentrations are not equal to activities for gases. The value of K_c determined here would have to be converted to a K_p to obtain the value used in $\Delta G^\circ = -RT \ln K$.

Example 5.11

A sealed container is filled with 0.750 atm of N_2O_4 . What is the equilibrium constant for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ if the total pressure at equilibrium is 0.946 atm?

The initial partial pressures are given, but the final total pressure is given instead of an individual partial pressure, so a reaction table must be constructed in order to determine the equilibrium partial pressures of each gas from the total pressure.[†]

	$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	$2\text{NO}_2(\text{g})$	
in	0.750		0	atm
Δ	-x		+2x	atm
eq	0.750 - x		+2x	atm

The total pressure is the sum of the equilibrium partial pressures of the two gases,

$$P_{\text{tot}} = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2} = 0.946 = (0.750 - x) + 2x = 0.750 + x$$

Solving the total pressure expression for x,

$$x = 0.946 - 0.750 = 0.196 \text{ atm}$$

The equilibrium partial pressures can then be determined from the entries on the equilibrium line and the value of x.

$$P_{\text{N}_2\text{O}_4} = 0.750 - 0.196 = 0.554 \text{ atm} \quad \text{and} \quad P_{\text{NO}_2} = 2(0.196) = 0.392 \text{ atm}$$

Using the partial pressure values for activities, we obtain the equilibrium constant

$$K = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(0.392)^2}{0.554} = 0.277$$

DETERMINING EQUILIBRIUM AMOUNTS

1. Put the initial activities in the reaction table.
2. If both reactants and products are present, calculate Q and compare it to K to determine to direction in which the reaction is proceeding. This step allows you to determine the sign of each entry on the Δ line, which should guarantee that x is positive.
3. Complete the Δ line using an unknown (we will use x). The stoichiometric relationships can be assured if the coefficient of each entry is the same as the coefficient in the balanced equation.
4. Add the initial and final lines to obtain the equilibrium line.
5. Substitute the equilibrium entries into the equilibrium constant expression and solve for x.
6. Use the value of x in the equilibrium line expression to determine the requested amount.

[†] K is the unknown in this example, but we also have unknowns in the reaction table. This may seem to violate our rule that there can be no unknowns in the reaction table if the equilibrium constant is not known. However, unlike most equilibrium problems, the unknowns in this reaction table can be determined strictly from stoichiometry without knowledge of the value of the equilibrium constant.

PRACTICE EXAMPLE 5.6

SO_3 is added to a container until the pressure is 12.5 atm and then allowed to decompose. What is the equilibrium constant for the following decomposition at the temperature of the reaction if the total pressure at equilibrium is 15.0 atm?

Construct the reaction table to establish partial pressures.



in

Δ

eq

Express the total pressure in terms of x and solve for x.

$$15.0 =$$

$$x = \text{_____ atm}$$

Equilibrium partial pressures

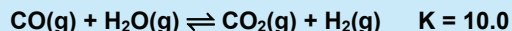
$$P_{\text{O}_2} = \text{_____ atm}; \quad P_{\text{SO}_2} = \text{_____ atm}; \quad P_{\text{SO}_3} = \text{_____ atm}$$

Equilibrium constant

$$K = \text{_____} = \text{_____}$$

Example 5.12

CO and H₂O are allowed to react as shown below. What are their equilibrium pressures if their initial pressures were each 0.200 atm?



1-4. Construct the reaction table.

	CO(g)	+	H ₂ O(g)	⇌	CO ₂ (g)	+	H ₂ (g)	
initial	0.200		0.200		0		0	atm
Δ	-x		-x		+x		+x	atm
eq	0.200 - x		0.200 - x		x		x	atm

5. Substitute the eq line entries into K and solve for x.

$$K = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} = \frac{(x)(x)}{(0.200 - x)(0.200 - x)} = \frac{x^2}{(0.200 - x)^2} = 10.0$$

The equation is a perfect square that is most easily solved by taking the square root of

$$\text{both sides: } \frac{x}{0.200 - x} = \sqrt{10.0} = 3.16$$

Multiplication of both sides by (0.200 - x) yields x = 0.632 - 3.16 x, or

$$x = \frac{0.632}{4.16} = 0.152 \text{ atm} = P_{\text{CO}_2} = P_{\text{H}_2}$$

6. Use the value of x to determine the requested pressures.

$$P_{\text{CO}} = P_{\text{H}_2\text{O}} = 0.200 - 0.152 = 0.048 \text{ atm}$$

Example 5.13

An equilibrium is 0.70 M in HI(g) and 0.10 M in each of I₂(g) and H₂(g). What are the equilibrium concentrations after the addition of 0.30 mol·L⁻¹ of H₂, 0.60 mol·L⁻¹ of I₂, and 0.20 mol·L⁻¹ HI?

We must decide a direction to write the chemical equation and then determine the value of K for the equation as written. We arbitrarily write the reaction as the decomposition of HI.

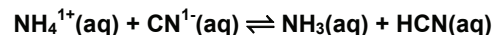
	2HI(g)	⇌	H ₂ (g)	+	I ₂ (g)	
eq	0.70		0.10		0.10	M

Δn_g = 0, so K = K_c = K_p. Thus, no subscript is required for K even when concentrations are used in its determination. K for the reaction is

$$K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.10)(0.10)}{(0.70)^2} = 0.020$$

PRACTICE EXAMPLE 5.7

10. mmol of NH₄Cl and 15 mmol of KCN are dissolved in enough water to make 200. mL of solution. What is the value of the equilibrium constant of the following reaction if [NH₄¹⁺] = 0.018 M at equilibrium?

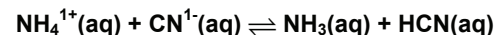


Initial concentrations:

$$[\text{NH}_4^{1+}] =$$

$$[\text{CN}^{1-}] =$$

Reaction Table



in

Δ

eq

Equilibrium constant expression

K =

Value of equilibrium constant

K = _____

1. Put the initial concentrations into the reaction table. Initial conditions are not equilibrium conditions, so add the moles of each gas to establish the initial non-equilibrium conditions. This is not the Δ line because this change is not due to the reaction.

	$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$			
eq	0.70	0.10	0.10	M
add	0.20	0.30	0.60	M
initial	0.90	0.40	0.70	M

2. Compare Q and K to determine the direction of the reaction. The reaction quotient for this initial set of conditions is

$$Q = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.40)(0.70)}{(0.90)^2} = 0.35 > K. \text{ Reaction is producing HI.}$$

- 3 & 4. Complete the Δ and equilibrium lines. From Step 2, we know that the reaction proceeds to the left, so we know the signs of the entries on the Δ line. Adding the initial and Δ lines produces the equilibrium line.

	$2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$			
initial	0.90	0.40	0.70	M
Δ	+2x	-x	-x	M
eq	0.90 + 2x	0.40 - x	0.70 - x	M

5. Substitute the equilibrium entries into K and solve for x .

$$K = 0.020 = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.40 - x)(0.70 - x)}{(0.90 + 2x)^2} = \frac{0.28 - 1.10x + x^2}{0.81 + 3.6x + 4x^2}$$

Multiply both sides by $(0.81 + 3.6x + 4x^2)$ to eliminate the denominator.

$$0.0162 + 0.072x + 0.080x^2 = 0.28 - 1.10x + x^2$$

Gather terms and rearrange to the form of a quadratic equation.*

$$0.92x^2 - 1.172x + 0.2738 = 0$$

Use the quadratic formula to solve for x .

$$x = \frac{-(-1.172) \pm \sqrt{(-1.172)^2 - 4(0.92)(0.2738)}}{2(0.92)} = 0.97 \text{ or } 0.31$$

The answer cannot exceed 0.40 because the equilibrium concentration of H_2 cannot be negative. Thus, $x = 0.31$ M.

6. Use the value of x to determine the requested amounts.

$$[\text{HI}] = 0.90 + 2(0.31) = 1.52 \text{ M}; [\text{I}_2] = 0.70 - 0.31 = 0.39 \text{ M}; [\text{H}_2] = 0.40 - 0.31 = 0.09 \text{ M}$$

Check your answer by substituting these concentrations into the equilibrium constant expression. The result is good to only one significant figure, but it agrees with the given K .

$$\text{Check: } K = \frac{(0.39)(0.09)}{1.52^2} = 0.02 \quad \checkmark$$

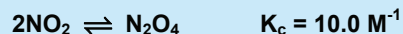
* **Quadratic equations** are solved by rearranging them so they have the following form: $ax^2 + bx + c = 0$. The two solutions are then given by the following expression:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In chemical problems, only one of the roots is usually valid as the other produces a value of x that is too large or negative.

Example 5.14

What are the new equilibrium concentrations after the volume of an equilibrium in which $[\text{NO}_2] = 0.200 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.400 \text{ M}$ is doubled?



- 1-4) Doubling the volumes halves the concentrations, so the initial concentrations are $[\text{NO}_2] = 0.100 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.200 \text{ M}$, so

$$Q_c = \frac{0.200}{0.100^2} = 20.0 \text{ M}^{-1} > K_c, \text{ so the reaction proceeds } 2\text{NO}_2 \leftarrow \text{N}_2\text{O}_4$$

and the reaction table is

	2NO_2	\rightleftharpoons	N_2O_4
in	0.100		0.200
Δ	+2x		-x
eq	$0.100 + 2x$		$0.200 - x$

- 5) Solve the equilibrium constant expression for x.

$$\text{setup expression for } K: \quad K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{0.200 - x}{(0.100 + 2x)^2} = 10.0$$

$$\text{rearrange to a quadratic equation: } 40x^2 + 5x - 0.100 = 0$$

$$\text{solve the quadratic: } x = \frac{-5 + \sqrt{5^2 - 4(40)(-0.100)}}{2(40)} = 0.0175 \text{ M}$$

- 6) Determine requested concentrations.

$$[\text{NO}_2] = 0.100 + 2(0.0175) = 0.135 \text{ M} \text{ and } [\text{N}_2\text{O}_4] = 0.200 - 0.0175 = 0.182 \text{ M}$$

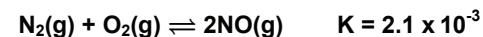
$$\text{Check: } K = \frac{0.1825}{0.135^2} = 10.0 \quad \checkmark$$

DETERMINING HOW MUCH TO ADD TO OBTAIN A GIVEN EQUILIBRIUM CONCENTRATION:

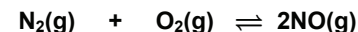
- Put the given information into the reaction table. The unknown goes into the initial line.
- Determine the entry on the Δ line for the substance whose final concentration is given.
- Use stoichiometry and the result of Step 2 to complete the Δ line.
- Add the initial and Δ lines to obtain the equilibrium line.
- Substitute the equilibrium line entries into the equilibrium constant expression and solve for the unknown.

PRACTICE EXAMPLE 5.8

0.80 mol N_2 and 0.80 mol O_2 are mixed and allowed to react in a 10-L vessel at 2500°C . How many moles of NO would be present at equilibrium?



Reaction Table (let x = change in O_2 concentration)



in

Δ

eq

Equilibrium constant expression in terms of x

$$2.1 \times 10^{-3} =$$

Square root of the above:

Solve for x:

$$x = \text{_____ M}$$

Moles of NO:

$$[\text{NO}] = \text{_____ M}$$

$$\text{moles of NO} = \text{_____ mol}$$

Example 5.15

How many moles of H_2 would have to be added to 1.00 mol I_2 in a 1.00-L flask to produce 1.80 mol HI at equilibrium? $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ $K = 49.0$

$n_g = 0$, so $K = K_p = K_c$. Thus, we can use concentrations with the given K .

- 1/2. Put the given information into the reaction table with x in the initial line and then determine the entry on the Δ line for the known substance.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$	
Initial	x		1.00		0	$\text{mol}\cdot\text{L}^{-1}$
Δ					+1.80	$\text{mol}\cdot\text{L}^{-1}$
Eq					1.80	$\text{mol}\cdot\text{L}^{-1}$

- 3/4. Use stoichiometry and the Δ line entry above to complete the Δ line then add the initial and Δ lines to obtain the equilibrium line.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$	
Initial	x		1.00		0	$\text{mol}\cdot\text{L}^{-1}$
Δ	-0.90		-0.90		+1.80	$\text{mol}\cdot\text{L}^{-1}$
Eq	$x-0.90$		0.10		1.80	$\text{mol}\cdot\text{L}^{-1}$

5. Setup the equilibrium constant expression and solve for x .

$$\text{Equilibrium constant expression: } 49.0 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1.80^2}{(x-0.90)(0.10)}$$

$$\text{Solve for } x: x = 0.90 + \frac{1.80^2}{(49.0)(0.10)} = 0.90 + 0.66 = 1.56 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2$$

Simple stoichiometry predicts that only 0.90 mol H_2 are required to react with 0.90 mol I_2 ; but, because the equilibrium constant is not very large, an excess of H_2 is required to drive the reaction to just 90% completion.

Example 5.16

What are the equilibrium concentrations in a solution made by mixing 100. mL each of 0.100 M KF and 0.100 M HNO_2 ? The chemical equation and its K are given below.

Mixing two solutions of equal volume results in a 1:2 dilution because the volume of solution is doubled from 100 to 200 mL. Set up the reaction table.

	$\text{F}^{1-}(\text{aq})$	+	$\text{HNO}_2(\text{aq})$	\rightleftharpoons	$\text{HF}(\text{aq})$	+	$\text{NO}_2^{1-}(\text{aq})$	$K = 0.56$
initial	0.0500		0.0500		0		0	M
Δ	-x		-x		+x		+x	M
eq	$0.0500 - x$		$0.0500 - x$		x		x	M

Solve the equilibrium expression for x .

PRACTICE EXAMPLE 5.9

What are the concentrations of ClF_3 and ClF in an equilibrium mixture produced by the decomposition of 1.84 M ClF_3 at a temperature where $K_c = 2.76$ M for the decomposition?

Construct the reaction table to establish partial pressures



in

Δ

eq

Equilibrium constant expression in terms of x :

$$K = 2.76 =$$

Eliminate the denominator:

Write the equation in the form of a quadratic equation:

Solve for x

$$[\text{ClF}_3] = \underline{\hspace{2cm}} \text{ M}$$

$$[\text{ClF}] = [\text{F}_2] = \underline{\hspace{2cm}} \text{ M}$$

$$K = 0.56 = \frac{[\text{HF}][\text{NO}_2^{1-}]}{[\text{F}^{1-}][\text{HNO}_2]} = \frac{(x)(x)}{(0.050 - x)(0.050 - x)} = \frac{x^2}{(0.050 - x)^2}$$

The numerator and denominator are perfect squares, so the algebra can be simplified by taking the square root of both sides to eliminate squared terms,

$$\sqrt{0.56} = 0.75 = \frac{x}{0.050 - x}$$

Multiply both sides of the equation by 0.050-x to obtain 0.037-0.75 x = x, and solve.

$$x = \frac{0.037}{1.75} = 0.021 \text{ M}$$

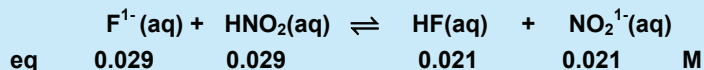
The equilibrium concentrations are:

$$[\text{F}^{1-}] = [\text{HNO}_2] = 0.050 - x = 0.050 - 0.021 = 0.029 \text{ M} \quad [\text{HF}] = [\text{NO}_2^{1-}] = x = 0.021 \text{ M.}$$

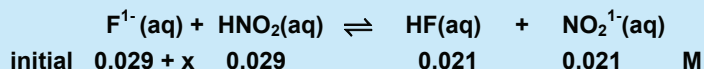
Example 5.17

How many moles per liter of fluoride ion should be added to the equilibrium solution discussed in Example 5.16 to increase the HF concentration to 0.040 M?

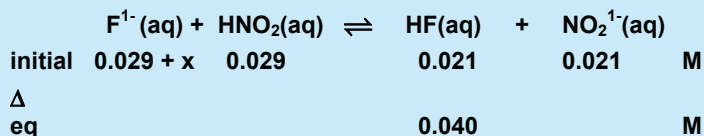
First, recognize that we are asked for the amount to be added, so the unknown is in the initial line. We start with the equilibrium concentrations from Example 5.16.



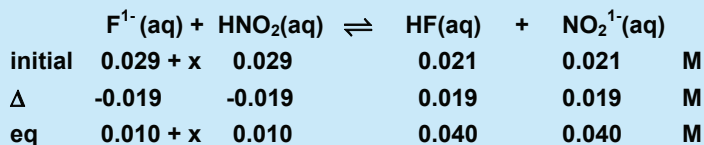
Add the unknown amount of fluoride ion to convert the equilibrium line to an initial line.



Enter the given equilibrium concentration.

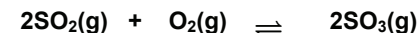


The concentration of HF increases by 0.019 M. The other Δ -line entries are then determined by applying stoichiometry to this entry. The equilibrium line is found by summing the initial and Δ lines.



PRACTICE EXAMPLE 5.10

The following equilibrium mixture was found in a 1.00-L flask at some temperature.



eq 0.0500 0.0250 0.0180 mol

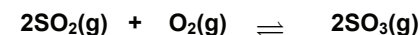
How many moles of O_2 must be added to double the number of moles of SO_3 at equilibrium?

Evaluate the equilibrium constant (K_c).

$K =$

On which line of the reaction table is the unknown?

Reaction Table



in

Δ

eq

Solve the equilibrium constant expression for the number of moles added.

The unknown is determined by evaluation of the equilibrium constant expression with these equilibrium concentrations.

$$K = 0.56 = \frac{[\text{HF}][\text{NO}_2^{1-}]}{[\text{F}^{1-}][\text{HNO}_2]} = \frac{(0.040)(0.040)}{(0.010 + x)(0.010)} = \frac{0.0016}{(0.010 + x)(0.010)} = \frac{0.16}{0.010 + x}$$

$$0.010 + x = \frac{0.16}{0.56} = 0.29 \Rightarrow x = 0.29 - 0.01 = 0.28 \text{ M}$$

The molarity of the fluoride ion must be increased by $0.28 \text{ mol}\cdot\text{L}^{-1}$, which is over 1.5 times the amount that reacts ($0.19 \text{ mol}\cdot\text{L}^{-1}$). In other words, *only about 68% of the added fluoride ion reacts!*

Hopefully, you have noticed that equilibrium problems are done in the same way whether they deal with gas-phase or aqueous equilibria. These same methods are applied in Chapters 6 - 8 in dealing with acid-base and metal ion equilibria. In this chapter, the equilibrium constants are neither very large nor very small; but, in the following chapters, the equilibrium constants are typically very small. The difference in magnitude allows us to make approximations to simplify the algebra, but it does not affect the way the problem is done.

5.4 CHAPTER SUMMARY AND OBJECTIVES

The activity of gases in equilibrium constants derived from standard free energies of formation are numerically equal to the pressures expressed in atmospheres. However, we can define the equilibrium constant in terms of concentrations, as well. The two values are designated as K_p (activities are in pressures) and K_c (activities are in concentrations), and they are related by the expression

$$K_p = K_c(RT)^{\Delta n_g}$$

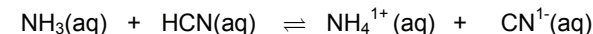
The equilibrium constant for a reaction depends upon how the reaction is expressed. If a reaction is multiplied by a number n , then the resulting equilibrium constant is the original K raised to the n^{th} power. If the reaction is written in the reverse direction, the equilibrium constant is the reciprocal of the original. Finally, the equilibrium constant of a reaction that is the sum of two other reactions is the product of the equilibrium constants of the summed reactions.

Le Châtelier's principle states that when a stress is placed on a reaction at equilibrium, the reaction proceeds so as to minimize the effects of the stress. The shift can be

PRACTICE EXAMPLE 5.11

How many moles/liter of HCN should be added to 0.100 M NH_3 to prepare a solution in which $[\text{NH}_4^{1+}] = 0.065 \text{ M}$?

Reaction table ($K = 0.71$)



initial

Δ

eq

Equilibrium constant expression in terms of x .

$0.71 =$

Solve the equilibrium constant expression for the number of moles/liter added.

$x =$ _____ mol/L HCN

understood in terms of changing the reaction quotient and the effect that change has on the free energy of the system. The addition of a solid that is involved in the equilibrium does not result in any change because the solid is not included in the reaction quotient.

Three types of equilibrium problems involving reaction tables were discussed:

- i. Determining K from the initial concentrations and one final concentration.
- ii. Determining concentrations from K and the initial conditions.
- iii. Determining how much of one substance must be added or removed to produce a desired equilibrium concentration.

After studying the material presented in this chapter, you should be able to:

1. convert between K_p and K_c (Section 5.1);
2. determine the value of K for a reaction given the value of K for a related reaction that differs only by a multiple and/or direction (Section 5.1);
3. determine the equilibrium constant of a reaction that is the sum of several other reactions (Section 5.1);
4. relate Le Châtelier's principle to the relationship between Q and K (Section 5.2);
5. predict the direction of the shift in equilibrium caused by stress placed on the equilibrium (Section 5.2);
6. calculate the concentrations of one substance in an equilibrium mixture from the other concentrations and the equilibrium constant (Example 5.8);
7. determine the equilibrium constant for a reaction given the initial amounts and one equilibrium amount (Examples 5.9 and 5.10);
8. determine the equilibrium composition from the initial composition and the equilibrium constant (Example 5.11);
9. calculate the amount of one reactant required to react with a given amount of another reactant to produce a given amount of product (Example 5.12);
10. determine the extent of the change caused by the addition of known amounts of reactants or products to an equilibrium mixture, given K and the initial equilibrium concentrations (Example 5.13);
11. calculate the concentrations resulting from a volume change (Example 5.14); and
12. calculate the amount of one substance that would have to be added to an equilibrium mixture to change the concentration of another substance in the equilibrium by a given amount (Example 5.16).

ANSWERS TO PRACTICE EXAMPLES

- 5.1 $\Delta G^\circ = +3.79 \text{ kJ}$; $K = 0.272$; $K_p = 0.272 \text{ atm}^{-1}$; $K_c = 7.81 \text{ M}^{-1}$
- 5.2 $\Delta G^\circ = -1.89 \text{ kJ}$; $K = 1.92$; $K = 1.92$
- 5.3 $K = 7.5 \times 10^{-5}$
- 5.4 a) $[\text{HSO}_4^{1-}]$ decreases; K unchanged
b) $[\text{HSO}_4^{1-}]$ increases; K unchanged
c) $[\text{HSO}_4^{1-}]$ increases; K decreases
- 5.5 $[\text{Ca}^{2+}] = 1.9 \times 10^{-5} \text{ M}$
- 5.6 $P_{\text{O}_2} = 2.5 \text{ atm}$; $P_{\text{SO}_2} = 5.0 \text{ atm}$; $P_{\text{SO}_3} = 7.5 \text{ atm}$; $K = 1.1$
- 5.7 $K = 1.3$
- 5.8 0.036 mol NO
- 5.9 $x^2 + 2.76x - 5.08 = 0$; $x = 1.26 \text{ M}$
 $[\text{ClF}_3] = 0.58 \text{ M}$; $[\text{ClF}] = [\text{F}_2] = 1.26 \text{ M}$
- 5.10 0.228 mol O_2
- 5.11 $0.24 \text{ mol} \cdot \text{L}^{-1} \text{ HCN}$

5.5 EXERCISES

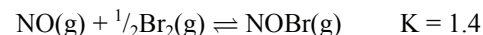
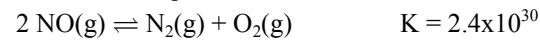
K_p VERSUS K_c

- What are the units of K_p and K_c for each of the following?
 - $2\text{H}_2\text{S}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{S}_2(\text{g})$
 - $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- What are the units of K_p and K_c for each of the following?
 - $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$
 - $\text{P}_4(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons \text{P}_4\text{O}_{10}(\text{s})$
- Determine K_c values for the following at 298 K:
 - $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ K_p = 0.15 atm
 - $\text{NO}_2(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}_3(\text{g})$ K_p = 0.86 atm⁻¹
- Determine the value of K_c for each of the following:
 - $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ K_p = 2.9 × 10⁻² atm at 30 °C
 - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ K_p = 1.48 × 10⁴ atm⁻¹ at 184 °C
- Determine the value of K_p for each of the following:
 - $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ K_c = 23.2 at 600 K
 - $2\text{H}_2\text{S}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{S}_2(\text{g})$ K_c = 2.3 × 10⁻⁴ M at 1405 K

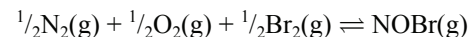
PROPERTIES OF THE EQUILIBRIUM CONSTANT

- If equal number of moles of reactants are used, do the following equilibrium mixtures contain primarily reactants or products?
 - $\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CN}^{1-}(\text{aq}) + \text{H}_3\text{O}^{1+}(\text{aq})$ K = 6.2 × 10⁻¹⁰
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ K = 2.51 × 10⁴
- Determine K for: $\text{HI}(\text{g}) \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{I}_2(\text{s})$, given
 $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2\text{HI}(\text{g})$ K = 8.6
 - Determine K_c for: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$, given
 $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$ K_c = 3.61 M^{-1/2}
- Use the K_p values in Exercise 3 to determine K_p values of the following.
 - $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
 - $\text{NO}_2(\text{g}) \rightleftharpoons \frac{1}{2}\text{N}_2\text{O}_4(\text{g})$
 - $2\text{NO}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{N}_2\text{O}_3(\text{g})$
 - $\text{N}_2\text{O}_4(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{N}_2\text{O}_3(\text{g})$

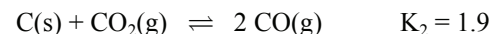
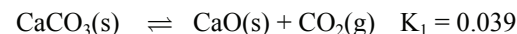
- Given the following:



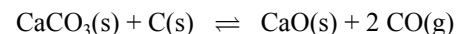
Determine K for



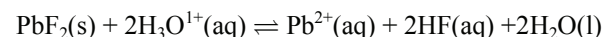
- Given the following information at 1000 K:



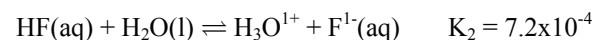
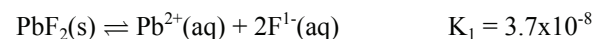
Determine the equilibrium constant at 1000 K for:



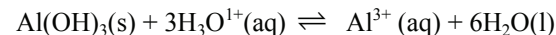
- Lead fluoride dissolves in strong acid by the following reaction:



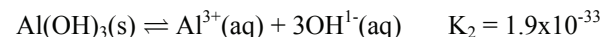
- What is the equilibrium constant *expression* for the reaction?
- Use the following equilibrium constants to determine the value of the equilibrium constant of the above reaction:



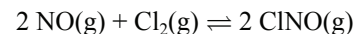
- Aluminum hydroxide dissolves in strong acid by the following reaction:



- What is the equilibrium constant *expression* for the reaction?
- Use the following equilibrium constants to calculate the value of K for the above reaction



- Equal numbers of moles of Cl₂ and NO are placed in a vessel at some temperature where they reach the following equilibrium:



Indicate whether each of the following statements about the resulting equilibrium mixture is true, false, or depends upon the value of the equilibrium constant.

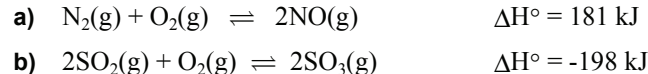
- [NO] > [ClNO] b) [Cl₂] < [NO] c) [Cl₂] > [ClNO]

14. Equal number of moles of NH_3 and N_2 are added to a flask where they equilibrate according to: $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$. Indicate whether each of the following statements about the resulting equilibrium mixture is true, false, or depends upon the value of the equilibrium constant.
- a) $[\text{NH}_3] < [\text{H}_2]$ b) $[\text{H}_2] > [\text{N}_2]$ c) $[\text{NH}_3] > [\text{N}_2]$

LE CHÂTELIER'S PRINCIPLE

15. What effect (increase, decrease, or no effect) does increasing the volume of the following equilibrium mixtures at constant temperature have on Q ? What effect does each have on K ?
- a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $\Delta H^\circ = +53 \text{ kJ}$
b) $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $\Delta H^\circ = -92 \text{ kJ}$
c) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ $\Delta H^\circ = +58 \text{ kJ}$
16. What effect does increasing the temperature at constant volume of each of the equilibrium mixtures in Exercise 15 have on Q and K ?
17. Does increasing the volume of each of the equilibria in Exercise 15 increase the number of moles of reactant, product, or neither?
18. Does increasing the temperature of each of the equilibria in Exercise 15 increase the number of moles of reactant or product?
19. Consider the equilibrium, $\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{NH}_4\text{HS}(\text{s})$, $\Delta H^\circ < 0$. Which of the following would *increase* the number of moles of ammonia in the equilibrium mixture?
- a) increasing the temperature
b) increasing the volume of the container
c) adding more H_2S gas
d) adding more NH_4HS solid
20. Methanol is manufactured by the following reaction:
- $$\text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \quad \Delta H^\circ = -91 \text{ kJ}$$
- Does the amount of methanol increase, decrease, or remain the same when an equilibrium mixture is subjected to the following changes?
- a) the temperature is increased
b) the volume of the container is decreased
c) CO is added
d) CH_3OH is added
21. Consider the following: $\text{P}_4(\text{s}) + 6\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{PCl}_3(\text{l})$ $\Delta H < 0$
- What happens to the mass of phosphorus in each of the following?
- a) the volume is increased b) chlorine is removed
c) phosphorus trichloride is added d) the mixture is cooled

22. Predict how an increase in temperature will change K for the following chemical reactions:



SOLVING FOR AN UNKNOWN EQUILIBRIUM CONCENTRATION

23. What is the concentration of ammonia in an equilibrium mixture that is 0.015 M in H_2 and 0.250 M in N_2 ?
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad K_c = 473 \text{ M}^{-2}$$
24. What is the equilibrium concentration of hydronium ion in a solution that 0.0867 M HF and 0.108 M F^{1-} ?
- $$\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^{1+}(\text{aq}) + \text{F}^{1-}(\text{aq}) \quad K_c = 7.2 \times 10^{-4} \text{ M}$$
25. What is the partial pressure of H_2 if the equilibrium partial pressures of I_2 and HI are 485 torr and 1293 torr, respectively?
- $$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \quad K = 12.0$$
26. What is the equilibrium concentration of Pb^{2+} in a solution of PbCl_2 that is 0.11 M in chloride ion?
- $$\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^{1-}(\text{aq}) \quad K_c = 1.7 \times 10^{-5} \text{ M}^3$$

DETERMINING THE VALUE OF K

27. A mixture that contains 1.00 mol of NH_3 and 0.400 mol of N_2 in a 5.00-L container is left to equilibrate. At equilibrium, it contains only 0.780 mol of NH_3 . The reaction is $2\text{NH}_3(\text{g}) \rightleftharpoons 3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$
- a) What are the equilibrium concentrations of the gases?
b) What is the value of K_c for the reaction shown above?
28. At a particular temperature, a 3.0-L flask contains 3.0 mol HI , 4.0 mol H_2 and 0.25 mol I_2 at equilibrium. Calculate K at this temperature for the reaction: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
29. Phosgene, a toxic gas used in the synthesis of many organic compounds, decomposes according to the reaction: $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$
- Phosgene is heated in a flask. At a certain temperature, the equilibrium mixture is found to contain 0.050 M CO , 0.050 M Cl_2 , and 0.50 M COCl_2 . What is the value of K_c at this temperature?
30. A sealed container is filled with 5.00 atm of NH_3 . What is the equilibrium constant for the following reaction at the temperature of the experiment if the total pressure of all gases is 8.54 atm at equilibrium?
- $$2\text{NH}_3(\text{g}) \rightleftharpoons 3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$$

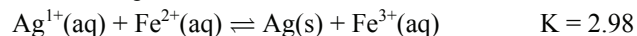
31. A sealed container is filled with 1.40 atm of PCl_5 and heated until the PCl_5 decomposes. What is the equilibrium constant for the following reaction at the temperature of the experiment if the total pressure inside the container is 2.60 atm at equilibrium? $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
32. 8.0 mol NH_3 are placed in a 10.0-L container at some temperature and allowed to equilibrate. At equilibrium, 2.0 moles remained. What is the value of K_c for the following reaction at the temperature of the experiment?
- $$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$$
33. At some temperature, 0.400 mol NO , 0.300 mol Cl_2 and 0.700 mol ClNO are introduced into a 20.0-L flask and allowed to react. What is the value of K_c for the following reaction at this temperature if the equilibrium mixture contained 0.900 mol ClNO ? $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{ClNO}(\text{g})$
34. Iron(III) oxalate decomposes as follows:
- $$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) + 3\text{CO}_2(\text{g})$$
- What is the value of K_p at a temperature where the total pressure of an equilibrium mixture is 0.868 atm?
35. What is the value of K_c for the reaction $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ at a temperature where 24.0 % of 0.600 mol·L⁻¹ SO_3 decomposes?
36. 4.00 mol CO_2 is placed in a 6.00-L container at a temperature where 12.3% of it decomposes. What is the value of K_c for the following at this temperature? $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$
37. At 2000. °C, water decomposes into hydrogen and oxygen. When 3.00 mol H_2O is heated in a sealed, 5.00-L container to 2000 °C, 2.00% of the water decomposes.
- What is value of K_c for $2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ at 2000 °C?
 - What is the value of K_p at this temperature?
 - What is the standard free energy of formation of $\text{H}_2\text{O}(\text{g})$ at 2000 °C?
38. Sulfuric acid has many uses, making it the most produced chemical in the world (over 150 million tons a year). One of the steps in the manufacture of sulfuric acid is $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$. A sealed flask at 627 °C is loaded with 1.48 atm of SO_2 and 0.74 atm of O_2 . After reaction, the equilibrium pressure of SO_3 is found to be 1.10 atm. What is the value of K_p for this reaction at 627 °C?

EQUILIBRIUM COMPOSITION

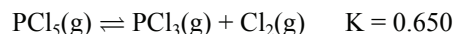
Problems identified with an asterisk require use of the quadratic formula.

39. For the reaction: $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ $K_c = 0.0160$ at 520. °C
- Calculate the concentration of all of the gases at equilibrium in a 6.00-L container with the following initial conditions:
- 0.400 mol HI
 - 0.200 mol H_2 and 0.200 mol I_2
 - 0.200 mol H_2 , 0.200 mol I_2 , and 0.400 mol HI
 - * 0.200 mol H_2 and 0.300 mol I_2
 - * 0.100 mol H_2 , 0.200 mol I_2 , and 0.300 mol HI
40. At a certain temperature, $K = 1.0 \times 10^2$ for the reaction:
- $$\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g})$$
- Calculate the equilibrium concentrations (or pressures) of all species in the equilibrium mixtures produced by mixing the following amounts of gas:
- 3.0 mol H_2 + 3.0 mol F_2 in a 2.0-L container
 - * 0.20 M H_2 + 0.35 M F_2
 - * 0.80 atm H_2 + 0.60 atm F_2 + 1.00 atm HF
41. An equilibrium mixture is found to contain 1.200 mol each CO_2 and H_2 and 0.155 mol each CO and H_2O . Assume that all substances are gases.
- What is the equilibrium constant for $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$?
 - What is the value of the reaction quotient immediately after the addition of 0.800 mol of each gas to this equilibrium mixture? How many moles of each gas are present when equilibrium is reestablished?
42. What is the equilibrium concentration of CN^{1-} ion after mixing the following solutions? Hint: Mixing the solutions dilutes the reactants.
- mixing 50.0 mL of 0.100 M HCN with 50.0 mL of 0.100 M NH_3 ?
 $\text{NH}_3(\text{aq}) + \text{HCN}(\text{aq}) \rightleftharpoons \text{NH}_4^{1+}(\text{aq}) + \text{CN}^{1-}(\text{aq})$ $K = 0.71$
 - mixing 50.0 mL of 0.100 M HCN with 50.0 mL of 0.100 M K_2S ?
 $\text{S}^{2-}(\text{aq}) + \text{HCN}(\text{aq}) \rightleftharpoons \text{HS}^{1-} + \text{CN}^{1-}(\text{aq})$ $K = 3.1 \times 10^3$
 - mixing 50.0 mL of 0.100 M HCN with 50.0 mL of 0.100 M KF ?
 $\text{F}^{1-}(\text{aq}) + \text{HCN}(\text{aq}) \rightleftharpoons \text{HF} + \text{CN}^{1-}(\text{aq})$ $K = 5.6 \times 10^{-7}$
43. What is the equilibrium concentration of F^{1-} ion after mixing the following solutions? Hint: Mixing the solutions dilutes the reactants.
- mixing 75.0 mL of 0.100 M HF with 75.0 mL of 0.100 M NH_3 ?
 $\text{NH}_3(\text{aq}) + \text{HF}(\text{aq}) \rightleftharpoons \text{NH}_4^{1+}(\text{aq}) + \text{F}^{1-}(\text{aq})$ $K = 1.3 \times 10^7$
 - mixing 75.0 mL of 0.100 M HF with 75.0 mL of 0.100 M KNO_2 ?
 $\text{NO}_2^{1-}(\text{aq}) + \text{HF}(\text{aq}) \rightleftharpoons \text{HNO}_2 + \text{F}^{1-}(\text{aq})$ $K = 1.8$
 - mixing 75.0 mL of 0.100 M HF with 75.0 mL of 0.100 M K_2SO_4 ?
 $\text{SO}_4^{2-}(\text{aq}) + \text{HF}(\text{aq}) \rightleftharpoons \text{HSO}_4^{1-} + \text{F}^{1-}(\text{aq})$ $K = 0.060$

- 44.* An aqueous solution is made 1.00 M in AgNO_3 and 1.00 M in $\text{Fe}(\text{NO}_3)_2$ and allowed to come to equilibrium. What are the concentrations of the ions present when equilibrium is established?



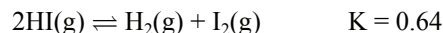
- 45.* Consider the following equilibrium at a temperature near 500 K:



How many moles of PCl_3 would be in the equilibrium mixture produced by

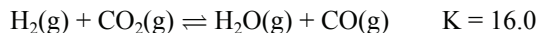
- placing 3.36 mol PCl_5 into an empty 4.82-L flask?
- placing 2.68 mol PCl_3 and 3.65 mol Cl_2 into an empty 6.15-L flask?

Use the following equilibrium for Exercises 46 - 49



- What are the partial pressures of the gases in an equilibrium mixture produced by the decomposition of HI with an initial pressure of 2.86 atm?
- What is the concentration of H_2 in an equilibrium mixture formed by the decomposition of 0.100 M HI?
- 0.40 mol of H_2 and 0.40 mol of I_2 are placed in 1.0-L container and allowed to react. How many moles of HI are in the equilibrium mixture?
- * How many moles of I_2 are in the equilibrium mixture produced by 0.20 mol H_2 and 0.40 mol HI in a 2.0-L flask?

Use the following equilibrium for Exercises 50 - 53



- The initial partial pressures of H_2 and CO_2 in a reaction flask are each 1.64 atm. What is the equilibrium pressure of CO? What is the total pressure at equilibrium?
- If a reaction mixture is 0.200 M H_2 , 0.200 M CO_2 , 0.400 M CO and 0.400 M H_2O , what will the equilibrium concentrations be?
- How many moles of CO_2 would be present at equilibrium after 0.200 mol H_2O and 0.200 mol CO equilibrate in a 1.00-L container?
- * What are the equilibrium concentrations resulting from the equilibration of 0.300 M H_2 , 0.500 M CO_2 , 0.100 M CO and 0.600 M H_2O ?

HOW MUCH TO ADD OR REMOVE

- An equilibrium mixture is 0.088 M NH_3 , 0.088 M H_2 , and 0.160 M N_2 . How many $\text{mol}\cdot\text{L}^{-1}$ of N_2 must be removed to increase the equilibrium concentration of H_2 to 0.130 M?

- An equilibrium mixture contains 0.800 mol HI, 0.200 mol I_2 , and 0.200 mol H_2 in a 1.00-L container. How many moles of I_2 must be removed in order to double the number of moles of H_2 at equilibrium?
- How many $\text{mol}\cdot\text{L}^{-1}$ of CO must be withdrawn from the equilibrium described in Exercise 29 to triple the equilibrium concentration of chlorine?
- An equilibrium mixture is 0.117 M NOBr, 0.364 M NO, and 0.205 M Br_2 .
 - What is the value of K_c for the reaction $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$?
 - How many moles per liter of NOBr must be added to the equilibrium mixture to produce an equilibrium mixture that is 0.360 M in Br_2 ?
 - The equilibrium temperature is 373 K. What is K_p ?
 - What is ΔG° at 373 K?
- How many moles of H_2 must be added to 0.656 moles of CO_2 in a 6.49-L flask in order to reduce 96.0 % of the CO_2 to CO at a temperature where $K = 4.0$ for the following: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$?

MISCELLANEOUS

- At 25 °C, the solubility of I_2 is $3.0 \times 10^{-4} \text{ g}\cdot\text{mL}^{-1}$ in water and $2.9 \times 10^{-2} \text{ g}\cdot\text{mL}^{-1}$ in CCl_4 . Iodine is readily extracted from water with CCl_4 . The amount of I_2 remaining in each solvent after an extraction is dictated by the equilibrium constant for the extraction process: $\text{I}_2(\text{H}_2\text{O}) \rightleftharpoons \text{I}_2(\text{CCl}_4)$.
 - Use the solubility of I_2 in each solvent to determine the equilibrium constant for the extraction at 25 °C.
 - What mass of I_2 remains in the water when 200. mL of an aqueous solution containing 55.0 mg of I_2 is extracted with 20. mL of CCl_4 ?
 - What mass of I_2 remains in the water after two extractions of 200. mL of an aqueous solution containing 55.0 mg of I_2 with 10. mL of CCl_4 ?
 - What volume of CCl_4 would have to be used to extract 50.0 mg of the I_2 from the original aqueous solution (Part c) in one extraction?
- Consider the following equilibrium: $\text{CS}_2(\text{g}) \rightleftharpoons \text{S}_2(\text{g}) + \text{C}(\text{s}) \quad K = 0.40$
 - How many grams of carbon form in the decomposition of 3.0 mol of CS_2 in a 6.0-L container?
 - What mass of carbon would be present at equilibrium if 0.50 mol $\text{S}_2(\text{g})$ is removed from the equilibrium in Part a?
 - What are the partial pressures of the two gases in an equilibrium mixture with a total pressure of 1.8 atm?

61. Consider the following equilibrium at 400 K:



- A mixture contains 1.80 mol BrCl, 0.60 mol of Br₂, and 1.40 mol Cl₂ in a 4.26-L container. How many moles of Cl₂ must be removed to obtain an equilibrium mixture that contains 1.00 mol Br₂?
- How many moles of chlorine should be added to 0.424 moles of bromine at 400 K to produce 0.500 mol of BrCl at equilibrium?
- What are the partial pressures of the gases in an equilibrium mixture formed from the decomposition of BrCl if the initial pressure of BrCl was 1.84 atm?

62. Consider the following equilibrium at 250 °C:



- What is the value of K_c at 250 °C?
- What would be the total pressure at equilibrium if excess NH₄HS is placed in the container at 250 °C?
- What minimum mass of NH₄HS is required to achieve equilibrium in a 12.0-L container at 250 °C?
- 30.0 g of NH₄HS are placed in a container at 250 °C. To what minimum volume would the container have to be adjusted to make all of the solid disappear?

63. PCl₅ is added to a container at some temperature to a total pressure of 1.000 atm where it decompose by the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. At equilibrium, the total pressure in the container is 1.544 atm. What is the value of the equilibrium constant for the decomposition at this temperature?

64. An equilibrium mixture contains 0.220 mol PCl₅(g) and 0.120 mol each of PCl₃(g) and Cl₂(g) in a 2.00-L flask. How many moles of each gas would be present in an equilibrium mixture if the volume of the container were changed to 6.00 L? ... to 0.200 L?

65. The following equilibrium pressures were measured in a 5.00 L container at 350 K: P_{N₂O₄} = 0.226 atm and P_{NO₂} = 0.914 atm. What would the equilibrium pressures be if the volume were increased to 20.0 L? ... decreased to 1.00 L?

66. Consider the equilibrium described in Exercise 65. What would the partial pressures of the gases be in the equilibrium mixture if the 5.00-L container were heated to 400 K? Assume that ΔH° and ΔS° are independent of temperature.

CHAPTER 6

Acids and Bases

6.0	Introduction
6.1	Autoionization of Water
6.2	The <i>p</i> -Scale
6.3	Strong Acids
6.4	Weak Acids
6.5	Polyprotic Acids

6.6	Strong Bases
6.7	Weak Bases
6.8	Salts of Weak Acids and Bases
6.9	Amphiprotic Salts
6.10	Chapter Summary and Objectives
6.11	Exercises

6.0 INTRODUCTION

A Lewis base is a substance that contains a lone pair that can be used in a coordinate covalent bond,* and a Lewis acid is a substance that has an empty orbital that can be used to share the lone pair in the bond. A Lewis acid-base reaction is the formation of the bond between the acid and the base. The Lewis acid-base reaction between ammonia and acetic acid is represented in Figure 6.1a. In it, the lone pair on ammonia is used to form a covalent bond to a hydrogen atom on the acetic acid. Ammonia contains the lone pair, so it is the base, and acetic acid accepts the lone pair, so it is the acid. This very broad classification allows us to treat many reactions as acid-base reactions. However, the reaction in Figure 6.1 can also be viewed as a proton transfer from the acid to the base. Although proton transfer reactions can be viewed as Lewis acid-base reactions, a different acid-base theory was developed for this very important branch of chemistry.†

In Brønsted-Lowry or simply Brønsted theory, an acid is a proton donor and a base is a proton acceptor. Acetic acid has a proton that it can transfer, so it is an acid, while ammonia can accept a proton, so it is a base. The loss of a proton converts the acid into its **conjugate base**, and the gain of the proton converts the base into its **conjugate acid** (Figure 6.1b). An acid and a base differ by one proton only and are said to be a **conjugate acid-base pair**. *The only reactants and products present in a Brønsted acid-base reaction are an acid, a base, and their conjugate base and acid.* In this chapter, we examine the concentrations of reactants and products in aqueous solutions of Brønsted acids and bases.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- explain how water is involved in aqueous acid-base chemistry;
- define pH and pOH and demonstrate their use;
- show how to calculate the concentrations of all species present in an equilibrium mixture of an acid and a base; and
- describe the solution of acids with more than one proton.

* Coordinate covalent bonds are covalent bonds in which both bonding electrons come from the same atom – the base in a Lewis acid-base reaction.

† Both Brønsted and Lewis theories were introduced in detail in Chapter 12 of CAMS.

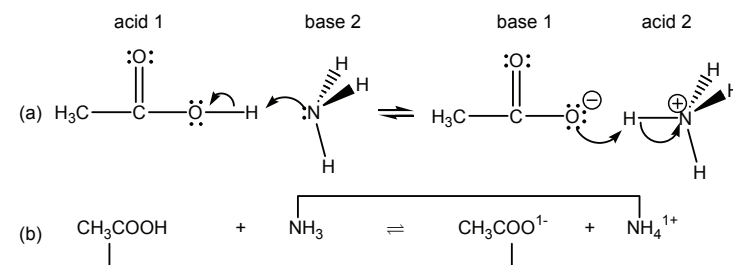
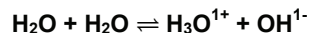


Figure 6.1 Acid-base reaction between acetic acid and ammonia

- (a) Lewis formalism in which the lone pair on N becomes an N-H bond.
- (b) Brønsted formalism in which a proton is transferred from the acid to the base. The conjugate acid-base pairs ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^{1-}$ and $\text{NH}_4^{1+}/\text{NH}_3$) are identified by brackets.

6.1 AUTOIONIZATION OF WATER

Aqueous acid-base chemistry is the focus of this chapter, and water plays an important role in that chemistry because in addition to being the solvent, water is also an acid and a base; that is, water is **amphiprotic**. In fact, the acidity or basicity of an aqueous solution is defined by the extent to which water reacts to produce its conjugate acid, H_3O^{1+} , or its conjugate base, OH^{1-} , respectively. Because it is amphiprotic, water can react with itself in a process called **autoionization**.



Rxn. 6.1*

The equilibrium constant expression for Reaction 6.1 is known as the **ion product constant of water** and given the symbol K_w . Water is the solvent and considered to be a pure liquid, so its activity is unity and the equilibrium constant is the following:

$$K_w = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

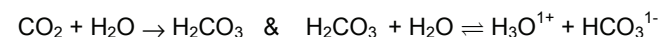
Eq. 6.1

The K_w expression must be obeyed in all aqueous solutions, but equilibrium constants are functions of temperature, so $K_w = 1.0 \times 10^{-14}$ only at 25°C . If no temperature is given, assume a temperature of 25°C and a K_w of 1.0×10^{-14}

Reaction 6.1 indicates a 1:1 stoichiometry between H_3O^{1+} and OH^{1-} , so their concentrations are equal in pure water. Solutions in which $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$ are said to be **neutral** because they are neither acidic nor basic. Pure water is neutral,[†] but when an acid is added, a proton transfer from the acid to water increases the hydronium ion concentration, which makes the solution acidic. Equation 6.1 indicates that an increase in $[\text{H}_3\text{O}^{1+}]$ must be accompanied by a decrease in $[\text{OH}^{1-}]$, so $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$ in **acidic** solutions. Similarly, adding a base to water results in a proton transfer from water to the base, which produces OH^{1-} and makes the solution basic. Consequently, $[\text{OH}^{1-}] > [\text{H}_3\text{O}^{1+}]$ in **basic** solutions. As demonstrated in Example 6.1, the hydronium and hydroxide ion concentrations can be determined from one another with K_w .

* The remainder of the text deals with aqueous chemistry, so water is always considered to be a pure liquid and ions are only present when dissolved in water. Therefore, we will drop the (l) tag for water and the (aq) tags for ions. However, other neutral species can be solid, liquid, gas, or aqueous, so the phase tag will be used with them.

† Tap water is usually slightly acidic due to dissolved CO_2 , which reacts with water to produce carbonic acid.



Boiling the water drives off the CO_2 and makes the water neutral.

Example 6.1

a) What are the hydronium and hydroxide ion concentrations in water at 25°C ?

Let $x = [\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$ and substitute into Equation 6.1 to obtain

$$[\text{H}_3\text{O}^{1+}][\text{OH}^{1-}] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

$$x = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M} \quad \text{M} = [\text{OH}^{1-}] = [\text{H}_3\text{O}^{1+}]$$

$[\text{OH}^{1-}] = [\text{H}_3\text{O}^{1+}] = 1.0 \times 10^{-7} \text{ M}$ at 25°C in a neutral aqueous solution.

- b) HCl is added to water until $[\text{H}_3\text{O}^{1+}] = 0.042 \text{ M}$. What is the concentration of the hydroxide ion in the resulting solution at 25°C ?

Solving Equation 6.1 for the hydroxide ion concentration, we obtain

$$[\text{OH}^{1-}] = \frac{K_w}{[\text{H}_3\text{O}^{1+}]} = \frac{1.0 \times 10^{-14}}{0.042} = 2.4 \times 10^{-13} \text{ M}$$

- c) What is $[\text{H}_3\text{O}^{1+}]$ in a solution that is 0.50 M in hydroxide ion at 25°C ?

Solving Equation 6.1 for the hydronium ion concentration, we obtain

$$[\text{H}_3\text{O}^{1+}] = \frac{K_w}{[\text{OH}^{1-}]} = \frac{1.0 \times 10^{-14}}{0.50} = 2.0 \times 10^{-14} \text{ M}$$

6.2 THE p-SCALE

The hydroxide and hydronium ion concentrations are important characteristics of the solution even at very low concentrations, but negative exponentials are usually avoided in discussions of these small concentrations by converting them to the p-scale. The **p-scale** is the negative base-10 logarithm of the number.

$$\text{pX} = -\log X \quad \text{Eq. 6.2}$$

Thus, $\text{pH} = -\log [\text{H}_3\text{O}^{1+}]$ and $\text{pOH} = -\log [\text{OH}^{1-}]$. Taking the antilogarithm of both sides yields Equation 6.3, which allows the value of X to be determined from its pX.

$$X = 10^{-\text{pX}} \quad \text{Eq. 6.3}$$

For example, $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}}$ and $[\text{OH}^{1-}] = 10^{-\text{pOH}}$. The digits to the left of the decimal in a value of X determined from its pX with Equation 6.3 are used for the exponent of 10, so *only those digits to the right of the decimal in a pX are significant digits*. For example, if $\text{pH} = 12.65$ then $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-12.65} = 2.2 \times 10^{-13} \text{ M}$, which is good to only two significant figures because only two of the digits of the pH are to the right of the decimal.

Example 6.2

What are the pH and pOH of the solutions discussed in Example 6.1?

- a) $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7} \text{ M}$

$$\text{pH} = \text{pOH} = -\log (1.0 \times 10^{-7}) = 7.00$$

The pH of a neutral solution is 7.00 at 25°C .

- b) $[\text{H}_3\text{O}^{1+}] = 0.042 \text{ M}$ and $[\text{OH}^{1-}] = 2.4 \times 10^{-13} \text{ M}$
 $\text{pH} = -\log(0.042) = 1.38$ and $\text{pOH} = -\log(2.4 \times 10^{-13}) = 12.62$
 $\text{pH} < 7$, $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$, and the solution is acidic.
- c) $[\text{H}_3\text{O}^{1+}] = 2.0 \times 10^{-14} \text{ M}$ and $[\text{OH}^{1-}] = 0.50$
 $\text{pH} = -\log(2.0 \times 10^{-14}) = 13.70$ and $\text{pOH} = -\log(0.50) = 0.30$
 $\text{pH} > 7$, $[\text{OH}^{1-}] > [\text{H}_3\text{O}^{1+}]$, and it is a basic solution.

As shown in Figure 6.2, an acidic solution is characterized by a pH of less than seven, while a pH greater than seven implies a basic solution. In more general terms, as the pH of a solution decreases, it becomes more acidic (less basic) and, as the pH increases, the solution becomes more basic (less acidic). Note that the pH range for most aqueous solutions is 0 to 14, but pH values greater than 14 and less than 0 result when $[\text{H}_3\text{O}^{1+}]$ or $[\text{OH}^{1-}] > 1 \text{ M}$. For example, the pH of a solution that is 2 M in H_3O^{1+} is $-\log 2 = -0.3$, and the pH of 2 M OH^{1-} is $14.0 - (-0.3) = 14.3$.

The p-scale can also be applied to equilibrium constants. Thus, if we take the negative logarithm of both sides of Equation 6.1, we obtain

$$\text{pK}_w = \text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C} \quad \text{Eq. 6.4}$$

As is true for all equilibrium constants, K_w varies with temperature, and pK_w is equal to 14.00 at 25°C only. The value of pK_w at several temperatures is given in Table 6.1. If the pH or the pOH is known, the other can be determined by subtraction of the known quantity from pK_w . For example, consider Example 6.2c. Once the pOH of the solution had been determined to be 0.30, the pH could have been determined as $\text{pH} = 14.00 - 0.30 = 13.70$.

Example 6.3

What are $[\text{H}_3\text{O}^{1+}]$ and $[\text{OH}^{1-}]$ in a solution with a pH of 8.62 at 25°C ?

We apply Equation 6.3 to determine the hydronium ion concentration.

$$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-8.62} = 2.4 \times 10^{-9} \text{ M}$$

We can now determine the hydroxide ion concentration by using Equation 6.1.

$$[\text{OH}^{1-}] = \frac{K_w}{[\text{H}_3\text{O}^{1+}]} = \frac{1.0 \times 10^{-14}}{2.4 \times 10^{-9}} = 4.2 \times 10^{-6} \text{ M}$$

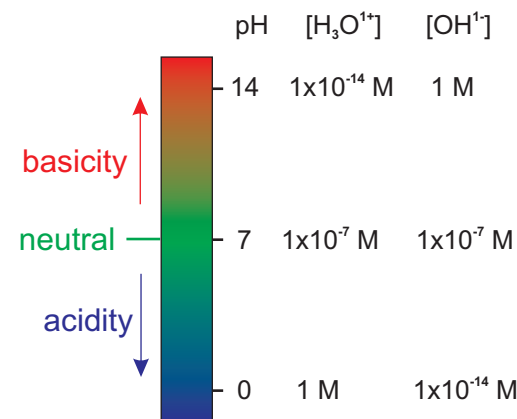


Figure 6.2 Relationship between pH, acidity and basicity

An increase in pH implies a decrease in the acidity of the solution or an increase in its basicity.

Table 6.1 pK_w at various temperatures.

T ($^\circ\text{C}$)	pK_w	K_w
0	14.94	1.15×10^{-15}
25	14.00	1.00×10^{-14}
50	13.28	5.25×10^{-14}
75	12.71	1.95×10^{-13}
100	12.26	5.50×10^{-13}

Or, use Equation 6.4 to get the pOH and then Equation 6.3 to get $[\text{OH}^{1-}]$.

$$\text{pOH} = \text{pK}_w - \text{pH} = 14.00 - 8.62 = 5.38; [\text{OH}^{1-}] = 10^{-\text{pOH}} = 10^{-5.38} = 4.2 \times 10^{-6} \text{ M}$$

The advantage to the second method is that it does not rely on a previous calculation. Thus, the hydroxide concentration could be correct even if a mistake is made in the calculation of the hydronium ion concentration.

Example 6.4

What are the pH, $[\text{H}_3\text{O}^{1+}]$, and $[\text{OH}^{1-}]$ in pure water at 75 °C?

Determine pH and pOH from Equation 6.4 by using the value of pK_w at 75 °C given in Table 6.1 and the fact that $\text{pH} = \text{pOH} = x$ in pure water.

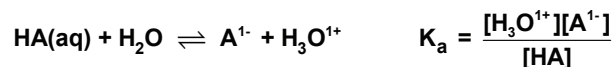
$$\text{pK}_w = 12.71 = \text{pH} + \text{pOH} = 2x; x = \text{pH} = \text{pOH} = \frac{1}{2}(12.71) = 6.35$$

Use Equation 6.3 and the pH and pOH values determined above to find the concentrations.

$$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = [\text{OH}^{1-}] = 10^{-\text{pOH}} = 10^{-6.35} = 4.5 \times 10^{-7} \text{ M}$$

Thus, the hydronium and hydroxide ion concentrations are 4.5 times greater at 75 °C than at 25 °C.

The pH of an aqueous solution changes when an acid is added because the acid reacts with water. The equilibrium constant for the reaction is called the **acid dissociation** or **acid ionization constant*** and given the symbol K_a . Consider the chemical equation and acid dissociation constant for the addition of a generic acid HA to water.



Acids are classified as either strong or weak based upon the extent of the above reaction. Strong acids are those for which $K_a \gg 1$, and weak acids are those for which $K_a \ll 1$.

6.3 STRONG ACIDS

The commonly encountered strong acids are perchloric acid (HClO_4), the hydrohalic acids (HI, HBr and HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3). Essentially all of a strong acid reacts with water to produce hydronium ion and the conjugate base of the strong acid. Indeed, the acid dissociation constants of weak acids are very large because the equilibrium concentration of the acid is nearly zero. Consider the following reaction table for the reaction between H_2O and HCl, a typical strong acid.

PRACTICE EXAMPLE 6.1

- a) The pH of a sample of lemon juice is found to be 2.32. What are the hydronium and hydroxide ion concentrations?

$$[\text{H}_3\text{O}^{1+}] =$$

$$\text{pOH} =$$

$$[\text{OH}^{1-}] =$$

- b) The hydroxide ion concentration in a bottle of household ammonia is 0.0083 M. What are the pH, pOH, and hydronium ion concentration?

$$\text{pH} =$$

$$\text{pOH} =$$

$$[\text{H}_3\text{O}^{1+}] =$$

* In Arrhenius acid-base theory acids dissociate or ionize in water not react with it. For example, $\text{HF} \rightarrow \text{H}^{1+} + \text{F}^{1-}$. Although, acids react with water in Brønsted theory, the terms 'acid dissociation' and 'acid ionization' are still in common use. Thus, K_a is commonly referred to as the acid dissociation or acid ionization constant of the acid.

	$\text{HCl(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{1+}(\text{aq}) + \text{Cl}^{1-}(\text{aq})$		
initial	c_o	0	0
Δ	$-c_o$	$+c_o$	$+c_o$
eq	~ 0	c_o	c_o

c_o is the original or *makeup* concentration of the acid. The concentration given on a bottle of acid is the makeup concentration, not the concentration of acid molecules at equilibrium. The concentration of hydronium ions in a solution of a strong monoprotic acid equals the makeup concentration. Thus, a bottle labeled 0.10 M HCl is 0.10 M in H_3O^{1+} and 0.10 M in Cl^{1-} , but it contains essentially no HCl molecules.

Example 6.5

What is the pH of a 0.16-M solution of hydrochloric acid?

HCl is a strong acid, so

$$[\text{H}_3\text{O}^{1+}] = c_o = 0.16 \text{ M, and } \text{pH} = -\log(0.16) = 0.80$$

6.4 WEAK ACIDS

Weak acids react to only a small extent with water, so the composition of their aqueous equilibria depends upon both their makeup concentration (c_o) and their dissociation constant (K_a). Water is again considered the solvent and treated as a pure liquid, so its activity does not appear in the reaction table. The initial concentration of the conjugate base (A^{1-}) is zero. The initial concentration of the hydronium ion in pure water is 1.0×10^{-7} M, but we enter zero because 10^{-7} M is negligibly small and does not impact the final hydronium ion concentration except for the most dilute acid solutions. The extent of reaction is unknown ($K_a \ll 1$), so the Δ line contains the unknown. Thus, the reaction table for the 'dissociation' of a generic weak acid HA in water has the following form:

	$\text{HA(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{A}^{1-} + \text{H}_3\text{O}^{1+}$		
initial	c_o	0	0 M
Δ	$-x$	$+x$	$+x$ M
eq	$c_o - x$	x	x M

The equilibrium constant expression can then be written as follows:

$$K_a = \frac{[\text{A}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HA}]} = \frac{(x)(x)}{c_o - x}$$

* Selected K_a 's can be found in Appendix C.

Thus, we must solve the following quadratic expression to determine the composition of the equilibrium mixture:

$$K_a = \frac{x^2}{c_o - x} \quad \text{Eq. 6.5}$$

Equation 6.5 is a quadratic equation,* so it has two solutions (\pm square root term). However, the restriction that $0 < x < c_o$ will be obeyed by only one solution.

* **Quadratic equations** are solved by rearranging them so they have the following form:

$$ax^2 + bx + c = 0$$

The two solutions are then given by the following quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The quadratic formula can also be found in the table of Fundamental Constants.

Example 6.6

What is the pH of 0.088 M HF?

Setup the reaction table and get the value of K_a from Appendix C.

	$\text{HF(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{F}^{1-} + \text{H}_3\text{O}^{1+}$	$K_a = 7.2 \times 10^{-4}$		
initial	0.088	0	0	M
Δ	-x	+x	+x	M
eq	0.088 - x	x	x	M

Setup the equilibrium constant expression (Equation 6.5)

$$K_a = \frac{[\text{F}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HF}]} = \frac{x^2}{0.088 - x} = 7.2 \times 10^{-4}$$

Multiply both sides by $0.088 - x$: $x^2 = (7.2 \times 10^{-4})(0.088) - 7.2 \times 10^{-4}x$

Get in the form of a quadratic equation*: $x^2 + 7.2 \times 10^{-4}x - (7.2 \times 10^{-4})(0.088) = 0$

Use the quadratic formula to solve: $x = \frac{-7.2 \times 10^{-4} \pm \sqrt{(7.2 \times 10^{-4})^2 + 4(7.2 \times 10^{-4})(0.088)}}{2}$

Discard the negative solution because x is a concentration and cannot be negative.

$$x = 7.6 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^{1+}] = [\text{F}^{1-}] \quad \& \quad [\text{HF}] = 0.088 - 0.0076 = 0.080 \text{ M}$$

Check your answer by calculating K_a with the answers: $K_a = \frac{(7.6 \times 10^{-3})^2}{0.080} = 7.2 \times 10^{-4} \checkmark$

$$\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log (7.6 \times 10^{-3}) = 2.12$$

If the extent of reaction is very small, the following approximation, known as the '**5% rule**', can be used to avoid solving a quadratic equation:

If less than 5% of a weak acid reacts, *i.e.*, if $x/c_o < 0.05$, then x can be assumed to be negligible in the subtraction from c_o ; that is, $c_o - x \sim c_o$.

Rewriting the expression for K_a for an acid obeying the 5% rule, we obtain the following:

$$K_a = \frac{(x)(x)}{c_o - x} \sim \frac{(x)(x)}{c_o} = \frac{x^2}{c_o}$$

Solving for x , we obtain the hydronium ion concentration and the conjugate base concentration in solutions of weak acids that dissociate less than 5% in water.

$$[H_3O^{1+}] = [\text{conjugate base}] = \sqrt{K_a c_o} \quad \text{Eq. 6.6}$$

The concentrations of the equilibrium species in a solution of c_o M HA are the following if the acid obeys the 5% rule:

$$[HA] = c_o \quad [A^1] = [H_3O^{1+}] = \sqrt{K_a c_o}$$

Although the use of Equation 6.6 is quick and greatly simplifies the algebra, care must be exercised in its use. Consider that the application of Equation 6.6 to the 0.088-M solution of HF presented in Example 6.6 yields $[HF] = 0.088\text{M}$ and $[F^1] = [H_3O^{1+}] = \sqrt{(7.2 \times 10^{-4})(0.088)} = 8.0 \times 10^{-3}\text{M}$, which differs from the concentrations obtained using the quadratic formula. The reason for the discrepancy is that $x/c_o = 0.086$ or 8.6%. More than 5% of the acid dissociates, so the approximation is not valid. **Whenever you use Equation 6.6 you must check your answer to make sure that x is less than 5% of c_o .**

There are three variables in equilibria involving weak acid solutions: the hydronium ion and/or conjugate base concentration (x); the initial or makeup concentration of the acid (c_o); and the K_a of the weak acid, so there are three types of problems involving weak acid solutions in which two of the variables are given and the third is to be determined.

Example 6.7

What is the pH of a 0.10-M solution of acetic acid?

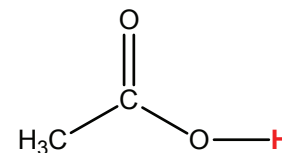
We are given $c_o = 0.10\text{M}$ and that the acid is acetic acid, which allows us to use Appendix C to determine that $K_a = 1.8 \times 10^{-5}$. The reaction table for the dissociation is



initial	0.10	0	0
Δ	-x	+x	+x
eq.	0.10 - x	x	x

Assume that x is negligible in the subtraction in the denominator K_a expression to obtain

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.10 - x)} \sim \frac{x^2}{0.10}$$



Acetic acid

Acetic acid is a carboxylic acid ($-\text{COOH}$ group). It is responsible for the tart taste and pungent odor of vinegar, which is a $\sim 4.5\%$ solution of acetic acid. Acetic acid is also used in the manufacture of acetates and pharmaceuticals. The acidic proton is shown in red.

PRACTICE EXAMPLE 6.2

What is the pH of a 0.080-M solution of ammonium nitrate?

K_a of $\text{NH}_4^{1+} =$ _____ from Appendix C

K_a reaction: _____

if $[\text{NH}_3] = [\text{H}_3\text{O}^{1+}] = x$, then $[\text{NH}_4^{1+}] =$ _____

K_a expression in terms of x :

$K_a =$

$[\text{H}_3\text{O}^{1+}] = x =$ _____ M

Is approximation acceptable? ____

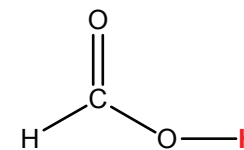
pH =

Solve for the hydronium ion concentration, x.

$$[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_o} = \sqrt{(1.8 \times 10^{-5})(0.10)} = \sqrt{1.8 \times 10^{-6}} = 0.0013 \text{ M}$$

Check the approximation: $x/c_o = 0.0013/0.10 = 0.013 < 0.05$ ✓

The pH of the solution is $\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log (0.0013) = 2.87$



Formic acid

Formic acid is the simplest carboxylic acid. It is a colorless liquid that is widely used in the chemical dyeing and tanning industries. It can also be found in the poisons of some insects and nettles. The acidic proton is shown in red.

Example 6.8

How many grams of formic acid are required to prepare 500.0 mL of a pH = 2.447 solution? $K_a = 1.79 \times 10^{-4}$

We are asked for c_o given the K_a and the pH of the solution (x).

1) Convert the pH to the concentrations.

$$[\text{H}_3\text{O}^{1+}] = [\text{HCOO}^1] = 10^{-\text{pH}} = 10^{-2.447} = 0.00357 \text{ M}$$

2) Setup the reaction table.

	$\text{HCOOH(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{HCOO}^{1-} + \text{H}_3\text{O}^{1+}$		
initial	c_o	0	0
Δ	-0.00357	+0.00357	+0.00357
eq.	$c_o - 0.00357$	+0.00357	+0.00357

3) Substitute the known quantities into K_a .

$$K_a = \frac{(0.00357)^2}{c_o - 0.00357} = 1.79 \times 10^{-4}$$

Note that Equation 6.6 should be used only when the amount reacting is to be determined because it allows us to reduce the algebra. However, there is no quadratic equation required in the determination of either K_a or c_o , so there is no reason to use the approximation.

4) Solve for c_o .

$$c_o = 0.00357 + \frac{(0.00357)^2}{1.79 \times 10^{-4}} = 0.0748 \text{ M}$$

If Equation 6.6 had been used, $c_o = 0.0712 \text{ M}$ and $x/c_o = 0.0501 > 0.05$.

5) Use the volume and molarity of the solution and the molar mass of HCHO_2 to determine the mass of HCHO_2 .

$$0.5000 \text{ L} \times \frac{0.0748 \text{ mol}}{\text{L}} \times \frac{46.03 \text{ g}}{\text{mol}} = 1.72 \text{ g}$$

PRACTICE EXAMPLE 6.3

What initial concentration of a KHSO_4 solution would be required to make a pH = 2.00 solution?

$K_a =$

K_a reaction:

$[\text{H}_3\text{O}^{1+}] =$

$[\text{SO}_4^{2-}] =$

$[\text{HSO}_4^{1-}]$ in terms of $c_o =$

K_a expression in terms of unknown c_o :

$K_a =$

Solve for c_o

Example 6.9

What is the K_a of iodic acid (HIO_3) if the pH of a 0.140-M solution is 1.040?

We are given the makeup and equilibrium concentrations and are asked for K_a . First convert the pH to the equilibrium concentrations:

$$x = [\text{IO}_3^{1-}] = [\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-1.040} = 0.0912 \text{ M}$$

then setup the reaction table.

	$\text{HIO}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons$	IO_3^{1-}	+	H_3O^{1+}	
initial	0.140	0		0	M
Δ	-0.0912	+0.0912		+0.0912	M
eq.	0.049	+0.0912		+0.0912	M

Substitute these values into the K_a expression:

$$K_a = \frac{[\text{IO}_3^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HIO}_3]} = \frac{(0.0912)^2}{0.049} = 0.17$$

The fraction of a weak acid that reacts with or dissociates in water is x/c_o , where x is the equilibrium concentration of the hydronium ion (or conjugate base). If the acid ionization is negligible ($< 5\%$), we can substitute, $\sqrt{K_a c_o}$ for x to obtain

$$\text{fraction of acid reacting} = \frac{x}{c_o} = \frac{\sqrt{K_a c_o}}{c_o} = \sqrt{\frac{K_a}{c_o}} = \sqrt{\frac{K_a}{c_o}}$$

Multiplying the preceding fraction by 100%, we obtain Equation 6.7 for the percent ionization.

$$\text{percent ionization of a weak acid} = \sqrt{\frac{K_a}{c_o}} \times 100\% \quad \text{Eq. 6.7}$$

Table 6.2 shows the percent ionization of several solutions of nitrous acid, acetic acid and hypochlorous acid solutions as determined by Equation 6.7. Note that for most common concentrations ($0.010 \text{ M} < c_o < 1.0 \text{ M}$), acids with $K_a < 10^{-5}$ obey the 5% rule, but more dilute and/or stronger acids probably will not.

Example 6.10

a) What are the percent ionization and pH of 0.026 M HCN ($K_a = 4.0 \times 10^{-10}$)?

$$\text{Equation 6.7 yields } \% = \sqrt{\frac{4.0 \times 10^{-10}}{0.026}} \times 100\% = 0.012\%$$

The above is well below 5% ✓, so Equation 6.6 is valid and can be used to determine the

Table 6.2 Percent ionization of nitrous, acetic and hypochlorous acids as a function of their concentrations

Molarity	HNO_2 $K_a = 4.0 \times 10^{-4}$	CH_3COOH $K_a = 1.8 \times 10^{-5}$	HOCl $K_a = 3.5 \times 10^{-8}$
1.0	2.0%	0.42%	0.019%
0.10	6.1% [†]	1.3%	0.059%
0.010	18% [†]	4.2%*	0.19%
0.0001	83% [†]	34% [†]	1.9%

* Note that the percent is close to but less than 5% in 0.01 M acetic acid. We conclude that the dissociation of any acid that is weaker than acetic acid and whose concentration is greater than 0.01 M can be assumed to be negligible.

† Equation 6.7 cannot be used because over 5% reacts. Indeed, the tabulated value was obtained by calculating x with the quadratic equation.

hydronium ion concentration and the pH:

$$[\text{H}_3\text{O}^{1+}] = \sqrt{(4.0 \times 10^{-10})(0.026)} = 3.2 \times 10^{-6} \text{ M}; \text{pH} = -\log(3.2 \times 10^{-6}) = 5.49$$

b) What are the percent ionization and pH of 0.026 M HF ($K_a = 7.2 \times 10^{-4}$)?

Equation 6.7 yields $\% = \sqrt{\frac{7.2 \times 10^{-4}}{0.026}} \times 100\% = 17\%$, which exceeds 5%. Thus, we cannot

assume x is negligible. The reaction table is

	HF	+	H ₂ O	\rightleftharpoons	F ¹⁻	+	H ₃ O ¹⁺
initial	0.026				0		0
Δ	-x				+x		+x
eq.	0.026-x				x		x

Setup the K_a expression:

$$7.2 \times 10^{-4} = \frac{x^2}{(0.026 - x)}$$

Eliminate the denominator:

$$(7.2 \times 10^{-4})(0.026) - 7.2 \times 10^{-4}x = x^2$$

Rearrange to the quadratic form:

$$x^2 + 7.2 \times 10^{-4}x - 1.87 \times 10^{-5} = 0$$

Use the quadratic formula to solve for $x = [\text{H}_3\text{O}^{1+}]$.

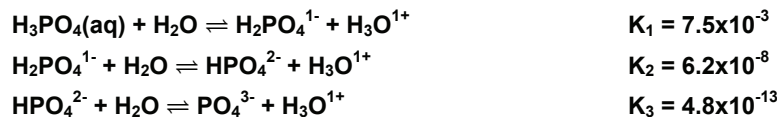
$$[\text{H}_3\text{O}^{1+}] = \frac{-7.2 \times 10^{-4} + \sqrt{(7.2 \times 10^{-4})^2 - 4(1)(-1.87 \times 10^{-5})}}{2} = 4.0 \times 10^{-3} \text{ M}$$

Determine the percent ionization of the acid and the pH of the solution.

$$\% = \frac{0.0040 \text{ M}}{0.026 \text{ M}} \times 100\% = 15\% \quad \& \quad \text{pH} = -\log(4.0 \times 10^{-3}) = 2.40$$

6.5 POLYPROTIC ACIDS

Polyprotic acids* have two or more acidic protons that they lose one at a time. Removal of a proton strengthens the remaining O–H bonds, which makes each subsequent acid weaker. Consider the step-wise dissociation of the triprotic acid H_3PO_4 .

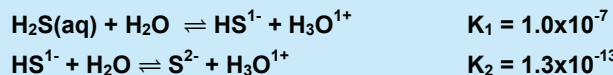


Each K_a is smaller by a factor of $\sim 10^5$, which means that the amount of any species formed in one dissociation is unaffected by subsequent reactions. Consequently, the *hydronium ion concentration in most polyprotic acids can be determined from the first ionization in the same way that it is determined for a monoprotic acid because the amount of hydronium ion produced after the first ionization is negligible.*

* Polyprotic is a general term meaning many protons. Most polyprotic acids have two or three protons. Those with two are said to be **diprotic** (H_2A) and those with three are **triprotic** (H_3A).

Example 6.11

What are the concentrations of all species present in 0.10 M H_2S ?



1) Create the reaction table for the first equilibrium.

	$\text{H}_2\text{S}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HS}^{1-} + \text{H}_3\text{O}^{1+}$		
initial	0.10	0	0
Δ	-x	+x	+x
eq.	0.10 - x	+x	+x

2) Assume that $0.10 - x = 0.10$ and substitute the eq line into the K_1 expression.

$$1.0 \times 10^{-7} = \frac{x^2}{0.10} \Rightarrow x = [\text{H}_3\text{O}^{1+}] = [\text{HS}^{1-}] = \sqrt{(1.0 \times 10^{-7})(0.10)} = 1.0 \times 10^{-4} \text{ M}$$

$$1.0 \times 10^{-4} / 0.10 = 1.0 \times 10^{-3} < 0.05, \text{ so approximation is valid. } \checkmark$$

3) The reaction table for the second equilibrium is

	$\text{HS}^{1-} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{S}^{2-} + \text{H}_3\text{O}^{1+} \quad K_2 = 1.3 \times 10^{-13}$		
initial	1.0×10^{-4}	0	1.0×10^{-4}
Δ	-y	+y	+y
eq.	$1.0 \times 10^{-4} - y$	+y	$1.0 \times 10^{-4} + y$

4) K_2 is very small, so y is probably negligible in both the addition and the subtraction,

$$1.0 \times 10^{-4} \pm y = 1.0 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^{1+}] = [\text{HS}^{1-}], \text{ so}$$

$$y = \frac{[\text{S}^{2-}][\cancel{1.0 \times 10^{-4}}]}{[\cancel{1.0 \times 10^{-4}}]} = 1.3 \times 10^{-13} \text{ M} = K_2 = [\text{S}^{2-}]$$

$$1.3 \times 10^{-13} \ll 1.0 \times 10^{-4}, \text{ so approximation is valid. } \checkmark$$

As shown in Example 6.11,

The concentration of the ion produced in the second ionization of a weak polyprotic acid equals the second ionization constant (K_2) of the acid.

For example, $K_2 = 6.2 \times 10^{-8}$ for H_3PO_4 , so $[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$ in a phosphoric acid solution and is independent of the concentration of phosphoric acid so long $[\text{H}_3\text{O}^{1+}] \gg K_2$.

PRACTICE EXAMPLE 6.4

What are the pH, and the concentrations of all carbon containing species in 0.18-M H_2CO_3 ?

Reaction table and equilibrium constant from Appendix C for the first dissociation:

Reaction _____ $K_1 =$
in
 Δ
eq

$$[\text{H}_3\text{O}^{1+}] = \text{_____} = \text{_____} \text{ M}$$

$$\text{pH} = \text{_____}$$

$$[\text{HCO}_3^{1-}] = \text{_____} \text{ M}$$

$$[\text{H}_2\text{CO}_3] = \text{_____} \text{ M}$$

Reaction table and equilibrium constant from Appendix C for the second dissociation:

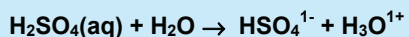
Reaction _____ $K_2 =$
in
 Δ
eq

$$[\text{CO}_3^{2-}] = \text{_____} \text{ M}$$

Example 6.12

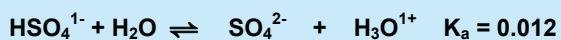
What are the H_3O^{1+} , HSO_4^{1-} , and SO_4^{2-} concentrations in 0.10 M sulfuric acid?

Sulfuric acid is a unique polyprotic acid because H_2SO_4 is a strong acid as the first ionization is complete.



initial	0.10	0	0	M
Δ	-0.10	+0.10	+0.10	M
eq	~0	0.10	0.10	M

HSO_4^{1-} is a weak acid, so its dissociation reaction must be considered next. The initial concentrations of the HSO_4^{1-} and H_3O^{1+} ions are 0.10 M due to the above.



Initial	0.10	0	0.10	M
Δ	-x	+x	+x	M
eq	0.10 - x	x	0.10 + x	M

If x is negligible, $[\text{SO}_4^{2-}] = K_a = 0.012$ M, but that is 12% of the initial concentration, and the assumption is not valid. Substitution of the above into the K_a expression and rearrangement to the form of a quadratic equation leads to the following:

$$0.012 = \frac{(0.10 + x)(x)}{(0.10 - x)} = \frac{0.10 + x^2}{0.10 - x} \Rightarrow x^2 + 0.112x - 0.0012 = 0$$

Use the quadratic formula to solve for x.

$$x = [\text{SO}_4^{2-}] = \frac{-0.112 \pm \sqrt{(0.112)^2 - 4(1)(-0.0012)}}{2(1)} = 0.0098 \text{ M}$$

Use the value of x obtained above to determine the other unknowns.

$$[\text{HSO}_4^{1-}] = 0.10 - 0.0098 = 0.09 \text{ M} ; [\text{H}_3\text{O}^{1+}] = 0.10 + 0.0098 = 0.11 \text{ M} ;$$

$$\text{pH} = -\log (0.11) = 0.96.$$

Example 6.13

What are the pH and concentrations of all phosphorus-containing species in a 1.00 M H_3PO_4 solution?

The first dissociation is $\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^{1-} + \text{H}_3\text{O}^{1+}$ $K_1 = 7.5 \times 10^{-3}$

Assume negligible reaction to obtain $[\text{H}_3\text{O}^{1+}] = \sqrt{(7.5 \times 10^{-3})(1.00)} = 0.087 \text{ M}$

x/c_0 is 0.087%, which is over 0.05, so we must solve the quadratic.

$$7.5 \times 10^{-3} = \frac{x^2}{1.00 - x}; \quad x^2 + 7.5 \times 10^{-3} x - 7.5 \times 10^{-3} = 0; \quad x = 0.083 \text{ M}$$

The concentrations of the other species involved in the first dissociation are

$$[\text{H}_3\text{PO}_4] = 1.00 - 0.083 = 0.92 \text{ M}; \quad [\text{H}_3\text{O}^{1+}] = [\text{H}_2\text{PO}_4^{1-}] = 0.083 \text{ M}$$

If the extent of the second dissociation is negligible compared to the first, then

$$[\text{HPO}_4^{2-}] = K_2 = 6.2 \times 10^{-8} \text{ M}$$

$6.2 \times 10^{-8} \text{ M}$ is negligible compared to 0.083 M and the assumption is valid. ✓

We now use the known concentrations in the third dissociation to determine the phosphate ion concentration.

	$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^{1+}$	$K_3 = 4.8 \times 10^{-13}$
in	6.2×10^{-8} 0 0.083	
Δ	-y +y +y	
eq	$6.2 \times 10^{-8} - y$ y $0.083 + y$	

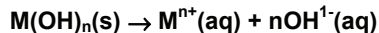
if y is negligible compared to 6.2×10^{-8} , then the K_a expression and y are

$$4.8 \times 10^{-13} = \frac{y(0.083)}{6.2 \times 10^{-8}}; \quad y = [\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.083} = 3.6 \times 10^{-19} \text{ M}$$

y is negligible compared to $6.2 \times 10^{-8} \text{ M}$, so the assumption is valid. ✓

6.6 STRONG BASES

Strong bases are derived from metal hydroxides, $\text{M}(\text{OH})_n$. However, most metal hydroxides are insoluble in water, so the common bases are restricted to the hydroxides of a relatively small number of metals that have soluble hydroxides. The most common strong bases are NaOH, KOH, and $\text{Ba}(\text{OH})_2$. The concentration on the label indicates the makeup concentration of the base, which is related to the hydroxide ion concentration by the stoichiometry of the metal hydroxide as shown in Reaction 6.2.



Rxn. 6.2

PRACTICE EXAMPLE 6.5

What are the pH, and the concentrations of all sulfur containing species in 0.064 M H_2SO_3 solution?

Reaction table and equilibrium constant from Appendix C for the first dissociation:

Reaction _____ $K_1 =$
in _____
 Δ _____
eq _____

a) Assume negligible reaction to determine $[\text{H}_3\text{O}^{1+}]$.

$$[\text{H}_3\text{O}^{1+}] = \text{_____} \text{ M}$$

% ionization = _____%

Is assumption valid? _____

b) Solve the quadratic equation.
equilibrium constant expression

quadratic equation in terms of x:

$$[\text{H}_3\text{O}^{1+}] = \text{_____} \text{ M}$$

$$\text{pH} = \text{_____}$$

$$[\text{HSO}_3^{1-}] = \text{_____} \text{ M}$$

$$[\text{H}_2\text{SO}_3] = \text{_____} \text{ M}$$

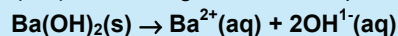
If K_2 reaction is negligible,

$$[\text{SO}_3^{2-}] = \text{_____} \text{ M}$$

Example 6.14

What is the pH of a solution labeled 0.16 M Ba(OH)₂ at 25 °C?

Ba(OH)₂ is a strong base and the process that occurs when it dissolves is



Thus, two moles of hydroxide ion are produced from each mole of Ba(OH)₂,

$$[\text{OH}^{1-}] = \frac{0.16 \text{ mol Ba(OH)}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol OH}^{1-}}{1 \text{ mol Ba(OH)}_2} = 0.32 \text{ M}$$

$$\text{pOH} = -\log(0.32) = 0.49; \quad \text{pH} = 14.00 - 0.49 = 13.51$$

6.7 WEAK BASES

Weak bases react with water to produce their conjugate acids and hydroxide ions. They can be treated in a manner analogous to weak acids. Consider the reaction table for the reaction of a generic base B¹⁻ with water.

	B ¹⁻	+	H ₂ O	⇌	HB(aq)	+	OH ¹⁻	
initial	c ₀				0		0	M
Δ	-x				+x		+x	M
eq	c ₀ - x				x		x	M

The equilibrium constant for the reaction is the K_b of the base. Setting up the equilibrium constant expression, we obtain

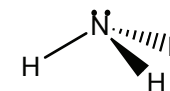
$$K_b = \frac{[\text{HB}][\text{OH}^{1-}]}{[\text{B}^{1-}]} = \frac{(x)(x)}{c_0 - x} = \frac{x^2}{c_0 - x}$$

The K_b expression is solved by using the quadratic formula or assuming that c₀ - x ≅ c₀, in which case Equation 6.8 can be used.

$$[\text{OH}^{1-}] = [\text{conjugate acid}] = \sqrt{K_b c_0} \quad \text{Eq. 6.8}$$

Equation 6.8 is valid only if less than 5% of the base reacts; *i.e.*, if x/c₀ < 0.05.*

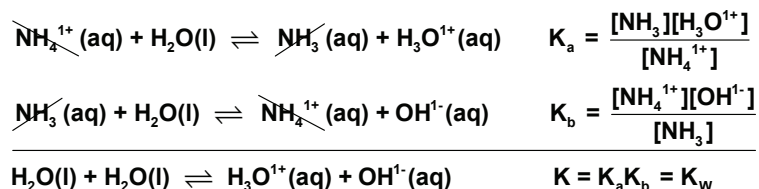
The K_b of a weak base is related to the K_a of its conjugate acid. The relationship can be seen by adding the K_a reaction of the weak acid and the K_b reaction of its conjugate base. The result is the autoionization reaction of water. For example, consider the sum of the K_a reaction of ammonium ion and the K_b reaction of ammonia.



Ammonia

Nitrogen atoms frequently have lone pairs in molecules, so their compounds are frequently weak bases. Ammonia is the simplest and most common such compound. It is a gas at normal conditions, but is most commonly encountered in aqueous solution, where its basicity makes it ideal for use as a cleaning fluid. Ammonia is the source of nitrogen in fertilizers, usually in the form of ammonium salts, plastics, vitamins, drugs, and many other chemicals. Large quantities of ammonia are also used in the production of nitric acid, which is needed to make such explosives as TNT (trinitrotoluene), nitroglycerin, and ammonium nitrate.

* The 5% rule applies to bases as well as to acids.



The autoionization reaction of water can be expressed as the sum of the K_a and K_b reactions of a conjugate acid-base pair, so K_w is the product of the K_a of an acid and the K_b of its conjugate base, i.e.,

$$K_a K_b = K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ \text{C} \quad \text{Eq. 6.9}$$

Typically, only the K_a of the acid or the K_b of its conjugate base is tabulated. The number that is not tabulated is then determined with Equation 6.9. For example, the K_a of ammonium ion is listed in Appendix C, but the K_b of ammonia is not. Thus, the ammonia K_b is determined as follows:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5}$$

K_a and K_b involve negative exponents, so they are frequently reported on the p-scale (Equation 6.2).

$$\text{p}K_a = -\log K_a \quad \text{and} \quad \text{p}K_b = -\log K_b \quad \text{Eq. 6.10}$$

Finally, we can take the logarithm of both sides of Equation 6.9 to obtain

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \text{ at } 25^\circ \text{C} \quad \text{Eq. 6.11}$$

Example 6.15

The $\text{p}K_a$ of lactic acid is 3.89. What is the K_a of lactic acid?

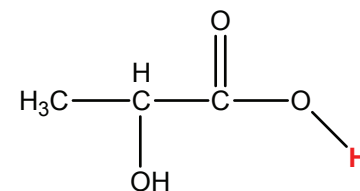
Use Equation 6.3 to convert the $\text{p}K_a$ to a K_a : $K_a = 10^{-\text{p}K_a} = 10^{-3.89} = 1.3 \times 10^{-4}$

What is the K_b of the lactate ion?

Use Equation 6.10 to convert the $\text{p}K_a$ of the acid into the $\text{p}K_b$ of the conjugate base and then Equation 6.3 to convert the $\text{p}K_b$ into the K_b :

$$\text{p}K_b = 14.00 - \text{p}K_a = 14.00 - 3.89 = 10.11$$

$$K_b = 10^{-\text{p}K_b} = 10^{-10.11} = 7.8 \times 10^{-11}$$



Lactic acid

Lactic acid is usually prepared by fermentation. It is the fermentation of lactose to lactic acid that is responsible for the souring of milk. Lactic acid is used in the preparation of food products. Also, it is the presence of lactic acid in muscle that causes fatigue and even cramps. The acidic proton is highlighted in red.

Example 6.16

What is the pH of a solution that is 0.12 M in NO_2^{1-} ?

The K_a of HNO_2 in Appendix C is 4.0×10^{-4} , so the K_b of the nitrite ion can be determined from Equation 6.9 to be

$$K_b = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$$

Proceed as with a weak acid and construct the reaction table for the reaction of nitrite ion with water.

	$\text{NO}_2^{1-}(\text{aq})$	$+\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{HNO}_2(\text{aq})$	$+\text{OH}^{1-}(\text{aq})$
initial	0.12			0	0
Δ	-x			+x	+x
eq.	0.12 - x			x	x

Substitute the concentrations into the K_b expression: $2.5 \times 10^{-11} = \frac{(x)(x)}{0.12-x}$

K_b is small and c_0 is large, so assume x is negligible compared to 0.12 and solve for $x = [\text{HNO}_2] = [\text{OH}^{1-}]$.

$$x^2 = (0.12)(2.5 \times 10^{-11}) \Rightarrow x = \sqrt{3.0 \times 10^{-12}} = 1.7 \times 10^{-6} \text{ M}$$

$x/0.12 \ll 0.05$, so assumption was valid. The hydroxide ion concentration is converted to pOH, which is then converted into the pH.

$$\text{pOH} = -\log [\text{OH}^{1-}] = -\log (1.7 \times 10^{-6}) = 5.76 \text{ and } \text{pH} = 14.00 - 5.76 = 8.24$$

Bases that can accept more than one proton are treated much the same way as polyprotic acids. Consider the case of the sulfide ion, which can accept two protons.



Note that the two K_b values differ by a factor of about a million. Thus, the hydroxide produced in the second step is negligible compared to that produced in the first step. Consequently, the hydroxide ion concentration in an aqueous solution of a base that can accept more than one proton salt can usually be determined by considering only the first step.

PRACTICE EXAMPLE 6.6

The pH of a 0.085-M solution of methyl amine is 11.77. What is the K_b of methyl amine (CH_3NH_2)?

K_b reaction:

$$[\text{OH}^{1-}] =$$

$$[\text{CH}_3\text{NH}_3^{1+}] =$$

$$[\text{CH}_3\text{NH}_2] =$$

$$K_b =$$

$$\text{p}K_b \text{ of } \text{CH}_3\text{NH}_2 =$$

Is $[\text{OH}^{1-}]$ negligible compared to c_0 in this solution?

What is the $\text{p}K_a$ of the methyl ammonium ion?

$$\text{p}K_a \text{ of } \text{CH}_3\text{NH}_3^{1+} =$$

Example 6.17**What is the pH of a 0.064-M solution of sulfide ion?**First determine the K_b of S^{2-} from the K_a or its conjugate acid, HS^{1-} , which is in Appendix C

$$K_b = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-13}} = 0.077$$

The reaction table for the reaction of sulfide ion and water is

	S^{2-}	$+ H_2O(l) \rightleftharpoons$	$HS^{1-}(aq) +$	$OH^{1-}(aq)$
initial	0.064		0	0
Δ	-x		+x	+x
eq.	0.064-x		x	x

Substitute the concentrations into the K_b expression. $0.077 = \frac{(x)(x)}{0.064 - x}$ If x is negligible compared to 0.064, then $x = \sqrt{(0.077)(0.064)} = 0.070 \text{ M}$, which is greater than c_0 , so the assumption is clearly not valid. Rewrite the K_b expression and rearrange.

$$(0.077)(0.064) - 0.077x = x \quad \text{so} \quad x^2 + 0.077x - 0.0049 = 0$$

Solve with quadratic formula: $x = \frac{-0.077 + \sqrt{(0.077)^2 - 4(1)(-0.0049)}}{2(1)} = 0.042 \text{ M}$ Check algebra: $K_b = \frac{(0.042)(0.042)}{(0.064 - 0.042)} = 0.077$ ✓ Extra significant digits were used with x .

$$pOH = -\log [OH^{1-}] = -\log (0.042) = 1.38; \quad pH = 14.00 - 1.38 = 12.62$$

PRACTICE EXAMPLE 6.7**What are the concentrations of all sulfur-containing species in a 0.12-M solution of K_2SO_3 ?** K_b for first step $K_1 =$ _____

reaction table for first step:

$$[HSO_3^{1-}] = \text{_____ M}$$

$$[SO_3^{2-}] = \text{_____ M}$$

 K_b for second step: $K_2 =$ _____

Reaction table for second step

$$[H_2SO_3] = \text{_____ M}$$

6.8 SALTS OF WEAK ACIDS AND BASES

A **salt** is an ionic compound that is produced in an acid-base reaction. The acid-base properties of a salt depend upon the nature of both the anion and the cation. Although small, highly-charged cations do have acid properties (Section 8.1), those of the 1A metals have no acid-base properties and can be ignored in deciding the properties of the salt. Consequently, the discussion in this section assumes that all metal-containing salts are formed with Group 1A metal ions.

A **neutral salt** is the salt of a strong acid and a strong base. They are neutral because the cation is a metal ion and the anion is the conjugate base of a strong acid, so it does not behave like a base in water. Thus, NaCl is a neutral salt because neither Na^{1+} nor Cl^{1-} have acid-base properties in water (chloride ion does not react with water to produce HCl because HCl is a strong acid).

Most anions accept the positive charge of a proton, so anions are usually good bases, and salts containing them are basic salts. **Basic salts** are formed in the reaction of weak acids with strong bases. For example, the reaction of HCN and NaOH produces the basic salt NaCN: $\text{HCN} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCN}$. NaCN produces Na^{1+} and CN^{1-} ions when it dissolves in water. The Na^{1+} ions can be ignored, but CN^{1-} is a weak base.



Basic salts are the most common source of weak bases.

Acidic salts are produced by the reaction of strong acids with weak bases. For example, the reaction of HCl with NH_3 produces the acidic salt NH_4Cl : $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$. NH_4Cl is an acidic salt because the ammonium ion is a weak acid, but chloride ion is not a weak base in water. Thus, dissolving NH_4Cl produces ammonium ions, which react with water to produce hydronium ions ($\text{NH}_4^{1+} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^{1+}$).

The acid-base properties of a salt formed from the reaction of a weak base and a weak acid depend upon the relative values of the K_a of the acid and the K_b of the base. They are acidic when $K_a > K_b$, basic when $K_b > K_a$, or neutral when $K_a = K_b$. Example 6.18 gives some examples.

Example 6.18

Indicate whether a solution of each of the following salts is acidic, basic, or neutral.

a) KClO_4

The cation is a 1A metal and ClO_4^{1-} is the conjugate base of a strong acid, so neither ion reacts with water, which makes KClO_4 a neutral salt.

b) Na_2S

The cation can be ignored but, S^{2-} is a weak base, so Na_2S is a basic salt.

c) NH_4NO_2

NH_4^{1+} is a weak acid, and NO_2^{1-} is a weak base. The K_a of NH_4^{1+} is 5.6×10^{-10} , and the K_b of NO_2^{1-} is $K_w/K_a(\text{HNO}_2) = (1.0 \times 10^{-14})/(4.0 \times 10^{-4}) = 2.5 \times 10^{-11}$. The K_a of NH_4^{1+} is greater than the K_b of NO_2^{1-} , so the salt is an acidic salt.

d) $(\text{NH}_4)_3\text{PO}_4$

NH_4^{1+} is a weak acid, and PO_4^{3-} is a weak base. The K_a of NH_4^{1+} is 5.6×10^{-10} , and the K_b of PO_4^{3-} is $K_w/K_a(\text{HPO}_4^{2-}) = (1.0 \times 10^{-14})/(4.8 \times 10^{-13}) = 2.1 \times 10^{-2}$. The K_b of PO_4^{3-} is greater than the K_a of NH_4^{1+} , so the salt is a basic salt.

PRACTICE EXAMPLE 6.8

What is the pH of a solution prepared by dissolving 3.5 g of KF ($M_m = 58.1 \text{ g}\cdot\text{mol}^{-1}$) in sufficient water to make 150 mL of solution?

KF is a(n) _____ salt because the _____ ion is a(n) _____, while the _____ ion is neither acidic nor basic in water.

$K_b =$ _____ $=$ _____

Moles of KF:

_____ x _____ $=$ _____ mol

Fluoride ion concentration:

$[\text{F}^{1-}] =$ _____ $=$ _____ M

Reaction Table:

Reaction:

In

Δ

Eq

Hydroxide ion concentration from Equation 6.8:

$[\text{OH}^{1-}] =$ _____ $=$ _____ M

Is the assumption made in Eq. 6.8 valid? _____

pOH =

pH =

e) $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$

NH_4^{1+} is a weak acid, and $\text{C}_2\text{H}_3\text{O}_2^{1-}$ is a weak base. The K_a of NH_4^{1+} is 5.6×10^{-10} , and the K_b of $\text{C}_2\text{H}_3\text{O}_2^{1-}$ is $K_w/K_a(\text{HC}_2\text{H}_3\text{O}_2) = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$. The $K_b(\text{C}_2\text{H}_3\text{O}_2^{1-}) = K_a(\text{NH}_4^{1+})$, so the salt is a neutral salt.

6.9 AMPHIPROTIC SALTS

As shown in Figure 6.3, HCO_3^{1-} is an amphiprotic substance because it can behave as both an acid and a base. It produces hydronium ion through its K_a reaction.



For every mole of hydronium produced, a mole of carbonate ion is also produced; *i.e.*,

$$[\text{H}_3\text{O}^{1+}]_{\text{produced}} = [\text{CO}_3^{2-}]$$

The concentration of hydronium ion produced in this step equals the equilibrium concentration of its conjugate base, carbonate ion. However, HCO_3^{1-} also produces hydroxide ion through its K_b reaction.



$K_{b1} = K_w/K_{a2} = 1.0 \times 10^{-14}/4.7 \times 10^{-11}$. For every mole of hydroxide ion produced, a mole of carbonic acid is also produced; *i.e.*, $[\text{OH}^{1-}]_{\text{produced}} = [\text{H}_2\text{CO}_3]$. Each mole of hydroxide ion that is produced, consumes a mole of hydronium ion ($\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$). Thus,

$$[\text{OH}^{1-}]_{\text{produced}} = [\text{H}_3\text{O}^{1+}]_{\text{consumed}} = [\text{H}_2\text{CO}_3]$$

The equilibrium hydronium ion concentration is determined from the following:

$$[\text{H}_3\text{O}^{1+}] = [\text{H}_3\text{O}^{1+}]_{\text{produced}} - [\text{H}_3\text{O}^{1+}]_{\text{consumed}} = [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3]$$

The concentrations of CO_3^{2-} and H_2CO_3 can be obtained from K_{a2} and K_{b1}

$$[\text{H}_3\text{O}^{1+}] = [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3] = \frac{K_{a2}[\text{HCO}_3^{1-}]}{[\text{H}_3\text{O}^{1+}]} - \frac{K_{b1}[\text{HCO}_3^{1-}]}{[\text{OH}^{1-}]}$$

Use $K_{b1} = K_w/K_{a1}$ and then $K_w = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$ to convert the second term from a function of K_{b1} and OH^{1-} to one of K_{a1} and $[\text{H}_3\text{O}^{1+}]$:

$$\frac{K_{b1}}{[\text{OH}^{1-}]} = \frac{K_w}{K_{a1}[\text{OH}^{1-}]} = \frac{[\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]}{K_{a1}[\text{OH}^{1-}]} = \frac{[\text{H}_3\text{O}^{1+}]}{K_{a1}}$$

* We use the following notation:

$$K_{a1} = K_a \text{ of } \text{H}_2\text{CO}_3$$

$$K_{a2} = K_a \text{ of } \text{HCO}_3^{1-}$$

$$K_{b1} = K_b \text{ of } \text{HCO}_3^{1-}$$

$$K_{b2} = K_b \text{ of } \text{CO}_3^{2-}$$

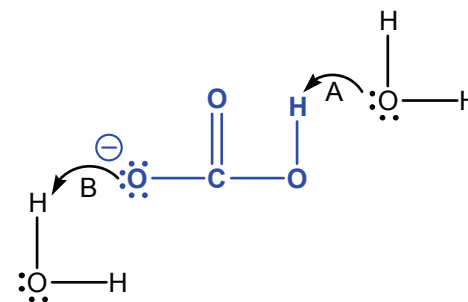


Figure 6.3 Amphiprotic substances are acids and bases

HCO_3^{1-} is amphiprotic because its acidic proton can be lost (Arrow A) or the lone pair on the oxygen with negative formal charge can accept a proton (Arrow B).

Express the hydronium ion concentration with the changes in the second term.

$$[\text{H}_3\text{O}^{1+}] = \frac{K_{a2}[\text{HCO}_3^{1-}]}{[\text{H}_3\text{O}^{1+}]} - \frac{[\text{H}_3\text{O}^{1+}][\text{HCO}_3^{1-}]}{K_{a1}}$$

Multiply both sides of the equation by the hydronium ion concentration to obtain

$$[\text{H}_3\text{O}^{1+}]^2 = K_{a2}[\text{HCO}_3^{1-}] - \frac{[\text{H}_3\text{O}^{1+}]^2[\text{HCO}_3^{1-}]}{K_{a1}}$$

Solve the preceding for the square of the hydronium ion concentration.

$$[\text{H}_3\text{O}^{1+}]^2 = \frac{K_{a1}K_{a2}[\text{HCO}_3^{1-}]}{K_{a1} + [\text{HCO}_3^{1-}]}$$

The extents of both the K_{a2} and K_{b1} reactions of HCO_3^{1-} are small, so little HCO_3^{1-} reacts and $[\text{HCO}_3^{1-}] \gg K_{a1}$ for normal concentrations. Thus, K_{a1} is negligible in the addition term in the denominator. Substitution of $[\text{HCO}_3^{1-}]$ for $K_{a1} + [\text{HCO}_3^{1-}]$ yields

$$[\text{H}_3\text{O}^{1+}]^2 = \frac{K_{a1}K_{a2}[\text{HCO}_3^{1-}]}{[\text{HCO}_3^{1-}]} = K_{a1}K_{a2}$$

Taking the negative *log* of both sides and solving for the pH, we obtain the final result.

$$\text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2}) \quad \text{Eq. 6.12}$$

The pH of an amphiprotic substance is half-way between its $\text{p}K_a$ ($\text{p}K_{a2}$) and that of its conjugate acid ($\text{p}K_{a1}$) so long as its concentration is much larger than the K_a of its conjugate acid, K_{a1} .

Example 6.19

What is the pH of a 0.116-M solution of K_2HPO_4 ?

First obtain the $\text{p}K_a$ values of the amphiprotic substance: $\text{p}K_2 = \text{p}K_a(\text{HPO}_4^{2-}) = 12.32$ and that of its conjugate acid: $\text{p}K_1 = \text{p}K_a(\text{H}_2\text{PO}_4^{1-}) = 7.21$. The concentration is irrelevant, and Equation 6.12 can be used to get the pH.

$$\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(7.21 + 12.32) = 9.77$$

6.10 CHAPTER SUMMARY AND OBJECTIVES

It takes only small concentrations of hydronium or hydroxide ion to make a solution acidic or basic. Because the concentrations are typically quite small, they are often expressed on the p-scale: $\text{pH} = -\log [\text{H}_3\text{O}^{1+}]$ and $\text{pOH} = -\log [\text{OH}^{1-}]$. Water is both a weak acid and a weak base. As a result, water molecules react with one another to a small extent. The equilibrium constant for the reaction, $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{1+} + \text{OH}^{1-}$, is $K_w = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}] = 1.0 \times 10^{-14}$. K_w must be satisfied in all aqueous solutions. Consequently, if either the hydronium or hydroxide ion concentration of a solution is known, the concentration of the other ion can be determined with K_w . In a neutral solution, $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$ and $\text{pH} = \text{pOH} = 7$.

Weak acids react to only a small extent with water, so their K_a values are less than one. The amount of acid reacting can be assumed to be negligible compared to its initial concentration if less than 5% reacts. In this case, the following approximation can be used: $[\text{H}_3\text{O}^{1+}] = [\text{conjugate base}] = \sqrt{K_a c_o}$. If more than 5% reacts, a quadratic equation must be solved.

Acids with more than one acidic proton are said to be polyprotic. The K_a values for the acids formed by removal of successive protons usually differ by several orders of magnitude, so the hydronium ion concentration in a polyprotic acid solution comes almost entirely from the first ionization reaction, and the pH is determined in the same way as a monoprotic acid. An important exception is the strong acid H_2SO_4 .

Bases react with water to produce OH^{1-} ion and the equilibrium constant for the reaction is termed the K_b of the base. The K_a of an acid and the K_b of its conjugate base are related by the expression: $K_a K_b = K_w$. Consequently, the K_b of a weak base can be determined from the K_a of its conjugate acid. Equilibria mixtures of bases are treated in a manner very similar to that of weak acids. When the extent of reaction is small, the following approximation can be used: $[\text{OH}^{1-}] = [\text{conjugate acid}] = \sqrt{K_b c_o}$. A quadratic equation must be solved if more than 5% of the base reacts.

Salts are the ionic products of acid-base reactions. They are frequently basic because most anions are weak bases. However, when the anion is the conjugate base of a strong acid, the salt is neutral because the anion is too weak a base to remove a proton from water and form OH^{1-} . Protonated anions can be acidic as is the ammonium ion. Consequently, salts like KHSO_4 and NH_4Cl are acidic salts. The acid-base properties of salts that contain

ANSWERS TO PRACTICE EXAMPLES

- 6.1 a) $[\text{H}_3\text{O}^{1+}] = 4.8 \times 10^{-3} \text{ M}$; $[\text{OH}^{1-}] = 2.1 \times 10^{-12} \text{ M}$
 b) $\text{pH} = 11.92$; $\text{pOH} = 2.08$; $[\text{H}_3\text{O}^{1+}] = 1.2 \times 10^{-12}$
- 6.2 $\text{pH} = 5.17$
- 6.3 $c_o = 0.018 \text{ M}$
- 6.4 $\text{pH} = 3.56$ $[\text{H}_2\text{CO}_3] = 0.18 \text{ M}$
 $[\text{HCO}_3^{1-}] = 2.8 \times 10^{-4} \text{ M}$ $[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M}$
- 6.5 a) $K_1 = 0.015$; $[\text{H}_3\text{O}^{1+}] = 0.031 \text{ M}$; No
 b) $[\text{H}_3\text{O}^{1+}] = 0.024 \text{ M} = [\text{HSO}_3^{1-}]$;
 $x^2 + 0.015x - 9.6 \times 10^{-4} = 0$
 $\text{pH} = 1.62$; $[\text{H}_2\text{SO}_3] = 0.040 \text{ M}$
 c) $[\text{SO}_3^{2-}] = K_2 = 1.0 \times 10^{-7} \text{ M}$
- 6.6 $K_b = 4.4 \times 10^{-4}$; $\text{p}K_b = 3.36$; $\text{p}K_a = 10.64$
- 6.7 $K_1 = 1.0 \times 10^{-7}$; $[\text{SO}_3^{2-}] = 0.12 \text{ M}$; $[\text{HSO}_3^{1-}] = 1.1 \times 10^{-4} \text{ M}$
 $[\text{H}_2\text{SO}_3] = 6.7 \times 10^{-13} \text{ M}$
- 6.8 KF is a basic salt because the fluoride ion is basic, while the potassium ion is neutral. $[\text{F}^{1-}] = 0.40 \text{ M}$;
 $[\text{OH}^{1-}] = 2.4 \times 10^{-6} \text{ M}$; $\text{pH} = 8.37$

both an acid and a base depend upon the relative strengths of the acid and the base.

Amphiprotic materials are anions with acidic protons, so they can act as both acids and bases. The pH of an amphiprotic substance is half-way between its pK_a (pK_2) and that of its conjugate acid (pK_1); *i.e.*, $pH = \frac{1}{2}(pK_1 + pK_2)$ for an amphiprotic substance.

After studying the material presented in this chapter, you should be able to:

1. convert between pH and $[H_3O^{1+}]$, pOH and $[OH^{1-}]$ (Section 6.1);
2. determine $[H_3O^{1+}]$, $[OH^{1-}]$, pH and pOH of a solution of a strong acid or strong base of known concentration (Section 6.2);
3. calculate the pH of a solution prepared by mixing a strong acid and a strong base (Section 6.3);
4. write the K_a expression for a weak acid (Sections 6.4);
5. determine the pH and equilibrium concentrations of all species present in solutions of weak acids (Sections 6.4);
6. determine one unknown (the pH of the solution, the K_a of the acid, or initial concentration of the acid) in a solution of a weak acid given the other two (Section 6.4);
7. calculate the percent ionization of a weak acid (Section 6.4);
8. convert between pK_a and K_a (Section 6.4);
9. determine the concentrations of all species in a solution of a polyprotic acid of known concentration (Section 6.5);
10. determine the pH of a strong base solution (Section 6.6);
11. write the K_b expression for a weak base (Sections 6.7);
12. determine the equilibrium concentrations of all species present in and the pH of solutions of weak bases (Sections 6.7);
13. determine one variable (the pH of the solution, the K_b of the base, or initial concentration of the base) in a solution of a weak base given the other two (Section 6.7);
14. convert between pK_b and K_b (Section 6.7);
15. convert between the K_a and K_b of a conjugate acid-base pair (Section 6.7);
16. define the term salt and predict whether a salt is neutral, basic, or acidic (Section 6.8);
and
17. determine the pH of a solution of an amphiprotic salt (Section 6.9).

6.9 EXERCISES

ACID-BASE TERMS AND A REVIEW OF ACID-BASE THEORY FROM CAMS CHAPTER 12

- Define a conjugate acid-base pair.
- Indicate the conjugate acid for each of the following:
a) OH^{1-} b) NO_2^{1-} c) NH_2^{1-} d) PO_4^{3-} e) HSO_3^{1-}
- Indicate the conjugate base for each of the following:
a) OH^{1-} b) H_2O_2 c) $\text{H}_2\text{PO}_4^{1-}$ d) H_3O^{1+} e) H_2SO_3
- Define a Lewis acid and a Brønsted acid. Give an example of a Lewis acid that is not a Brønsted acid.
- Are all Brønsted bases also Lewis bases? Explain.
- What distinguishes a weak acid from a strong one?
- Which of the following are Brønsted bases?
a) NaOH b) NaCl c) CH_3OH d) KCN e) KH_2PO_4
- Which of the following are Brønsted acids?
a) HClO b) CaH_2 c) $\text{CH}_3\text{CO}_2\text{H}$ d) KHSO_3 e) NH_4Cl
- Explain how the reaction $\text{Ag}^{1+} + \text{Cl}^{1-} \rightarrow \text{AgCl}$ is a Lewis acid-base reaction. Is it also a Brønsted acid-base reaction? Explain.
- Write Brønsted acid-base reactions or indicate *no reaction* if $K \ll 1$.
a) Hydrochloric acid and aqueous sodium hydroxide are mixed.
b) Aqueous potassium fluoride is added to perchloric acid.
c) Aqueous NH_4Cl is added to aqueous KHSO_4 .
d) Aqueous ammonia is added to hydrofluoric acid.
e) HNO_2 is added to aqueous KF .
- Write Brønsted acid-base reactions or indicate *no reaction* if $K \ll 1$.
a) Aqueous sodium sulfate is added to hydrobromic acid.
b) Aqueous NH_4Cl and aqueous KF are mixed.
c) Aqueous NaCN is added to a large excess of sulfurous acid.
d) Acetic acid and aqueous sodium hypochlorite are mixed.
e) Hydrogen sulfide is bubbled into water.
- Explain why HClO_4 is a strong acid, but HClO is a weak acid.
- Explain why HCl is a strong acid, but HF is a weak acid.
- What is the predominate phosphorus containing species in a solution prepared by adding sodium phosphate to an excess of carbonic acid?

- What is the predominate phosphorus containing species in a solution prepared by adding phosphoric acid to a large excess of ammonia?
- Define *amphiprotic*. Identify the amphiprotic species in Exercises 2 & 3.
- What is an *autoionization* reaction? Write the chemical equation for the autoionization of ammonia. H_3O^{1+} and OH^{1-} are the strongest acid and base that can exist in aqueous solutions because water reacts with any acids or bases that are stronger than these acids. This is known as the *leveling effect*. What are the strongest acid and base that can exist in liquid ammonia?

In the remaining exercises, assume a temperature of 25 °C if none is given; that is, assume that $K_w = 1.0 \times 10^{-14}$ if no temperature is given.

THE p-SCALE

- Determine the hydronium and hydroxide ion concentrations in the following solutions:
a) rainwater; pH = 5.3 b) household ammonia; pH = 11.9
c) vinegar; pH = 2.7 d) seawater; pH = 7.6
- Determine the hydronium and hydroxide ion concentrations in the following solutions:
a) detergent; pH = 10.3 b) stomach acid; pH = 2.4
c) beer; pH = 4.2 d) milk of magnesia; pH = 10.5
- Determine the pK_a of each of the following acids:
a) Hypiodous acid HIO $K_a = 2.3 \times 10^{-11}$
b) Iodic acid HIO_3 $K_a = 0.16$
- Determine the pK_a of each of the following acids:
a) Tartaric acid $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ $K_a = 1.0 \times 10^{-3}$
b) Boric acid H_3BO_3 $K_a = 5.8 \times 10^{-10}$
- Determine the K_a of each of the following acids:
a) Phenol $\text{C}_6\text{H}_5\text{OH}$ $\text{pK}_a = 10.00$
b) Ascorbic acid $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ $\text{pK}_a = 4.10$
- Determine the K_a of each of the following acids:
a) Hypobromous acid HOBr $\text{pK}_a = 8.64$
b) Saccharin $\text{HNC}_7\text{H}_4\text{SO}_3$ $\text{pK}_a = 11.68$
- What is the pK_b of the conjugate base of each acid in Exercise 20?
- What is the pK_b of the conjugate base of each acid in Exercise 21?

26. Determine the pH of solutions with the following pOH's:
 a) 12.32 b) 1.86 c) 4.37
27. What is the K_a of an acid whose conjugate base has the following pK_b ?
 a) 8.37 b) 12.66 c) 0.22

AUTOIONIZATION AND pH

28. Determine the pH and pOH of solutions with the following hydronium ion concentrations:
 a) 3.4×10^{-6} M b) 4.7×10^{-3} M c) 8.8×10^{-10} M
29. Determine the pH and pOH of solutions with the following hydroxide ion concentrations:
 a) 7.5×10^{-8} M b) 3.9×10^{-4} M c) 1.0×10^{-12} M
30. What is the pH of 1.0×10^{-8} M HCl at 25 °C? Hint: At such a low acid concentration water is the primary source of H_3O^{1+} in the solution.
31. The solubility of $Al(OH)_3$ in water is 2.9×10^{-9} M at 25 °C. What is the pH of a saturated solution of $Al(OH)_3$ at 25 °C? Hint: What is the primary source of hydroxide ion in the solution?
32. The pH of water at 100 °C is 6.13. What is the value of K_w at 100 °C?

Exercises 33-36 deal with solutions at 37 °C, the temperature of the human body. $K_w = 2.42 \times 10^{-14}$ at this temperature.

33. What is pH of a neutral solution at 37 °C?
34. What is the K_b of a base if $K_a = 5.0 \times 10^{-10}$ at 37 °C for its conjugate acid?
35. What is the pK_b of a base if the pK_a of its conjugate acid is 5.21 at 37 °C?
36. The hydroxide ion concentration in a weak base solution at 37 °C is 0.024. What is the pH of the solution?

STRONG ACIDS AND STRONG BASES

37. What is the pH of each of the following aqueous solutions?
 a) 0.066 M HCl b) 0.21 M KOH c) 0.11 M $Ba(OH)_2$
38. What is the pH of each of the following aqueous solutions?
 a) 0.57 M NaOH b) 1.3×10^{-4} M HNO_3 c) 2.1 M KOH
39. To what volume must 5.0 mL of 6.0 M HCl be diluted to prepare a solution with pH = 1.22?

40. How much water must be added to 25 mL of an HCl solution with a pH = 2.46 to make a pH = 4.00 solution? Assume the volumes are additive.
41. What volume of HCl gas measured at 300. K and 1 atm is required to prepare 5.0 L of hydrochloric acid with a pH of 3.84?
41. 512 mL of HCl gas at 300. K and 886 torr is dissolved in water. What is the pH of the resulting solution if the total volume is 653 mL?
43. How many grams of $Ba(OH)_2$ would have to be dissolved in water to prepare 500.0 mL of a pH = 9.80 solution?
44. To what volume should 2.6 mL of 0.11 M NaOH be diluted in order to make a pH = 12.00 solution?

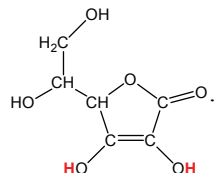
WEAK ACIDS

45. What is the 5% rule?
46. Use the 5% rule to determine if the equilibrium concentration of the acid can be approximated by its makeup concentration.
 a) 2.0 M HF b) 2.0×10^{-4} M H_2S c) 0.10 M HNO_2
47. Use the 5% rule to determine if the equilibrium concentration of the acid can be approximated by its makeup concentration.
 a) 0.80 M cyanic acid ($HCNO$, $pK_a = 3.46$)
 b) 4.4×10^{-3} M hydrazoic acid (HN_3 , $pK_a = 4.6$)
 c) 3.0 M arsenic acid (H_3AsO_4 , $pK_a = 2.26$)
48. Calculate the pH of a 0.25 M phenol (C_6H_5OH , $K_a = 1.0 \times 10^{-10}$), which is often used as an antiseptic.
49. What is the pH of vinegar, a 4.5% solution of acetic acid? Assume the density of the solution is $1.0 \text{ g} \cdot \text{mL}^{-1}$.
50. The pH of a 0.030 M benzoic acid solution is 2.85. What are K_a and pK_a of benzoic acid? What are K_b and pK_b of the benzoate ion?
51. What is the hypochlorite ion concentration in a 0.14 M solution of HOCl? What is the pH of the solution?
52. What is the fluoride ion concentration in 2.0 M HF?
53. What is the pH of 0.044 M HF?
54. What is the phosphate ion concentration in 0.066 M H_3PO_4 ?
55. What is the K_a of chloroacetic acid, $ClCH_2COOH$, if a 0.085-M solution has a pH of 2.00?

56. What is the K_a of an acid if a 0.21-M solution is 3.4% dissociated?
57. What is the pK_a of iodic acid if the iodate ion concentration in a 0.066-M solution of HIO_3 is 0.050 M?
58. What is the percent dissociation of 0.048 M propanoic acid ($pK_a = 4.86$)?
59. What is the percent dissociation of 0.26 M uric acid ($pK_a = 3.89$)?
60. What is the percent dissociation of 0.15 M iodic acid ($pK_a = 0.77$)?
61. What mass of ammonium chloride is required to prepare 500. mL of a solution with a pH of 4.62?
62. What mass of potassium hydrogensulfate is required to make 350. mL of a solution with a pH of 2.50?

POLYPROTIC ACIDS

63. Vitamin C is ascorbic acid, $H_2C_6H_6O_6$,



Calculate the pH, $[C_6H_8O_6]$, $[C_6H_7O_6^{1-}]$ and $[C_6H_5O_6^{2-}]$ in a 0.075-M solution of ascorbic acid.

64. Oxalic acid ($H_2C_2O_4$) is a diprotic acid with two carboxylic acid group that occurs naturally in some plants. Calculate the pH and the concentrations of all species present in a 0.25-M solution.
65. What are concentrations of all species in a 0.16-M solution of malonic acid ($H_2C_3H_2O_4$)? $K_1 = 1.5 \times 10^{-3}$ and $K_2 = 2.0 \times 10^{-6}$

WEAK BASES & BASIC SALTS

66. Calculate the pH of a 0.50-M solution of pyridine (C_6H_5N , $K_b = 1.7 \times 10^{-9}$).
67. Industrial bleach is 15% $NaClO$ by mass. What is the hypochlorous acid concentration in industrial bleach? Household bleach is a 5.25% solution of $NaOCl$. What is its pH? Assume a density of $1.0 \text{ g} \cdot \text{mL}^{-1}$ for each solution.
68. What are the HF concentration and pH of 0.32 M KF ?
69. What are the NH_4^{1+} concentration and pH of a 0.16-M solution of NH_3 ?
70. The pH of a 0.068-M solution of methyl amine (CH_3NH_2) is 11.72. What are the K_b and pK_b of methylamine? What are the K_a and pK_a of the methylammonium ion?
71. The pH of 0.083 M aniline ($C_6H_5NH_2$) is 8.76. What are its K_b and pK_b ?
72. How many grams of KCN are required to prepare 250. mL of a pH = 11.15 solution?
73. What percent of the ammonia molecules in a 0.12-M solution have reacted to produce ammonium ions?
74. What percent of the acetate ions in a 0.060-M solution of potassium acetate react to produce acetic acid molecules?
75. What are the concentrations of all phosphorus containing species in 0.084 M K_3PO_4 ? What is the pH of the solution?
76. What are the concentrations of all carbon-containing species in 0.041 M K_2CO_3 ?

SALTS

77. Define the term *salt*. Give an example of a neutral, a basic, and an acidic salt.
78. Explain why all anions are not bases in water. Give examples of two anions that are not bases for different reasons.
79. Indicate whether each salt is acidic, basic, or neutral.
- | | | |
|--------------|--------------|--------------|
| a) K_2SO_4 | b) K_2SO_3 | c) $KHSO_4$ |
| d) K_2CO_3 | e) $KClO$ | d) NH_4ClO |
80. Indicate whether each salt is acidic, basic, or neutral.
- | | | |
|------------|-------------------|-------------------|
| a) NH_4F | b) NH_4HSO_4 | c) $(NH_4)_3PO_4$ |
| d) KNO_3 | e) $(NH_4)_2CO_3$ | f) NaF |
81. What is the pH of each of the following salt solutions?
- | | | |
|--------------------|------------------|--------------------|
| a) 0.12 M NH_4Cl | b) 0.096 M KCN | c) 0.10 M $KHSO_3$ |
|--------------------|------------------|--------------------|
82. What is the pH of each of the following salt solutions?
- | | | |
|-----------------|-----------------------|-----------------------|
| a) 0.12 M KCl | b) 0.086 M KH_2PO_4 | c) 0.088 M Na_2SO_3 |
|-----------------|-----------------------|-----------------------|

CHAPTER 7

Mixtures of Acids and Bases

7.0 Introduction

7.1 The Common-Ion Effect

7.2 Buffers

7.3 Acid-Base Composition from Reactant Amounts

7.4 Acid-Base Composition from Equilibrium pH

7.5 Acid-Base Indicators

7.6 Chapter Summary and Objectives

7.7 Exercises

7.0 INTRODUCTION

In Chapter 6, we examined the equilibrium concentrations in solutions of acids and solutions of bases. In this chapter, we continue our discussion of acids and bases by focusing on the equilibrium concentrations of solutions formed by mixing acids and bases.

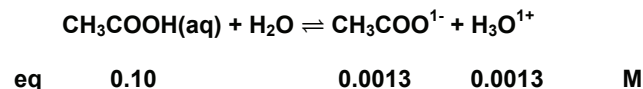
THE OBJECTIVES OF THIS CHAPTER ARE TO:

- explain the common ion effect;
- define buffers and explain their use;
- show how the composition of a mixture varies with its pH;
- describe titration curves, how they are generated, and what they mean; and
- describe acid-base indicators and explain their function.

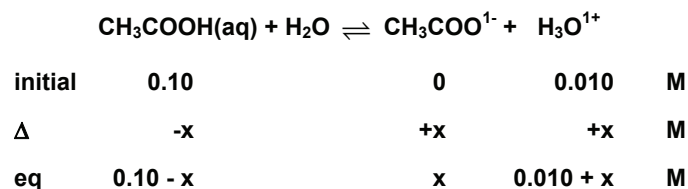
7.1 THE COMMON-ION EFFECT

When solutions are prepared in such a way that there are two or more separate sources of an ion in equilibrium, then that ion is referred to as a **common ion**. In this and the following chapters, we will have occasion to deal with the effect on an equilibrium mixture caused by the addition of a common ion. The effect can readily be predicted with Le Châtelier's principle, which predicts that the composition of the mixture shifts to counteract the addition. Consequently, *the addition of a common ion always produces more of the substances on the opposite side of the equilibrium and reduces the concentrations of the other substances on the same side of the equilibrium.*

In Example 6.7, we determined that the equilibrium concentrations in a 0.10 M solution of acetic acid are the following:



When hydrochloric acid is added to acetic acid, the H_3O^{1+} ion is common to both solutions, so it is a common ion. The additional hydronium ion from the hydrochloric acid reacts with the acetate ion above to increase the concentration of acetic acid and decrease the concentration of acetate ion. Thus, less acetic acid reacts with water to produce acetate ion in the presence of the common ion, or, said slightly differently, *addition of hydronium ion suppresses (reduces the extent of) the dissociation of the weak acid* as a result of the common-ion effect. For example, consider the following reaction table for the dissociation of 0.10 M acetic acid in the presence of 0.010 M hydronium ion:



$$K_a = \frac{[\text{CH}_3\text{COO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{CH}_3\text{COOH}]} = \frac{x(0.010 + x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

The common ion suppresses the dissociation, so $x < 0.0013$ M - its value in the absence of excess hydronium ion. If x is negligible compared to 0.01 then the equilibrium concentrations of acetic acid and hydronium ion are $[\text{CH}_3\text{COOH}] = 0.10 - x = 0.10$ M and $[\text{H}_3\text{O}^{1+}] = 0.01 + x = 0.01$ M. Solving the K_a expression for x , we obtain the following:

$$x = [\text{CH}_3\text{COO}^{1-}] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^{1+}]} = (1.8 \times 10^{-5}) \left(\frac{0.10}{0.010} \right) = 1.8 \times 10^{-4} \text{ M}$$

The hydronium ion concentration in the final solution is $0.010 + 0.00018 = 0.010$ M as x is negligible. We conclude that, *in a solution containing both a weak acid and a strong acid, the hydronium ion produced by the weak acid can usually be ignored because of the common-ion effect*. The same conclusion can be drawn for a solution containing both a strong base and a weak base. *The amount of hydroxide ion produced by a weak base in the presence of a strong base is usually negligible in determining the hydroxide ion concentration.*

7.2 BUFFERS

In Chapter 6, we treated in some detail four types of acid-base solutions: strong acid, strong base, weak acid, and weak base. We now treat buffers, the last type of acid-base solution to be considered. A buffer is defined in the dictionary as a “device that softens the shock of a blow.” A chemical buffer serves much the same purpose: it softens the effect of the shock caused by the addition of a strong acid or base. A **buffer** is a solution of a weak acid and its conjugate base in *comparable* and *appreciable* amounts. Buffers are very common both in and outside the chemistry laboratory. For example, aspirin is an acid that can upset the stomach, but Bufferin[®] contains buffers to reduce the pH changes that ordinarily accompany the addition of an acid. Much of the maintenance involved in the upkeep of an aquarium involves maintaining proper buffer levels in the water to assure that the pH stays in a range that is safe for the fish. Blood is also buffered, which is why it maintains a pH of about 7.4 even though many acid-base reactions take place in it.

Buffers are able to minimize changes in pH because they contain both a weak acid and a weak base. Thus, if a strong acid is added to a buffered solution, it reacts with the weak base component of the buffer, and if a strong base is added to a buffered solution, it reacts with the weak acid component of the buffer. Either way, the effect of the addition of hydroxide or hydronium ion on the solution is dramatically reduced because these strong acids and bases are converted into much weaker acids and bases by the action of the buffer.

Buffers contain both a weak acid and a weak base, so both K_a and K_b must be satisfied, and either can be used to determine the composition of the equilibrium mixture. However, pH is more common than pOH, so we use the acid dissociation reaction to discuss buffered solutions. Consider an acetic acid/acetate ion buffer in which the initial concentrations of the acid (c_a) and its conjugate base (c_b) are comparable. The reaction table for the acid dissociation of acetic acid in the presence of acetate ion has the following form:

	$\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^{1-} + \text{H}_3\text{O}^{1+}$			
initial	c_a	c_b	0	M
Δ	-x	+x	+x	M
Eq	$c_a - x$	$c_b + x$	x	M

The acetate ion suppresses the acid dissociation due to the common-ion effect, so x is very small. Thus, $c_a - x \sim c_a$ and $c_b + x \sim c_b$. The equilibrium constant expression is

$$K_a = \frac{[\text{CH}_3\text{COO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{CH}_3\text{COOH}]} = \frac{(c_b + x)x}{(c_a - x)} = \frac{c_b}{c_a} x = \frac{n_b}{n_a} x$$

n_b and n_a are the numbers of moles of base and acid, respectively. The ratio of concentrations is equal to the ratio of moles because the volumes cancel in the ratio:

$$\frac{c_b}{c_a} = \frac{n_b/V}{n_a/V} = \frac{n_b}{n_a}$$

Solving for x yields the hydronium ion concentration.

$$[\text{H}_3\text{O}^{1+}] = x = K_a \times \frac{c_a}{c_b} = K_a \times \frac{n_a}{n_b} \quad \text{Eq. 7.1}$$

Taking the negative logarithm of both sides of Equation 7.1, we obtain the pH of a buffer solution as a function of the $\text{p}K_a$ of the acid and the ratio of the numbers of moles or concentrations of the base and the acid.

$$\text{pH} = \text{p}K_a + \log\left(\frac{c_b}{c_a}\right) = \text{p}K_a + \log\left(\frac{n_b}{n_a}\right) \quad \text{Eq. 7.2}$$

Equation 7.2 is known as the **Henderson-Hasselbalch equation**.

Example 7.1

What is the pH of a solution that is 0.600 M potassium acetate and 0.750 M acetic acid?

This is a solution of a weak acid (acetic acid) and its conjugate base (acetate ion) in comparable and appreciable amounts. Consequently, it is a buffered solution, and Equation 7.2 can be used to determine the pH. The $\text{p}K_a$ of acetic acid is obtained from Appendix C to be 4.74. Substitution into Equation 7.2 yields

$$\text{pH} = \text{p}K_a + \log\left(\frac{c_b}{c_a}\right) = 4.74 + \log\left(\frac{0.600}{0.750}\right) = 4.64$$

BUFFER ACTION

Buffers act to protect the solution from drastic pH changes resulting from the addition of hydronium or hydroxide ions by converting the added ions into a weak acid or weak base. Unreacted hydronium or hydroxide ions produce large changes in pH, so the buffer must be in excess to function properly, which is why it must be present in appreciable amounts. When a strong acid is added to a buffer, it reacts with the weak base, but when a strong base is added, it reacts with the weak acid. *Acid-base reactions involving OH^{1-} or H_3O^{1+}*

PRACTICE EXAMPLE 7.1

What is the pH of a buffer prepared by dissolving 23.5 g of KNO_2 ($M_m = 85.1 \text{ g}\cdot\text{mol}^{-1}$) in 1.25 L of 0.0882 M HNO_2 ?

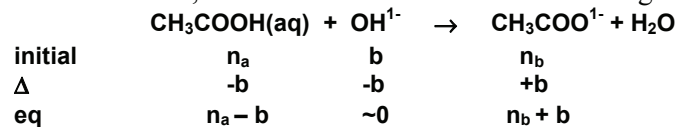
$\text{p}K_a$ of HNO_2 = _____ from Appendix C

moles of KNO_2 in solution :

moles of HNO_2 in solution = _____ mol

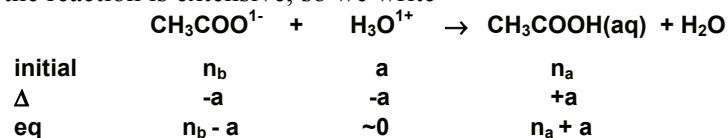
pH = _____ mol

ions are always extensive, so essentially all of the limiting reactant disappears, i.e., the delta line is known. Consider the case where **b** moles of OH¹⁻ ion are added to a buffer solution that contains **n_a** moles of acetic acid and **n_b** moles of acetate ion. The strong base reacts extensively with the weak acid in the buffer. Acetic acid must be in excess (**n_a** > **b**) to have proper buffer function, so the reaction table has the following form:



The reaction replaces the OH¹⁻ ion, a strong base, with CH₃COO¹⁻ ions, a weak base, which causes the pH change caused by the addition of the strong base to be considerably less than it would have been in the absence of the buffer.

If hydronium ion is added to the buffer solution, the weak base, which must be in excess, goes to work. The reaction table for the addition of **a** moles of acid to a buffer solution containing **n_b** moles of weak base and **n_a** moles of weak acid has the following form. Again, the reaction is extensive, so we write



The effect is to replace the strong acid with a weak acid, which minimizes the drop in pH.

Example 7.2

By how much would the pH of 200. mL of water change when 10. mL of 6.0 M NaOH is added to it?

We assume pure water at 25 °C, so the initial pH is 7.00. We determine the hydroxide ion concentration (the final solution contains 60. mmol of OH¹⁻ in 210 mL of solution), convert that to a pOH, and the pOH into the pH.

$$[\text{OH}^{1-}] = \frac{60 \text{ mmol}}{210 \text{ mL}} = 0.29 \text{ M}$$

$$\text{pOH} = -\log(0.29) = 0.54; \text{pH} = 14.00 - 0.54 = 13.46$$

The final pH is 13.46 and the initial pH was 7.00, so the pH change is

$$\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}} = 13.46 - 7.00 = 6.46$$

Example 7.3

By how much would the pH of 200. mL of the buffer described in Example 7.1 change when 10. mL of 6.0 M NaOH is added?

Dilution effects of mixing two solutions can be avoided by doing the problem in moles. Thus, we first determine the initial number of moles (or millimoles since the volumes are in mL) of the relevant species.

$$(200. \text{ mL})(0.750 \text{ mmol CH}_3\text{COOH/mL}) = 150. \text{ mmol CH}_3\text{COOH}$$

$$(200. \text{ mL})(0.600 \text{ mmol CH}_3\text{COO}^{\text{1-}}/\text{mL}) = 120. \text{ mmol CH}_3\text{COO}^{\text{1-}}$$

$$(10. \text{ mL})(6.0 \text{ mmol OH}^{\text{1-}}/\text{mL}) = 60. \text{ mmol OH}^{\text{1-}}$$

The reaction table for this extensive reaction is

	$\text{CH}_3\text{COOH(aq)} + \text{OH}^{\text{1-}}$		\rightleftharpoons	$\text{CH}_3\text{COO}^{\text{1-}} + \text{H}_2\text{O}$	
initial	150	60		120	mmol
Δ	-60	-60		+60	mmol
final	90	~ 0		180	mmol

The final mixture still contains appreciable and comparable amounts of the acid and its conjugate base, so it can still be treated as a buffer solution.

$$\text{pH} = \text{pK}_a + \log\left(\frac{n_b}{n_a}\right) = 4.74 + \log\left(\frac{180}{90}\right) = 5.04$$

The addition of the base caused the pH of the solution to rise from an original pH of 4.64 (Example 7.1) to a final pH of 5.04.

$$\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}} = 5.04 - 4.64 = 0.40$$

The function of a buffer can be seen clearly by comparing the results of Examples 7.2 and 7.3. Adding 60 mmol $\text{OH}^{\text{1-}}$ to 200 mL of water resulted in $\Delta\text{pH} = 6.46$, which implies a change in hydronium ion concentration by a factor of $10^{6.46}$, which is 2.9×10^6 or about three million. Adding the same 60 mmol of hydroxide to 200 mL of the buffer increased the pH by only 0.40 pH units, which is change in hydronium ion concentration by a factor of $10^{0.40} = 2.5$. Thus, adding 60 mmoles of hydroxide to this buffer decreases hydronium ion three-fold, while adding it to water decreases it by three million-fold! The effect of a strong acid on a buffer solution is examined in Example 7.4.

When a strong acid is added to a buffer, the resulting solution will be a buffer as long as the hydronium ion is the limiting reactant, but if the hydronium ion is in excess, then the resulting solution is a strong acid solution, and the pH is determined from the concentration of the excess hydronium ion. Similar considerations apply to the addition of a strong base to a buffer: if the hydroxide ion is in excess, the resulting solution is a strong base and the pH is determined from the concentration of the excess hydroxide ion.

Example 7.4

By how much would the pH of 200. mL of the buffer described in Example 7.1 change when 10. mL of 6.0 M HCl is added?

The initial number of mmol of hydronium is (10. mL)(6.0 mmol H₃O¹⁺/mL) = 60. mmol H₃O¹⁺. (See Example 7.3 for the determination of the initial numbers of millimoles of acetic acid and acetate ion.) The reaction table for the extensive reaction between the added acid and the base component of the buffer is

	H ₃ O ¹⁺	+ CH ₃ COO ¹⁻	→ CH ₃ COOH(aq)	+ H ₂ O	
initial	60	120	150		mmol
Δ	-60	-60	+60		mmol
Final	~0	60	210		mmol

The resulting solution is still a buffer because it still has appreciable and comparable amounts of the weak acid and its conjugate base. Thus, Equation 7.2 can be used to obtain the pH.

$$\text{pH} = \text{pK}_a + \log\left(\frac{n_b}{n_a}\right) = 4.74 + \log\left(\frac{60.}{210.}\right) = 4.20$$

The initial pH was 4.64 (Example 7.1), so the addition of the strong acid results in a decrease of 0.44 pH units.

Example 7.5

What is the pH of a solution prepared by adding 30.0 mL of 12.0 M HCl to 576 mL of a buffer solution that is 0.600 M in HClO and 0.500 M in KClO?

The strong acid reacts with ClO¹⁻. The number of millimoles of each substance is determined by multiplying its volume by its molarity. The reaction table is

	H ₃ O ¹⁺	+ ClO ¹⁻	→ HClO(aq)	+ H ₂ O	
Initial	360	288	346		mmol
Δ	-288	-288	+288		mmol
final	72	~0	634		mmol

There is insufficient buffer capacity, so the resulting solution is a strong acid.*

$$[\text{H}_3\text{O}^{1+}] = \frac{72 \text{ mmol}}{606 \text{ mL}} = 0.12 \text{ M}; \text{pH} = -\log(0.12) = 0.92$$

The pK_a of HClO is 7.46, so the pH of the initial buffer is $\text{pH} = 7.46 + \log\left(\frac{0.500}{0.600}\right) = 7.38$

Thus, addition of the acid lowered the pH by 6.46 units, which is over a million-fold increase in [H₃O¹⁺]. The large increase is due to an insufficient buffer capacity.

PRACTICE EXAMPLE 7.2

A buffer is 0.18 M in NO₂¹⁻ and 0.22 M in HNO₂.

a) What is the pH of the buffer?

pH = _____

b) What is the pH of a solution prepared by mixing 5.0 mL of 6.0 M NaOH with 250. mL of the buffer?

Reaction Table

in

Δ

Eq

Type of solution at equilibrium: _____

pH = _____

c) What is the pH of a solution prepared by mixing 15.0 mL of 1.0 M HCl with 150. mL of the buffer?

Reaction Table

in

Δ

Eq

Type of solution at equilibrium: _____

pH = _____

* Recall that the weak acid can be ignored in the presence of the strong acid due to the common ion effect.

PREPARING BUFFER SOLUTIONS

There must be appreciable amounts of the acid and its conjugate base in a buffer to assure that it has acceptable **buffer capacity**, the amount of hydronium or hydroxide ion that can be buffered without destroying the buffer's effectiveness. The buffer capacity of the buffer in Example 7.5 was exceeded because there was insufficient weak base in the buffer to handle the added acid, so the additional acid resulted in a large change in pH. A buffer solution has a large buffer capacity if it contains a large number of moles of weak acid and conjugate base; *i.e.*, if the weak acid and weak base are present in appreciable amounts.

A buffer functions best when the addition of large amounts of acid or base result in only small pH changes. The pH range over which the buffer is effective is called the **buffer range**. Figure 7.1 shows the relationship between pH and the mole fractions of the acid and the base in an acetic acid/acetate ion buffer. The buffer range is the pH range over which the mole fractions change most dramatically with pH. This assures that the pH change is small even when there is substantial reaction (large changes in mole fractions). This region is highlighted by the yellow box in Figure 7.1. The center of the buffer range is where the two mole fractions (or concentrations) are equal ($c_A/c_B = 1$). Application of Equation 7.2 to the midpoint of the buffer range along with the fact that $\log 1 = 0$ yields

$$\text{pH} = \text{pK}_a + \log 1 = \text{pK}_a$$

As shown in Figure 7.1, buffers operate acceptably in the range where the mole fractions of the acid and base lie between ~ 0.1 and ~ 0.9 , so the effective buffer range is usually assumed to be $0.1 < c_a/c_b < 10$. $\log(10) = -\log(0.10) = 1$, so we conclude that *buffers are effective within one pH unit of their pK_a , i.e.,*

$$(\text{pK}_a - 1) \leq \text{effective pH range for a buffer} \leq (\text{pK}_a + 1)$$

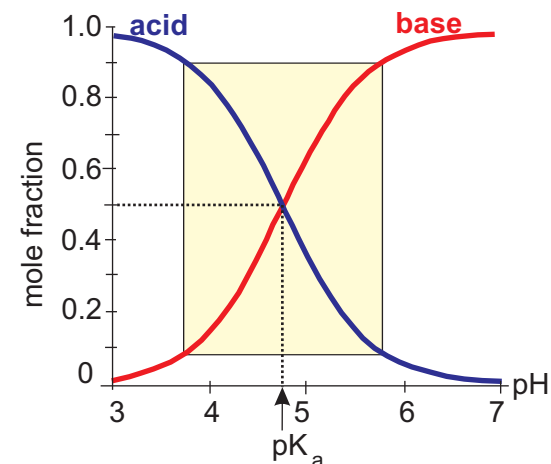


Figure 7.1 Mole fractions of acetic acid and acetate ion as a function of pH

The effective buffer range is indicated by the yellow box.

Example 7.6

Select a good buffer system from Appendix C for each of the following pH's.

pH = 4.50

The pK_a of the weak acid should fall between 3.5 and 5.5. There are 8 acids in Appendix C with pK_a 's in this range. Two choices include $\text{HC}_2\text{H}_3\text{O}_2/\text{C}_2\text{H}_3\text{O}_2^{1-}$ ($\text{pK}_a = 4.74$) and $\text{HCHO}_2/\text{CHO}_2^{1-}$ ($\text{pK}_a = 3.74$)

pH = 8.50

There are four weak acids in Appendix C with pK_a 's between 7.5 and 9.5. Some examples are $\text{HBrO}/\text{BrO}^{1-}$ ($\text{pK}_a = 8.70$), $\text{NH}_4^{1+}/\text{NH}_3$ ($\text{pK}_a = 9.25$) and $\text{H}_3\text{BO}_3/\text{H}_2\text{BO}_3^{1-}$ ($\text{pK}_a = 9.27$)

Once the conjugate acid-base pair has been selected, the ratio of their concentrations or moles that produces the desired pH must be determined by Equation 7.1, Equation 7.2, or Equation 7.3, which is obtained by rearranging either of those equations.

$$\frac{n_b}{n_a} = \frac{c_b}{c_a} = K_a \times 10^{\text{pH}} \quad \text{Eq. 7.3}$$

The ratio of the number of moles (or molarities) of base to acid required to produce a given pH equals the K_a of the acid times ten raised to the desired pH. Direct mixing of a conjugate acid and base in the ratio specified in Equation 7.3 is demonstrated in Example 7.7. It is the first of three methods to be demonstrated in this chapter.

Example 7.7

How many grams of K_2HPO_4 ($M_m = 174.17 \text{ g}\cdot\text{mol}^{-1}$) must be added to 1.00 L of 0.860 M $\text{H}_2\text{PO}_4^{1-}$ to prepare a pH = 7.00 buffer?

Equations 7.1, 7.2 or 7.3 can be used to do the problem. We will use Equation 7.3 here to demonstrate its utility. The $\text{H}_2\text{PO}_4^{1-}$ ion is the acid in this phosphate buffer, while HPO_4^{2-} is the base, so we get the K_a and $\text{p}K_a$ of $\text{H}_2\text{PO}_4^{1-}$ from Appendix C. $K_a = 6.2 \times 10^{-8}$ and $\text{p}K_a = 7.21$, and pH is given as 7.00. Substitution into Equation 7.3 yields

$$\frac{n_b}{n_a} = 6.2 \times 10^{-8} \times 10^{7.00} = \frac{0.62 \text{ mol HPO}_4^{2-}}{1 \text{ mol H}_2\text{PO}_4^{1-}}$$

Alternatively, n_b/n_a can be found with Equation 7.2 and the $\text{p}K_a$ as follows:

$$\log \frac{n_b}{n_a} = \text{pH} - \text{p}K_a = 7.00 - 7.21 = -0.21; \quad \frac{n_b}{n_a} = 10^{-0.21} = \frac{0.62 \text{ mol HPO}_4^{2-}}{1 \text{ mol H}_2\text{PO}_4^{1-}}$$

Next, determine n_a with the given volume and acid concentration.

$$n_a = 1.00 \text{ L sol'n} \times \frac{0.860 \text{ mol H}_2\text{PO}_4^{1-}}{1 \text{ L sol'n}} = 0.860 \text{ mol H}_2\text{PO}_4^{1-}$$

The given number of moles of acid is converted to mass of K_2HPO_4 with the ratio of base to acid, the number of moles of HPO_4^{2-} ion in a mole of K_2HPO_4 , and the molar mass of the base, K_2HPO_4 .

$$0.860 \text{ mol H}_2\text{PO}_4^{1-} \times \frac{0.62 \text{ mol HPO}_4^{2-}}{1 \text{ mol H}_2\text{PO}_4^{1-}} \times \frac{1 \text{ mol K}_2\text{HPO}_4}{1 \text{ mol HPO}_4^{2-}} \times \frac{174.17 \text{ g K}_2\text{HPO}_4}{1 \text{ mol K}_2\text{HPO}_4} = 93 \text{ g K}_2\text{HPO}_4$$

PRACTICE EXAMPLE 7.3

Select a conjugate acid-base pair from Appendix H to use to prepare a solution buffered to pH = 9.80.

buffer acid: _____ buffer base: _____

How many moles of the base would have to be added to 500. mL of a 0.222-M solution of the acid to prepare the buffer?

$\text{p}K_a =$ _____ from Appendix C

Use Equation 7.2 to calculate the ratio of number of moles of base to acid.

$$\log \left(\frac{n_b}{n_a} \right) =$$

$$\frac{n_b}{n_a} =$$

from the problem, $n_a =$ _____ = _____ mol

$n_b =$ _____ = _____ mol

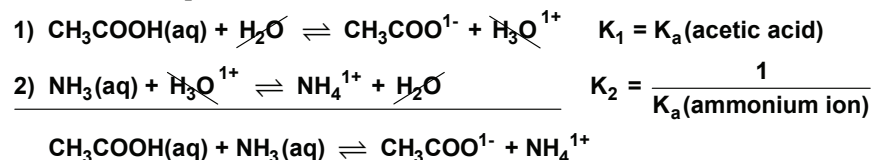
7.3 ACID-BASE COMPOSITION FROM REACTANT AMOUNTS

There are four types of acid-base reactions:

1. weak acid - weak base
2. strong acid - strong base
3. weak acid - strong base
4. strong acid - weak base

WEAK ACID - WEAK BASE REACTIONS

Reactions types 2-4 involve a strong acid and/or a strong base, so they are all extensive. However, the equilibrium constant for a weak acid and a weak base can vary from very large to very small, so it must be determined before the equilibrium composition can be determined. The equilibrium constants for weak acid-weak base reactions can be determined from the K_a 's of the reacting and produced acids because any weak acid-weak base reaction can be expressed as the sum of the acid dissociation reaction of the reacting acid and the reverse of the acid dissociation reaction of the produced acid. For example, summing the chemical equations for the acid dissociation of CH_3COOH (the reacting acid) and the reverse of the dissociation equation for NH_4^{1+} (the produced acid) produces the overall chemical equation for the reaction of acetic acid and ammonia:



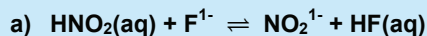
Reaction 2 is the reverse of the acid dissociation reaction of the produced acid (ammonium ion), so its equilibrium constant is the reciprocal of the K_a of the produced acid. In the addition of the two reactions, the H_2O molecules and H_3O^{1+} ions on each side of the reaction cancel to produce the desired acid-base reaction. The reaction is expressed as the sum of two reactions, so its equilibrium constant is equal to the product of the two equilibrium constants. We conclude that *the equilibrium constant of any acid-base reaction is the ratio of the reacting acid K_a to the produced acid K_a .*

$$K = K_1 \times K_2 = \frac{K_a(\text{reacting acid})}{K_a(\text{produced acid})} \quad \text{Eq. 7.4}$$

Equilibrium constants for weak acid-weak base reactions vary from very large when the reacting acid is much stronger than the produced acid to very small when the produced acid is the stronger acid. The composition of the equilibrium mixture varies accordingly.

Example 7.8

Indicate the equilibrium constant for each of the following reactions:

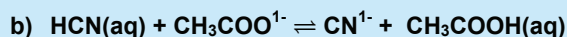


First, identify the reacting and produced acids, then obtain their K_a values from Appendix C, then use Equation 7.4 to obtain the equilibrium constant.

Reacting Acid: HNO_2 , $K_a = 4.0 \times 10^{-4}$ Produced Acid: HF , $K_a = 7.2 \times 10^{-4}$

$$K = \frac{K_a(\text{HNO}_2)}{K_a(\text{HF})} = \frac{4.0 \times 10^{-4}}{7.2 \times 10^{-4}} = 0.56$$

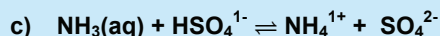
If the two acids have similar acid strengths, then $K \sim 1$.



Reacting Acid: HCN , $K_a = 4.0 \times 10^{-10}$ Produced Acid: CH_3COOH , $K_a = 1.8 \times 10^{-5}$

$$K = \frac{K_a(\text{HCN})}{K_a(\text{CH}_3\text{COOH})} = \frac{4.0 \times 10^{-10}}{1.8 \times 10^{-5}} = 2.2 \times 10^{-5}$$

If the reacting acid is much weaker than the produced acid, then $K \ll 1$.



Reacting Acid: HSO_4^{1-} , $K_a = 1.2 \times 10^{-2}$ Produced Acid: NH_4^{1+} , $K_a = 5.6 \times 10^{-10}$

$$K = \frac{K_a(\text{HSO}_4^{1-})}{K_a(\text{NH}_4^{1+})} = \frac{1.2 \times 10^{-2}}{5.6 \times 10^{-10}} = 2.1 \times 10^7$$

If the reacting acid is much stronger than the produced acid, then $K \gg 1$.

PRACTICE EXAMPLE 7.4

What is the NO_2^{1-} ion concentration in a solution prepared by mixing 75 mL of 0.10 M HNO_2 and 75 mL of 0.10 M KF ?

Initial concentrations after dilution of mixing:

$$[\text{HNO}_2] = [\text{F}^{1-}] = \text{_____ M}$$

Let x = change in concentration of $[\text{NO}_2^{1-}]$ and construct the reaction table:

rxn:

in

Δ

eq

value of K = _____ (From Example 7.8)

Equilibrium constant expression in terms of x :

$$K = \text{_____} = \text{_____}$$

Take square root of both sides.

Solve for x .

$$x = [\text{NO}_2^{1-}] = \text{_____}$$

* An extra significant figure has been included to avoid rounding errors.

Example 7.9

What are the equilibrium concentrations in a solution prepared by mixing 50.0 mL each of 0.10 M HBrO and 0.10 M NH_3 ?

The chemical equation: $\text{HBrO}(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{BrO}^{1-} + \text{NH}_4^{1+}$

The equilibrium constant for the reaction: $K = \frac{K_a(\text{HBrO})}{K_a(\text{NH}_4^{1+})} = \frac{2.0 \times 10^{-9}}{5.6 \times 10^{-10}} = 3.57^*$

K is not large, so the extent of reaction is unknown. Mixing the two solutions doubles their volumes, which dilutes each by a half. The reaction table therefore has the following form.

	HBrO(aq)	+	$\text{NH}_3(\text{aq})$	\rightleftharpoons	BrO^{1-}	+	NH_4^{1+}	
in	0.050		0.050		0		0	M
Δ	-x		-x		+x		+x	M
eq	0.050-x		0.050-x		x		x	M

The equilibrium constant expression: $K = 3.57 = \frac{x^2}{(0.050-x)^2}$

Taking the square-root of both sides: $K = \sqrt{3.57} = 1.89 = \frac{x}{(0.050-x)}$

$$x = \frac{0.0945}{2.89} = 0.033 \text{ M} = [\text{BrO}^{1-}] = [\text{NH}_4^{1+}]; [\text{HBrO}] = 0.050 - 0.033 = 0.017 \text{ M}$$

Check: $\frac{(0.0327)^2}{(0.0173)^2} = 3.57$ * ✓ The calculated concentrations reproduce K, so the algebra is correct. Note that extra significant figures are used in all concentrations.

* Extra significant digits are included in the concentrations to avoid rounding errors. Using the concentrations to two significant digits results in $K = 3.8$.

The three remaining types of acid-base reactions all involve a strong acid and/or a strong base, so they are representative of the reactions in most acid-base titrations.[†] Titrations are most commonly used to find the equivalence point of the reaction. However, a **titration curve**, which is a plot of solution pH versus the volume of titrant added, is an excellent way to monitor the composition of the solution, so our discussions of the remaining acid-base reactions will also include a titration curve for each type.

[†] Titrations were introduced in Section 2.4.

Reactions containing a strong acid and/or strong base are all characterized by large equilibrium constants, so, unlike the reaction in Example 7.9, the limiting reactant essentially disappears completely and there are no unknowns in the reaction table. The following abbreviations are used in order to discuss the various mixing problems in the most general way:

n_a = number of moles of acid added

n_b = number of moles of base added

STRONG ACID - STRONG BASE REACTIONS

Strong acids react as H_3O^{1+} in water and strong bases react as OH^{1-} , so the reaction table for the reaction n_a mol of acid and n_b mol of base if the base is the limiting reactant is

	H_3O^{1+}	+	OH^{1-}	\rightarrow	$2\text{H}_2\text{O}$
initial	n_a		n_b		
Δ	- n_b		- n_b		
eq	$n_a - n_b$		~0		

The resulting solution is a strong acid containing $(n_a - n_b)$ moles of hydronium ion. If the acid is the limiting reactant, then each entry on the Δ line would be $-n_a$ and the resulting solution would be a strong base containing $(n_b - n_a)$ moles of hydroxide ion. If $n_a = n_b$ (the equivalence point), both hydronium and hydroxide ions disappear and the resulting solution is pure water with a pH of 7. These three possibilities are summarized in Table 7.1 and demonstrated in Example 7.10.

Example 7.10

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 M HCl with 0.100 M NaOH that is shown in Figure 7.2.

The number of moles of acid is constant, so we determine it first:

$$n_a = (20.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 2.00 \text{ mmol H}_3\text{O}^{1+}$$

a) 10.0 mL of base

The number of moles of base: $(10.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 1.00 \text{ mmol OH}^{1-}$

The base is the limiting reactant ($n_b < n_a$), so the reaction table is

	$\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$		
initial	2.00	1.00	mmol
Δ	-1.00	-1.00	mmol
eq	1.00	~0	mmol

The final solution is a strong acid solution containing 1.0 mmol of hydronium ions in a total volume of $20.0 + 10.0 = 30.0 \text{ mL}$. The hydronium ion concentration and pH are

$$[\text{H}_3\text{O}^{1+}] = \frac{1.00 \text{ mmol}}{30.0 \text{ mL}} = 0.033 \text{ M} \quad \text{and} \quad \text{pH} = -\log(0.033) = 1.48$$

b) 20.0 mL of base

The number of moles of base: $(20.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 2.00 \text{ mmol OH}^{1-}$

The number moles of acid = the number of moles of base, so this is the equivalence point.

	$\text{H}_3\text{O}^{1+} + \text{OH}^{1-} \rightarrow 2\text{H}_2\text{O}$		
initial	2.00	2.00	mmol
Δ	-2.00	-2.00	mmol
eq	~0	~0	mmol

No excess acid or base is present, so the solution is pure water, which has a pH = 7.00.

Table 7.1 Solution type resulting from the reaction of n_a moles of a strong acid with n_b moles of a strong base

a) $n_a > n_b$	Strong acid solution with $[\text{H}_3\text{O}^{1+}] = \frac{n_a - n_b}{\text{total volume}}$
b) $n_a = n_b$	Water with pH = 7.00
c) $n_a < n_b$	Strong base solution with $[\text{OH}^{1-}] = \frac{n_b - n_a}{\text{total volume}}$

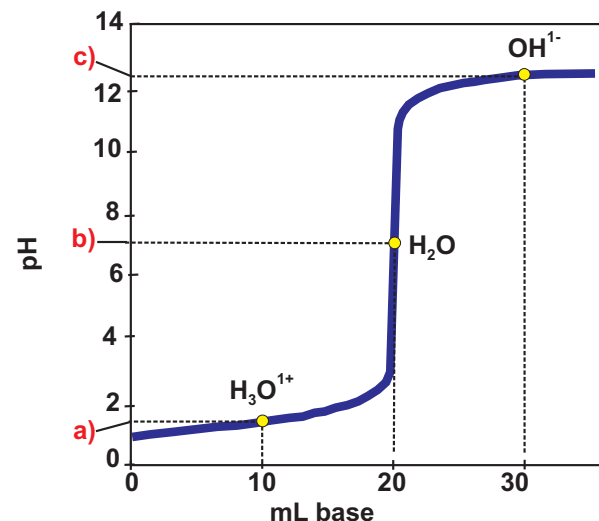


Figure 7.2 Strong acid-strong base titration curve.

Titration of 20.0 mL of 0.100 M HCl with 0.100 M NaOH. The equivalence point (yellow circle) in a strong acid-strong base titration is pure water, so the pH is 7.00. Points a, b, and c lie in regions a, b, and c of Table 7.1 and correspond to points a, b, and c in Example 7.10.

c) 30.0 mL of base

The number of moles of base: $(30.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 3.00 \text{ mmol OH}^{1-}$

The base is the limiting reactant ($n_a < n_b$), so the reaction table is

	H_3O^{1+}	$+$	OH^{1-}	\rightarrow	$2\text{H}_2\text{O}$	
initial	2.00		3.00			mmol
Δ	-2.00		-2.00			mmol
eq	~0		1.00			mmol

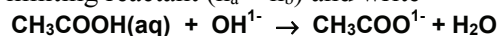
The concentration of the excess hydroxide and the resulting pH are

$$[\text{OH}^{1-}] = \frac{1.00 \text{ mmol}}{50.0 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pOH} = -\log(0.0200) = 1.70 \text{ and } \text{pH} = 14.00 - 1.70 = 12.30$$

WEAK ACID - STRONG BASE REACTIONS

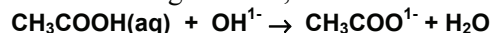
Consider the reaction of n_a moles of acetic acid with n_b moles of hydroxide ion. The reaction is the reverse of the K_b reaction of acetate ion, $K = (K_b)^{-1} = K_a/K_w = 1.8 \times 10^9$. The large value of K means that the limiting reactant essentially disappears. We consider the case where the acid is the limiting reactant ($n_a < n_b$) and write



initial	n_a	n_b	0	mol
Δ	$-n_a$	$-n_a$	$+n_a$	mol
eq	~0	$n_b - n_a$	n_a	mol

The resulting solution contains $(n_b - n_a)$ moles of hydroxide ion and is, therefore, a solution of a strong base.* The acetate ion has no effect on the pH of the solution due to the common-ion effect exerted by the excess hydroxide ion.

When $n_b < n_a$, the base is the limiting reactant, and the table takes the following form:



initial	n_a	n_b	0	mol
Δ	$-n_b$	$-n_b$	$+n_b$	mol
eq	$n_a - n_b$	~0	n_b	mol

The solution contains a weak acid and its conjugate base, so it is a buffer solution that contains $(n_a - n_b)$ moles of the weak acid and n_b moles of its conjugate base.[†] Thus, *adding a strong base to an excess of weak acid is another way to make a buffer solution.* Halfway to the equivalence point in the titration of a weak acid with a strong base, $n_b = \frac{1}{2} n_a$, so $n_b/(n_a - n_b) = 1$. $\log(1) = 0$, so $\text{pH} = \text{p}K_a + 0$ at that point. We conclude that

The pH at the midpoint of the titration (half-way to the equivalence point) of a weak acid and a strong base equals the $\text{p}K_a$ of the weak acid.

$$* \text{ Strong base: } [\text{OH}^{1-}] = \frac{n_b - n_a}{\text{total volume}} \text{ and } \text{pH} = 14.00 - \log[\text{OH}^{1-}].$$

$$† \text{ Buffer: } \text{pH} = \text{p}K_a + \log\left(\frac{n_b}{n_a - n_b}\right)$$

n_a is the initial number of moles of acid. The equilibrium number of moles of acid is $n_a - n_b$, which was represented by n_a in Equation 7.2. n_b is the initial number of moles of strong base, but it is also the equilibrium number of moles of weak base that are produced.

At the equivalence point in a titration, $n_a = n_b$, so the reaction table becomes

	CH_3COOH	+	OH^{1-}	\rightarrow	$\text{CH}_3\text{COO}^{1-}$	+	H_2O
Initial	n_a		n_b		0		mol
Δ	$-n_a$		$-n_b$		$+n_b$		mol
Eq	~ 0		~ 0		n_b		mol

The solution in this case is that of a weak base containing n_b (or n_a) moles of the acetate ion. The solution types that can result from the reaction of a weak acid and a strong base are summarized in Table 7.2 and demonstrated in the titration curve in Example 7.11.

Example 7.11

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH (Figure 7.3).

The parts of this example correspond to Points a – d of Figure 7.3 and lie in the regions a – d that are defined in Table 7.2. First, determine the number of moles of acid:

$$n_a = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol CH}_3\text{COOH}$$

a) 0 mL ($n_b = 0$)

No acid has been added, so the initial solution is a weak acid

$$[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_a} = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.3 \times 10^{-3} \text{ M and pH} = 2.87$$

b) 10.0 mL ($n_a > n_b$)

The number of moles of base added is

$$n_b = (10.0 \text{ mL})(0.100 \text{ M}) = 1.00 \text{ mmol OH}^{1-}$$

The base is the limiting reactant ($n_b < n_a$), so the reaction table is

	CH_3COOH	+	OH^{1-}	\rightarrow	$\text{CH}_3\text{COO}^{1-}$	+	H_2O
Initial	2.00		1.00		0		mmol
Δ	-1.00		-1.00		+1.00		mmol
Eq	1.00		~ 0		1.00		mmol

The result is a buffer solution containing 1.00 mmol of acetic acid and 1.00 mmol of its conjugate base. The second way to prepare a buffer is to add hydroxide ion to an excess of weak acid.

The pK_a of acetic acid is $-\log(1.8 \times 10^{-5}) = 4.74$, so the pH is

$$\text{pH} = 4.74 + \log\left(\frac{1.00}{1.00}\right) = 4.74$$

$\log(1) = 0$, so $\text{pH} = \text{pK}_a$ when the equilibrium number of moles of the acid and its conjugate base are identical, which occurs half-way to the equivalence point. We conclude that **the pH at the midpoint of a titration of a weak acid and a strong base equals the pK_a of the acid.**

Table 7.2 The type of solution resulting from the reaction of n_a moles of weak acid with n_b moles of a strong base

a) $n_b = 0$: Weak acid solution with n_a moles of acid.

$$[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_a}; c_a = \frac{n_a}{V}$$

b) $n_a > n_b$: Buffer solution with $n_a - n_b$ moles of acid and n_b moles of conjugate base: $\text{pH} = \text{pK}_a + \log\left(\frac{n_b}{n_a - n_b}\right)$

c) $n_a = n_b$: Weak base solution containing $n_b = n_a$ moles of the weak base $\text{pH} > 7$;

$$[\text{OH}^{1-}] = \sqrt{K_b c_b}; c_b = \frac{n_b}{\text{total volume}}$$

d) $n_a < n_b$: Strong base solution with $n_b - n_a$ moles of OH^{1-} .

$$[\text{OH}^{1-}] = \frac{n_b - n_a}{\text{total volume}} \text{ and } \text{pH} = 14.00 - \log[\text{OH}^{1-}]$$

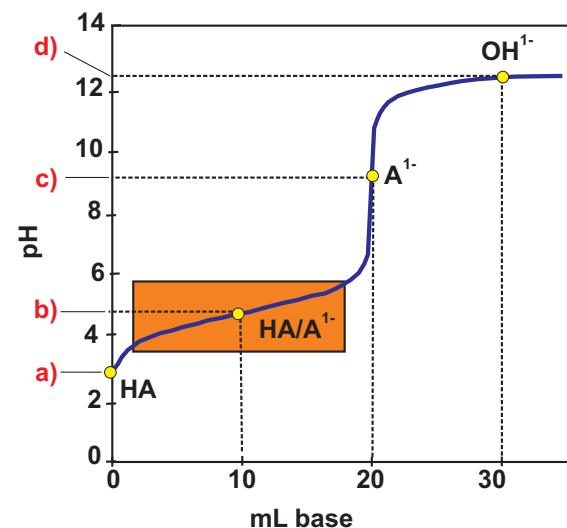


Figure 7.3 Weak acid-strong base titration curve

Titration of 20.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH. Points a – d lie in regions defined in Table 7.2 and correspond to Parts a – d in Example 7.11. The orange rectangle outlines the buffer range of the acetic acid/acetate ion buffer.

a) $n_b = 0$; a solution of the weak acid HA.

b) $n_b < n_a$; a buffer solution. Point b is the midpoint of the titration, so $\text{pH} = \text{pK}_a$, which is 4.74 for acetic acid.

c) $n_b = n_a$; the equivalence point is a solution of the weak base A^{1-} .

d) $n_b > n_a$; excess OH^{1-} makes the solution a strong base.

c) 20.0 mL ($n_a = n_b$)

$$n_b = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol OH}^{1-}$$

$n_b = n_a$, so this is the equivalence point. The reaction table is

	$\text{CH}_3\text{COOH} +$	$\text{OH}^{1-} \rightarrow$	$\text{CH}_3\text{COO}^{1-} + \text{H}_2\text{O}$	
Initial	2.00	2.00	0	mmol
Δ	-2.00	-2.00	+2.00	mmol
Eq	~ 0	~ 0	2.00	mmol

The resulting solution is a **weak base** that contains 2.00 mmol of the base ($\text{CH}_3\text{COO}^{1-}$) in $20.0 + 20.0 = 40.0 \text{ mL}$ of solution. $K_b = 5.6 \times 10^{-10}$, so the hydroxide ion concentration is

$$[\text{OH}^{1-}] = \sqrt{K_b \times c} = \sqrt{(5.6 \times 10^{-10}) \left(\frac{2.00 \text{ mmol}}{40.0 \text{ mL}} \right)} = 5.3 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28 \text{ and } \text{pH} = 14.00 - 5.28 = 8.72$$

d) 30.0 mL ($n_a < n_b$)

$$n_b = (30.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 3.00 \text{ mmol OH}^{1-}$$

The base is the limiting reactant ($n_a < n_b$), so the reaction table is

	$\text{CH}_3\text{COOH} +$	$\text{OH}^{1-} \rightarrow$	$\text{CH}_3\text{COO}^{1-} + \text{H}_2\text{O}$	
Initial	2.00	3.00	0	mmol
Δ	-2.00	-2.00	+2.00	mmol
Eq	~ 0	1.00	2.00	mmol

The excess hydroxide ion suppresses any reaction of acetate ion, so the solution is a **strong base** with the following concentration and pH:

$$[\text{OH}^{1-}] = \frac{1.00 \text{ mmol}}{50.0 \text{ mL}} = 0.0200 \text{ M}$$

$$\text{pOH} = -\log(0.0200) = 1.70 \text{ and } \text{pH} = 14.00 - 1.70 = 12.30$$

Note that the pH at this point is identical to the strong acid-strong base titration.

PRACTICE EXAMPLE 7.5

What is the pH of a solution prepared by mixing 34.0 mL of 0.250 M NaOH and 16.5 mL of 0.515 M KHSO_4 ?

Reaction table:

Rxn:

in

Δ

eq

solution type: _____ solution volume: _____ mL

$$[\text{SO}_4^{2-}] = \text{_____} = \text{_____ M}$$

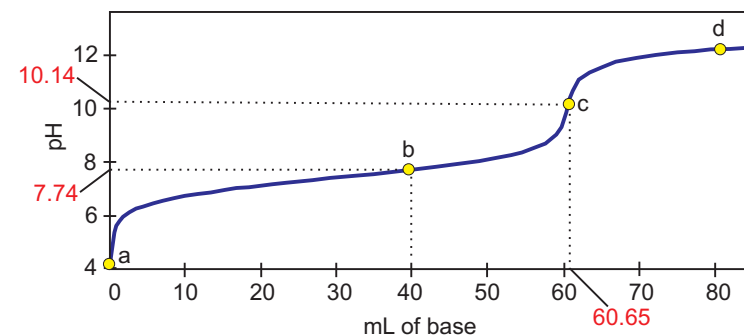
$$K_a \text{ of } \text{HSO}_4^{1-} = \text{_____} \text{ from Appendix C}$$

$$K_b \text{ of } \text{SO}_4^{2-} = \text{_____} = \text{_____}$$

$$[\text{OH}^{1-}] = \text{_____} = \text{_____ M}$$

$$\text{pOH} = \text{_____}$$

$$\text{pH} = \text{_____} = \text{_____}$$



Example 7.12

Example 7.12

The titration curve for the titration of 50.00 mL of an unknown acid with 0.122 M NaOH is shown in the margin. Determine the concentration and pK_a of the acid.

The concentration is determined from the equivalence point, which is at 60.65 mL of a 0.122 M base solution. Thus, the number of mmoles of base at the equivalence point is $n_b = (60.65 \text{ mL})(0.122 \text{ M}) = 7.40 \text{ mmol}$, which equals the number of mmoles of acid in 50 mL. Thus the concentration of the acid is

$$c_a = \frac{7.40 \text{ mmol}}{50.00 \text{ mL}} = 0.148 \text{ M}$$

The pK_a of the acid is most easily determined from a pH in the buffer range. Indeed, the pK_a is near 7.5 as that is the approximate pH at the midpoint of the titration. We use the fact that $pH = 7.74$ at the 40 mL point to determine the pH more precisely. $n_a = 7.40$ mmol and $n_b = (40.00 \text{ mL})(0.122 \text{ M}) = 4.88$ mmol at this point, so the reaction table is

	$HA(aq)$	$+$	OH^{1-}	\rightarrow	A^{1-}	$+$	H_2O	
in	7.40		4.88		0			mmol
Δ	-4.88		-4.88		+4.88			mmol
eq	2.52		~ 0		4.88			mmol

Solve Equation 7.2 for the pK_a of a buffer solution that has a $pH = 7.74$ and contains 2.52 mmol acid and 4.88 mmol base and solve for pK_a .

$$pK_a = pH - \log\left(\frac{n_b}{n_a}\right) = 7.74 - \log\left(\frac{4.88}{2.52}\right) = 7.45$$

Polyprotic acids dissociate one proton at a time, and they are deprotonated by OH^{1-} ion one proton at a time. The loss of each proton gives rise to one equivalence point. The equilibrium constants for the individual dissociations are usually very different, so only one or two species usually have non-negligible concentrations in polyprotic acid solutions. Indeed, their equilibria are identical to those of monoprotic acids except that the base may be amphiprotic. Example 7.13 shows how to treat the reaction of a polyprotic acid with hydroxide ion and gives an example of a titration curve.

Example 7.13

Determine the pH at various points in the titration curve for the titration of 20.0 mL of 0.100 M H_2A ($pK_1 = 4.00$, $pK_2 = 9.00$) with 0.100 M NaOH shown in Figure 7.4.

There are two equivalence points: 20 mL and 40 mL. H_2A is the weak acid up to the first equivalence point, but HA^{1-} is the acid between the first and the second.

b) 10.0 mL

This is half-way to the first equivalence point, so $[H_2A] = [HA^{1-}]$ and $pH = pK_1 = 4.00$

c) 15.0 mL

$$n_a = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol } H_2A \quad n_b = (15.0 \text{ mL})(0.100 \text{ M}) = 1.50 \text{ mmol } OH^{1-}$$

	H_2A	$+$	OH^{1-}	\rightarrow	HA^{1-}	$+$	H_2O	$pK_1 = 4.00$
initial	2.00		1.50		0			mmol
Δ	-1.50		-1.50		+1.50			mmol
eq	0.50		~ 0		1.50			mmol

$$\text{a buffer solution, so } pH = pK_1 + \log\left(\frac{\text{mol } HA^{1-}}{\text{mol } H_2A}\right) = 4.00 + \log\left(\frac{1.50}{0.50}\right) = 4.48$$

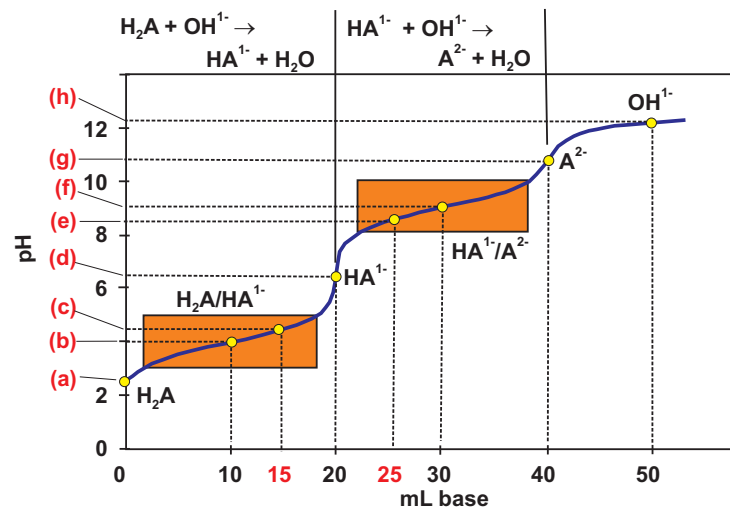


Figure 7.4 Diprotic acid-strong base titration curve

Titration of 20.0 mL of 0.100 M H_2A with 0.100 M NaOH. $pK_1 = 4.00$ and $pK_2 = 9.00$. The rectangles outline the two buffer ranges. See Example 7.13 for details of Points b - f.

- a) Solution of weak acid H_2A
- b & c) Buffer solution. Point b is half-way to the first equivalence point, so $pH = pK_1 = 4.00$.
- d) The first equivalence point is a solution of HA^{1-} , which is amphiprotic, so the pH of the solution is $\frac{1}{2}(pK_1 + pK_2) = 6.5$.
- e & f) Buffer solution. Point f is the midpoint between the first and second equivalence points, so $pH = pK_2 = 9.0$.
- g) The second equivalence point is a solution of A^{2-} , a weak base.
- h) Strong base solution that is characterized by the concentration of the excess hydroxide.

d) 20.0 mL

All of the H_2A has been converted to HA^{1-} at the equivalence point. HA^{1-} is an amphiprotic substance, so we use Equation 6.12 to determine the pH.

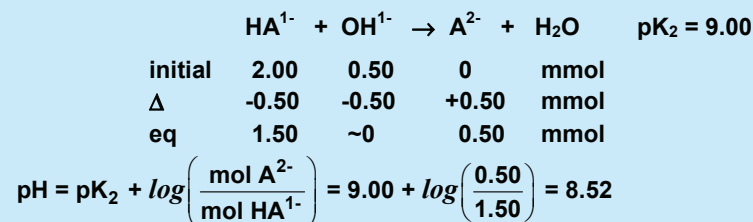
$$\text{pH} = \frac{1}{2}(\text{pK}_1 + \text{pK}_2) = \frac{1}{2}(4.00 + 9.00) = 6.50$$

e) 25.0 mL

This is after the first equivalence point, so the 2.00 mmol H_2A have been converted into 2.00 mmol HA^{1-} , which is now the reacting acid.

$$n_b = (25.0 \text{ mL})(0.100 \text{ M}) = 2.50 \text{ mmol OH}^{1-}$$

2.50 mmol OH^{1-} have been added, but 2.00 mmol were consumed in the reaction with H_2A to produce 2.00 mmol HA^{1-} . Thus, only 0.50 mmol OH^{1-} is available to react with HA^{1-} .



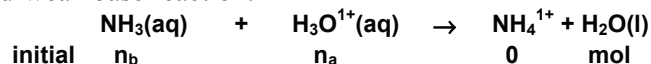
f) 30.0 mL

This is halfway between the first and second equivalence, so $\text{pH} = \text{pK}_2 = 9.00$

Note that the pH change at the two equivalence points in Figure 7.4 is less dramatic than for the monoprotic acid in Figure 7.3. This is to be expected because the pH range of the titrations are nearly the same ($\text{pH} = 2$ to 12), but the diprotic acid has two equivalence points while the monoprotic acid has only one.

STRONG ACID - WEAK BASE REACTIONS

We use the reaction of n_b moles of ammonia with n_a moles of HCl as our example of a strong acid-weak base reaction:



This reaction is the reverse of the K_a reaction for NH_4^{1+} , so $K = (K_a)^{-1} = (5.6 \times 10^{-10})^{-1} = 1.8 \times 10^9$. Using the same reasoning for this extensive reaction as in the reaction of a weak acid and a strong base, we obtain the results shown in Table 7.3. Note that when $n_a < n_b$, the result is a buffer. Thus, *adding a strong acid to an excess of weak base is the third way to make a buffer*.

Table 7.3 The type of solution resulting from the reaction of n_a moles of a strong acid with n_b moles of a weak base

- a) $n_a = 0$ A weak base: $[\text{OH}^{1-}] = \sqrt{K_b c_b}$; $\text{pH} = 14.00 - \log[\text{OH}^{1-}]$
- b) $n_a < n_b$ Buffer solution containing n_a moles of acid and $(n_b - n_a)$ moles of base: $\text{pH} = \text{pK}_a + \log\left(\frac{n_b - n_a}{n_a}\right)$
- c) $n_a = n_b$ Weak acid solution containing $n_b = n_a$ moles of the weak acid:
 $[\text{H}_3\text{O}^{1+}] = \sqrt{K_a c_a}$; $c_a = \frac{n_a}{\text{total volume}}$; $\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$
- d) $n_a > n_b$ Strong acid solution containing $n_a - n_b$ moles of H_3O^{1+}
 and $[\text{H}_3\text{O}^{1+}] = \frac{n_a - n_b}{\text{total volume}}$; $\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$

Example 7.14

Determine the pH at each of the following points in the titration curve for the titration of 20.0 mL of 0.100 M NH_3 with 0.100 M HCl.

The points are shown in Figure 7.5 and defined in Table 7.3. From Appendix C:

For NH_4^{1+} : $K_a = 5.6 \times 10^{-10}$ and $\text{p}K_a = 9.25$

a) 0 mL HCl ($n_a = 0$)

Prior to the addition of acid, the solution is one of NH_3 , which is a weak base.

$$[\text{OH}^{1-}] = \sqrt{K_b c_b}; \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{-5}$$

$$[\text{OH}^{1-}] = \sqrt{(1.8 \times 10^{-5})(0.100)} = 1.3 \times 10^{-3} \text{ M} \Rightarrow \text{pOH} = -\log(1.3 \times 10^{-3}) = 2.87$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.87 = 11.13$$

b) 10 mL ($n_a < n_b$)

$$n_a = (10.0 \text{ mL})(0.100 \text{ M}) = 1.00 \text{ mmol } \text{H}_3\text{O}^{1+}$$

The acid is the limiting reactant ($n_a < n_b$), so the reaction table is

	NH_3	+	H_3O^{1+}	\rightarrow	NH_4^{1+}	+	H_2O	
Initial	2.00		1.00		0			mmol
Δ	-1.00		-1.00		+1.00			mmol
Eq	1.00		~ 0		1.00			mmol

The result is a **buffer solution** containing 1.00 mmol of ammonia and 1.00 mmol of its conjugate acid. The $\text{p}K_a$ of the acid (NH_4^{1+}) is 9.25, so the pH is

$$\text{pH} = 9.25 + \log\left(\frac{1.00}{1.00}\right) = 9.25 \quad \text{This is the midpoint of the titration, so } \text{pH} = \text{p}K_a.$$

The third way to prepare a buffer is to add a strong acid to an **excess** of a weak base.

c) 20 mL ($n_a = n_b$)

$$n_a = (20.0 \text{ mL})(0.100 \text{ M}) = 2.00 \text{ mmol } \text{H}_3\text{O}^{1+}$$

$n_b = n_a$, so this is the equivalence point. The reaction table is

	NH_3	+	H_3O^{1+}	\rightarrow	NH_4^{1+}	+	H_2O	
Initial	2.00		2.00		0			mmol
Δ	-2.00		-2.00		+2.00			mmol
Eq	~ 0		~ 0		2.00			mmol

The resulting solution is a **weak acid** that contains 2.00 mmol of the acid (NH_4^{1+}) in 20.0 + 20.0 = 40.0 mL of solution. $K_a = 5.6 \times 10^{-10}$, so the hydronium ion concentration is

$$[\text{H}_3\text{O}^{1+}] = \sqrt{(5.6 \times 10^{-10})\left(\frac{2.00 \text{ mmol}}{40.0 \text{ mL}}\right)} = 5.3 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = -\log(5.3 \times 10^{-6}) = 5.28$$

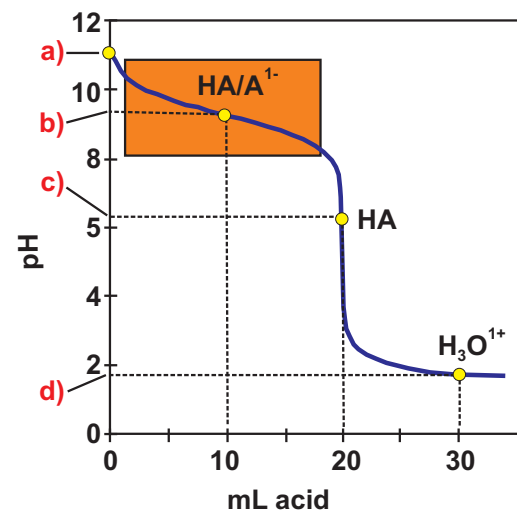


Figure 7.5 Weak-base-strong acid titration curve

Titration of 20.0 mL of 0.100 M NH_3 with 0.100 M HCl. See Example 7.14 for details on each point.

- a) $n_a = 0$ – a solution of the weak base NH_3
- b) $n_a < n_b$ – a buffer solution, Point b is the midpoint of the titration, so $\text{pH} = \text{p}K_a$, which is 9.25 for ammonium ion.
- c) $n_a = n_b$ – the equivalence point is a solution of the weak acid HA.
- d) $n_a > n_b$ – excess H_3O^{1+} makes the solution a strong acid.

d) 30 mL ($n_a > n_b$)

$$n_a = (30.0 \text{ mL})(0.100 \text{ mmol} \cdot \text{mL}^{-1}) = 3.00 \text{ mmol } \text{H}_3\text{O}^{1+}$$

The base is the limiting reactant ($n_a < n_b$), so the reaction table is

	NH_3	$+$	H_3O^{1+}	\rightarrow	$\text{NH}_4^{1+} + \text{H}_2\text{O}$	
Initial	2.00		3.00		0	mmol
Δ	-2.00		-2.00		+2.00	mmol
Eq	~0		1.00		2.00	mmol

The excess hydronium ion suppresses the reaction of ammonium ion with water, so the solution is a **strong acid** with the following concentration and pH:

$$[\text{H}_3\text{O}^{1+}] = \frac{1.00 \text{ mmol}}{50.0 \text{ mL}} = 0.0200 \text{ M} \quad \& \quad \text{pH} = -\log(0.0200) = 1.70$$

We have presented all three ways to make a buffer. In summary, they can be made by

- 1) adding the acid directly to its conjugate base,
- 2) adding a strong base to an excess of the weak acid, and
- 3) adding a strong acid to an excess of the weak base.

Example 7.15 demonstrates the second method.

Example 7.15

How many mL of 0.856 M HCl must be added to 250.0 mL of 0.116 M KClO to make a pH = 8.00 buffer? $\text{pK}_a = 7.46$ for HClO.

Set up the reaction table for the reaction of an unknown amount of acid with $n_b = (250 \text{ mL})(0.116 \text{ M}) = 29.0 \text{ mmol}$ of ClO^{1-} ion.

	ClO^{1-}	$+$	H_3O^{1+}	\rightarrow	HClO	$+$	H_2O	
In	29.0		x		0			mmol
Δ	-x		-x		+x			mmol
Eq	29.0-x		~0		x			mmol

Use the Henderson-Hasselbalch equation with pH = 8.00, $\text{pK}_a = 7.46$, $n_b = 29.0 - x$ and $n_a = x$ to solve for x.

$$8.00 = 7.46 + \log\left(\frac{29.0-x}{x}\right) \quad \text{or} \quad \log\left(\frac{29.0-x}{x}\right) = 8.00 - 7.46 = 0.54$$

$$\frac{29.0-x}{x} = 10^{0.54} = 3.47 \quad \Rightarrow \quad x = \frac{29.0}{4.47} = 6.49 \text{ mmol } \text{H}_3\text{O}^{1+}$$

$$\text{Determine the volume of acid required: } 6.49 \text{ mmol} \times \frac{1 \text{ mL}}{0.856 \text{ mmol}} = 7.58 \text{ mL}$$

7.4 ACID-BASE COMPOSITION FROM EQUILIBRIUM pH

Solutions are frequently prepared by adjusting the solution pH to a desired level rather than adding a known volume of acid or base. For example, the easiest way to make a buffer of a desired pH is to decide on the proper acid-base pair, make a solution that contains an appreciable amount of the acid or base and then add a strong base or acid until the solution has the required pH. The question then becomes: Once you have attained the appropriate pH, what are the concentrations of the acid(s) and base(s) in the solution?

One equation is required for each unknown concentration in a solution, so determining $[H_2X]$, $[HX^1]$, and $[X^2]$ in a solution of a diprotic acid involves three equations and three unknowns. The equilibrium constant expressions for K_1 and K_2 are two of the equations. The third equation is mass balance: $c_o = [H_2X] + [HX^1] + [X^2]$. Fortunately, chemistry can usually be used to simplify the algebra because only one or two of the concentrations are usually appreciable at any pH. Once the one or two appreciable concentrations have been determined at a given pH, the other concentrations can be readily determined from the given K 's, c_o , and pH. Thus, our first task is to identify these one or two species that dominate the concentration. We do so by assuming that the concentration of a substance is negligible if it is less than 1% of the concentration of either its conjugate acid or base.* Thus, the acid concentration is negligible if $[base]/[acid] > 100$, and the base concentration is negligible if $[base]/[acid] < 0.01$. The pH at which each ratio is achieved can be determined with Equation 7.2. Thus, the acid is negligible if $pH > pK_a + \log(100) = pK_a + 2$, and the base is negligible if $pH < pK_a + \log(0.01) = pK_a - 2$. We conclude that *the concentration of an acid and its conjugate base are both appreciable at pH's within 2 pH units of the pK_a of the acid, but only the acid can be appreciable below this pH range, and only the base can be appreciable above it.*

For example, consider the case of acetic acid in Figure 7.6. The pK_a of CH_3COOH is 4.7, so $[CH_3COOH] = c_o$ if $pH < 2.7$ ($pH = 4.7 - 2$), but $[CH_3COO^1] = c_o$ if $pH > 6.7$ ($4.7 + 2$). At intermediate pH values ($2.7 < pH < 6.7$), neither concentration is negligible, so we use $[CH_3COOH] + [CH_3COO^1] = c_o$. Figure 7.7 shows the concentrations in an H_2S ($pK_1 = 7.0$, $pK_2 = 12.9$) solution. The two yellow boxes represent the two pH ranges ($pK_a \pm 2$) in which both the acid (H_2S or HS^1) and its conjugate base (HS^1 or S^2) are appreciable. Only one substance is appreciable at all other pH values. The example of a triprotic acid, H_3PO_4 , is examined in Example 7.16. Even though there are four concentrations to determine, no more than two are appreciable at any pH.

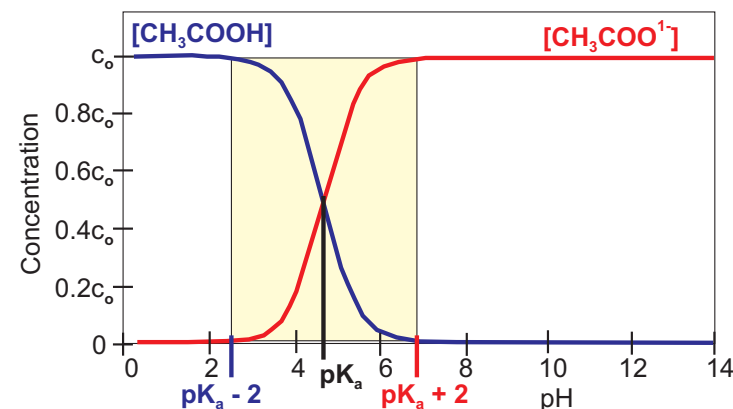


Figure 7.6 Concentrations in acetic acid as a function of pH

The $[acid] \sim c_o$ and $[base] \sim 0$ at pH's below ($pK_a - 2$), but $[acid] \sim 0$ and $[base] \sim c_o$ at pH's above ($pK_a + 2$). The concentrations of both substances are appreciable only in the yellow region. $pK_a = 4.74$

* Recall from Chapter 6 that we used the 5% rule, which stated that a concentration was negligible if it was less than 5% of its conjugate acid or base concentration, so a 1% cut-off is somewhat arbitrary.

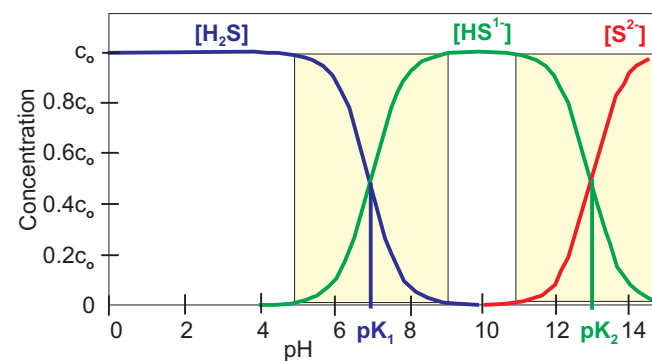
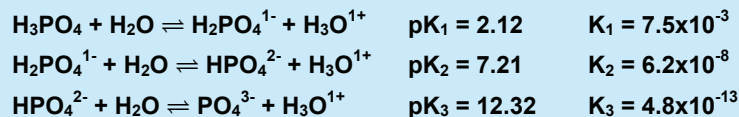


Figure 7.7 Concentrations in an H_2S solution as a function of pH

The concentrations of two substances are comparable and appreciable in the yellow boxes, but only one component is appreciable outside. The pH ranges of the yellow boxes are from $pH = pK_a - 2$ to $pH = pK_a + 2$.

Example 7.16

Solid NaOH is dissolved in a 0.10 M H_3PO_4 solution. Assume no volume change and calculate the concentrations of the phosphorus containing species at each pH.

**a) pH = 7.0**

pH = 7.0 is within 2 units of $\text{p}K_2$, so, in agreement with Figure 7.8, the concentrations of both the acid ($\text{H}_2\text{PO}_4^{1-}$) and the base (HPO_4^{2-}) in the K_2 equilibrium are appreciable. If $[\text{H}_2\text{PO}_4^{1-}] = x$, then $[\text{HPO}_4^{2-}] = 0.10 - x$. $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 1.0 \times 10^{-7}$ M. Writing the K_2 expression and solving it for x , we obtain the following:

$$\frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_2\text{PO}_4^{1-}]} = \frac{(0.10 - x)(1.0 \times 10^{-7})}{x} = 6.2 \times 10^{-8}$$

$$\frac{(0.10 - x)}{x} = \frac{6.2 \times 10^{-8}}{1.0 \times 10^{-7}} = 0.62, \text{ so } x = \frac{0.10}{1.62} = 0.062 \text{ M} = [\text{H}_2\text{PO}_4^{1-}]$$

$$[\text{HPO}_4^{2-}] = 0.100 - 0.062 = 0.038 \text{ M}$$

Use $[\text{H}_2\text{PO}_4^{1-}] = 0.062 \text{ M}$ and $[\text{H}_3\text{O}^{1+}] = 1.0 \times 10^{-7} \text{ M}$ in K_1 to obtain $[\text{H}_3\text{PO}_4]$.

$$\frac{[\text{H}_2\text{PO}_4^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_3\text{PO}_4]} = \frac{(0.062)(1.0 \times 10^{-7})}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$$

$$[\text{H}_3\text{PO}_4] = \frac{(0.062)(1.0 \times 10^{-7})}{7.5 \times 10^{-3}} = 8.3 \times 10^{-7} \text{ M}$$

Use the $[\text{HPO}_4^{2-}] = 0.038 \text{ M}$ and $[\text{H}_3\text{O}^{1+}] = 1.0 \times 10^{-7} \text{ M}$ in K_3 to obtain $[\text{PO}_4^{3-}]$.

$$\frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^{1+}]}{[\text{HPO}_4^{2-}]} = \frac{[\text{PO}_4^{3-}](1.0 \times 10^{-7})}{0.038} = 4.8 \times 10^{-13}$$

$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(0.038)}{1.0 \times 10^{-7}} = 1.8 \times 10^{-7} \text{ M}$$

b) pH = 10.0

pH = 10 is not within 2 units of any $\text{p}K_a$, so the concentration of only one species is appreciable at this pH. The pH lies between $\text{p}K_2$ and $\text{p}K_3$, so the dominant species is the one that is common to both the K_2 and K_3 equilibria. We conclude that $[\text{HPO}_4^{2-}] = c_0 = 0.10 \text{ M}$ at pH = 10. Again this is consistent with Figure 7.8.

We use $[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 1.0 \times 10^{-10} \text{ M}$ and $[\text{HPO}_4^{2-}] = 0.10 \text{ M}$ in the K_2 and K_3 equilibria to obtain the concentrations of the conjugate acid and base of HPO_4^{2-} .

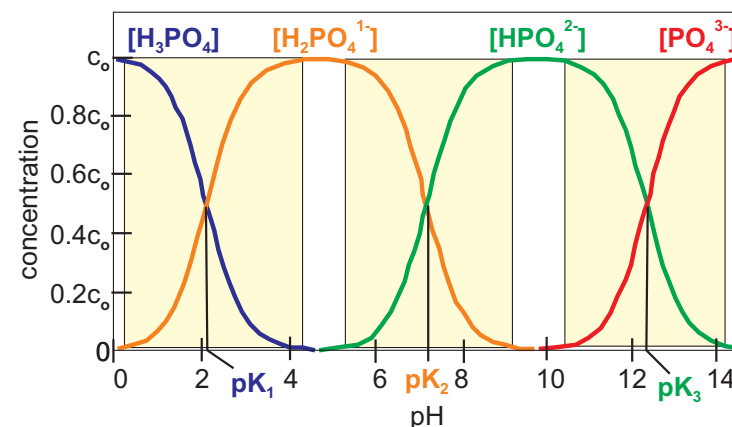


Figure 7.8 Phosphoric acid composition versus pH

See Example 7.14 for details. $\text{p}K_1 = 2.12$; $\text{p}K_2 = 7.21$; $\text{p}K_3 = 12.32$

Obtain $[\text{PO}_4^{3-}]$ from the K_3 equilibrium.

$$\frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^{1+}]}{[\text{HPO}_4^{2-}]} = \frac{[\text{PO}_4^{3-}](1.0 \times 10^{-10})}{0.10} = 4.8 \times 10^{-13}$$

$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(0.10 \text{ M})}{1.0 \times 10^{-10}} = 4.8 \times 10^{-4} \text{ M}$$

Obtain $[\text{H}_2\text{PO}_4^{1-}]$ from the K_2 equilibrium.

$$\frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_2\text{PO}_4^{1-}]} = \frac{(0.10 \text{ M})(1.0 \times 10^{-10})}{[\text{H}_2\text{PO}_4^{1-}]} = 6.2 \times 10^{-8}$$

$$[\text{H}_2\text{PO}_4^{1-}] = \frac{(0.10 \text{ M})(1.0 \times 10^{-10})}{6.2 \times 10^{-8}} = 1.6 \times 10^{-4} \text{ M}$$

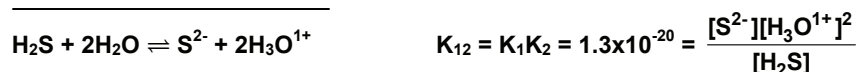
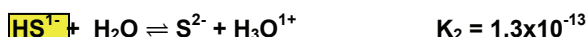
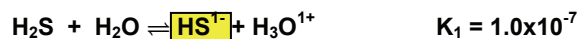
Use $[\text{H}_2\text{PO}_4^{1-}] = 1.6 \times 10^{-4} \text{ M}$ in the K_1 equilibrium to obtain $[\text{H}_3\text{PO}_4]$.

$$\frac{[\text{H}_2\text{PO}_4^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{H}_3\text{PO}_4]} = \frac{(1.6 \times 10^{-4})(1.0 \times 10^{-10})}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3}$$

$$[\text{H}_3\text{PO}_4] = \frac{(1.6 \times 10^{-4})(1.0 \times 10^{-10})}{7.5 \times 10^{-3}} = 2.1 \times 10^{-12} \text{ M}$$

It should be noted that, while the concentrations in Example 7.16 were determined for a solution formed by adding NaOH to H_3PO_4 , the compositions at a given pH would be identical if the solutions had been prepared by adding a strong acid to PO_4^{3-} .

While the protons of a polyprotic acid are removed individually, the individual equilibria can be combined to eliminate concentrations of intermediate ions. For example, consider the dissociation equilibria of H_2S .



Note that the HS^{1-} ion cancels in the sum, so adding the two equations produces a chemical equation without HS^{1-} . The new chemical equation is the result of adding two equations, so its equilibrium constant equals the product of the equilibrium constants of the added reactions. K_{12} does not include $[\text{HS}^{1-}]$, so its use affords us a quick way to determine the concentration of sulfide ion in a solution where $[\text{H}_3\text{O}^{1+}]$ and $[\text{H}_2\text{S}]$ are known. However, $[\text{H}_2\text{S}]$ is the *equilibrium* concentration of H_2S , not its makeup

PRACTICE EXAMPLE 7.6

What are the H_2SO_3 , HSO_3^{1-} , and SO_3^{2-} concentrations in a 0.100 M H_2SO_3 ($\text{p}K_1 = 1.82$ and $\text{p}K_2 = 7.00$) solution at the following pH's?

a) pH = 5.0

Major component(s) in solution: _____

Concentration(s) of major component(s): _____

Concentration(s) of other component(s): _____

b) pH = 8.0

Major component(s) in solution: _____

Concentration(s) of major component(s): _____

Concentration(s) of other component(s): _____

concentration. If the pH is low enough that only a negligible amount of H_2S reacts then $[\text{H}_2\text{S}] = c_0$, but such is not the case at higher pH. When determining a pH with K_{12} , you should always check that $[\text{HS}^{1-}]$ is negligible at that pH.

Example 7.17

Sulfide ion is used to selectively precipitate metal ions from solution, but the concentration of the sulfide ion must be adjusted carefully to select which metals will precipitate. This is done by adjusting the pH of the solution.

a) What is $[\text{S}^{2-}]$ in a saturated solution of H_2S (0.10 M) at a pH = 3.0?

H_2S is not deprotonated at pH values less than $\text{p}K_a - 2 = 7.00 - 2 = 5.00$ (also see Figure 7.7), so $[\text{H}_2\text{S}] = 0.10 \text{ M}$ at pH = 3.0. We use the equilibrium constant for the combined equations to solve for $[\text{S}^{2-}]$.

$$[\text{S}^{2-}] = \frac{K_{12}[\text{H}_2\text{S}]}{[\text{H}_3\text{O}^{1+}]^2} = \frac{(1.3 \times 10^{-20})(0.10)}{(1.0 \times 10^{-3})^2} = 1.3 \times 10^{-15} \text{ M}$$

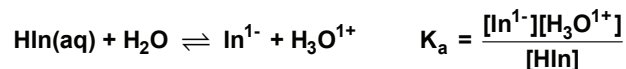
b) At what pH will the sulfide ion concentration be $1.0 \times 10^{-12} \text{ M}$?

$$[\text{H}_3\text{O}^{1+}] = \sqrt{\frac{K_{12}[\text{H}_2\text{S}]}{[\text{S}^{2-}]}} = \sqrt{\frac{(1.3 \times 10^{-20})(0.10)}{(1.0 \times 10^{-12})}} = 3.6 \times 10^{-5} \text{ M} \Rightarrow \text{pH} = 4.44$$

pH = 4.44 < 5.0 ($\text{p}K_a - 2$), so H_2S is not deprotonated at this pH, $[\text{HS}^{1-}]$ is negligible, and the assumption that $[\text{H}_2\text{S}] = 0.10 \text{ M}$ is valid. ✓

7.5 ACID-BASE INDICATORS

Indicators are organic dyes that are also weak acids. They function as acid-base indicators because the weak acid (HIn) and its conjugate base (In^{1-}) differ in color. Consider the K_a of the indicator HIn :



The base to acid ratio in solution varies with the pH as shown below (Equation 7.3):

$$\frac{[\text{In}^{1-}]}{[\text{HIn}]} = \frac{K_a}{[\text{H}_3\text{O}^{1+}]} = K_a \times 10^{\text{pH}}$$

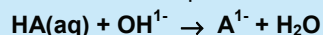
The human eye perceives the color of In^{1-} if this ratio is greater than 10 and the color of HIn if the ratio is less than 0.1. In order to change the ratio from 0.1 to 10, the hydronium ion concentration must decrease by a factor of 100, which means that the pH must increase by 2 pH units. For this reason, most indicators have a useful range of about 2 pH units.

Ideally, $[\text{HIn}] \sim [\text{In}^{1-}]$ at the equivalence point so, a *good indicator has a K_a that is close to the hydronium ion concentration at the equivalence point. Alternatively, a good indicator has a $\text{p}K_a$ that is close to the pH at the equivalence point.* Table 7.4 gives the useful range of a series of common acid-base indicators.

Example 7.18

- a) What is the molarity of a weak monoprotic acid HA if 25.00 mL of the acid require 35.22 mL of 0.1095 M NaOH to reach the equivalence point?

Determining the concentration of an acid or base is the most common application of a titration. This example involves the reaction of a strong acid and a strong base:



$$n_b = 35.22 \text{ mL base} \times \frac{0.1095 \text{ mmol OH}^{1-}}{\text{mL base}} = 3.857 \text{ mmol OH}^{1-}$$

The equivalence point is that point where the number of moles of base that is added equals the number of moles of acid in the original sample, so 3.857 mmol HA were present in the original 25.00 mL.

$$\text{Molarity of acid} = \frac{3.857 \text{ mmol acid}}{25.00 \text{ mL solution}} = 0.1543 \text{ M}$$

- b) What is the K_a of the acid if the pH of the solution was 5.26 after the addition of 20.00 mL of the base?

$(20.00 \text{ mL})(0.1095 \text{ M}) = 2.190 \text{ mmol OH}^{1-}$, and the reaction table for the reaction of 2.190 mmol OH^{1-} with 3.857 mmol HA is

	HA(aq)	+ OH ¹⁻	→	A ¹⁻	+ H ₂ O
in	3.857	2.190		0	mmol
Δ	-2.190	-2.190		+2.190	mmol
fin	1.667	~0		2.190	mmol

The solution contains appreciable amounts of both the acid and the base, so $\text{pH} = \text{p}K_a + \log(n_b/n_a)$. We are given the pH and have determined n_a and n_b , so we solve for the $\text{p}K_a$.

$$\text{p}K_a = \text{pH} - \log\left(\frac{n_b}{n_a}\right) = 5.26 - \log\left(\frac{2.190}{1.667}\right) = 5.14$$

Table 7.4 The pH range and color change of selected acid-base indicators

Indicator	pH range	color change
Methyl violet	1.0-1.6	yellow → blue
Thymol blue	1.2-2.8	red → yellow
Methyl orange	3.2-4.4	red → yellow
Bromocresol green	3.8-5.4	yellow → blue
Alizarin	5.4-6.6	colorless → yellow
Bromothymol blue	6.0-7.6	yellow → blue
Phenolphthalein	8.2-10.0	colorless → pink
Alizarin yellow R	10.1-12.0	yellow → red

PRACTICE EXAMPLE 7.7

An old sample of KHSO_4 is analyzed by dissolving 438.7 mg in ~50 mL of water and titrating the solution with 0.08221 M KOH. The endpoint was reached after the addition of 36.42 mL of the base. What is the percent purity of the KHSO_4 ?

Titration reaction:

$$\text{mmol OH}^{1-} \text{ added} = \quad = \quad \text{mmol}$$

$$\text{mmol of HSO}_4^{1-} \text{ in sample} = \quad \text{mmol}$$

$$\text{molar mass of KHSO}_4 = \quad \text{g} \cdot \text{mol}^{-1}$$

$$\text{mass of KHSO}_4 \text{ in sample:} \quad = \quad \text{mg}$$

percent purity of sample:

$$\% = \quad \times 100\% = \quad \%$$

c) What is the pH at the equivalence point?

The solution at the equivalence point has a volume of $25.00 + 35.22 = 60.22$ mL and it contains 3.857 mmol A^{1-} .

$$[A^{1-}] = \frac{3.857 \text{ mmol}}{60.22 \text{ mL}} = 0.06405 \text{ M}$$

$$pK_b = 14.00 - 5.14 = 8.86; K_b = 10^{-8.86} = 1.38 \times 10^{-9}$$

If we assume a negligible reaction of the base with water to produce OH^{1-} ,

$$[OH^{1-}] = \sqrt{(K_b)(c_o)} = \sqrt{(1.38 \times 10^{-9})(0.06405)} = 9.40 \times 10^{-6} \text{ M}$$

$[OH^{1-}]/[A^{1-}] = 1.5 \times 10^{-4}$, which is much less than 5%, so the assumption is valid. ✓

$$pH = 14.00 - \log[OH^{1-}] = 14.00 - \log(9.40 \times 10^{-6}) = 8.97$$

d) What indicator from Table 7.4 should be used to indicate the end point?

The best indicator from Table 7.4 to use at $pH \sim 9$ is phenolphthalein.

7.6 CHAPTER SUMMARY AND OBJECTIVES

Buffers are solutions of a weak acid and its conjugate base in comparable and appreciable amounts. They must be in comparable amounts to be effective. The effective buffer range is $0.10 < c_a/c_b < 10$. They must be present in appreciable amounts to have a good buffer capacity. Buffered solutions resist changes in pH brought on by the addition of either acid or base because the weak acid reacts with additional strong base while the weak base reacts with any additional strong acid. The result is the strong acid or base is converted into a weak base or acid.

One of five types of solutions result when acids and bases are mixed. The five types of solutions and how they are treated are as follows:

1. Strong acid solutions: $[H_3O^{1+}] = c_o$
2. Strong base solutions: $[OH^{1-}] = c_o$
3. Weak acid solution: $[H_3O^{1+}] = \sqrt{K_a c_o}$ (assumes very little reaction, so the equilibrium concentration of the weak acid = c_o)
4. Weak base solution: $[OH^{1-}] = \sqrt{K_b c_o}$ (assumes very little reaction, so the equilibrium concentration of the weak base = c_o)
5. Buffer solutions: $[H_3O^{1+}] = [H_3O^{1+}] = K_a \left(\frac{c_a}{c_b} \right)$ or $pH = pK_a + \log \left(\frac{c_b}{c_a} \right)$ (c_A and c_B are the makeup concentrations or number of moles of the acid and the base, respectively)

ANSWERS TO PRACTICE EXAMPLES

- 7.1 $pH = 3.80$
- 7.2 a) 3.31 b) 3.88 c) 2.80
- 7.3 NH_4^{1+}/NH_3 ; 0.39 mol NH_3 or
 HCO_3^{1-}/CO_3^{2-} ; 0.033 mol CO_3^{2-} or
 HCN/CN^{1-} ; 0.28 mol CN^{1-}
- 7.4 $[NO_2^{1-}] = 0.021 \text{ M}$
- 7.5 $[SO_4^{2-}] = 0.17 \text{ M}$ $pH = 7.58$
- 7.6 a) $[HSO_3^{1-}] = 0.10 \text{ M}$; $[H_2SO_3] = 6.7 \times 10^{-5} \text{ M}$; $[SO_3^{2-}] = 1.0 \times 10^{-3} \text{ M}$
 b) $[HSO_3^{1-}] = 0.0091 \text{ M}$; $[SO_3^{2-}] = 0.091 \text{ M}$; $[H_2SO_3] = 6.1 \times 10^{-9} \text{ M}$
- 7.7 92.94%

A titration curve is a plot of the pH of a solution as a function of the amount of titrant added. Titration curves are flat in buffer regions, but undergo dramatic pH changes near the equivalence points. There is one equivalence point for each acidic proton in the acid. The composition of an acid-base mixture at a given pH can be determined by comparing the pH with the pK_a values of the acid. If the pH is within 1.5 units of the pK_a , then both the acid and base are present in appreciable amounts, but if the pH is not within 1.5 units of a pK_a only one substance is present in appreciable amounts.

After studying the material presented in this chapter, you should be able to:

1. explain the common-ion effect and predict the effect of a common ion on an equilibrium mixture (Section 7.1);
2. define a buffer and explain how it works (Section 7.2);
3. choose an appropriate conjugate acid-base pair to use in the preparation of a buffer of a known pH (Section 7.2);
4. determine the base to acid ratio required to produce a buffer of a given pH (Section 7.2);
5. determine the pH of a buffer given the amounts of acid and base present (Section 7.2);
6. calculate the change in pH expected when a strong acid or base is added to a buffered solution (Section 7.2);
7. write acid-base reactions and determine their equilibrium constants from the K_a 's of the reacting and produced acids (Section 7.3);
8. determine the concentrations of all species in a solution prepared by mixing a strong acid (or base) with a strong base (or acid) or a weak base (or acid) (Section 7.3);
9. describe the three ways in which buffers can be made (Section 7.3);
10. define a titration curve and explain how it is determined (Section 7.3);
11. discuss how a titration curve varies with acid and base strengths (Section 7.3);
12. determine the pH at any point in the titration of a strong acid with a strong base, or a weak acid and a strong base, or a weak base and a strong acid (Section 7.3);
13. determine the concentrations of all species in an acid-base mixture given the initial concentration of the acid and the pH of the solution (Section 7.4);
14. describe the function of an indicator (Section 7.5); and
15. choose an indicator that is appropriate for a titration (Section 7.5).

7.7 EXERCISES

THE COMMON-ION EFFECT AND BUFFERS

1. What is a common ion and what is the common-ion effect?
2. Why can the dissociation of a weak base be ignored when calculating the pH of a solution that contains both a weak base and a strong base?
3. What is a buffer and how does it function?
4. Explain why the terms *appreciable* and *comparable* appear in the definition of a buffer.
5. Why is a solution that is 1.4 mM HF and 6.4 mM KF not a good buffer?
6. Why is a solution that is 1.3 M HF and 1.3 mM KF not a good buffer?
7. Explain why a solution of a strong acid and its conjugate base is not a buffer. Use a solution of HCl and KCl as an example.
8. Explain why a solution that is prepared by dissolving 0.1 mol of each of KH_2PO_4 and K_3PO_4 in 1 L of water is not a buffered solution.
9. Use Appendix C to determine the best acid/base pair to prepare buffers at the following pH's:
 - a) pH = 1.5
 - b) pH = 7.0
 - c) pH = 12.0
10. Select an acid-base pair from Appendix C that could be used to buffer a solution at each of the following pH's:
 - a) pH = 3.5
 - b) pH = 8.0
 - c) pH = 10.6
11. What is the pH of a solution that is 0.16 M NH_3 and 0.43 M NH_4Cl ?
12. What is the pH of a solution that is 0.21 M K_2HPO_4 and 0.096 M K_3PO_4 ?
13. What is the pH of a solution made by dissolving 7.6 g KNO_2 to 750 mL of 0.11 M HNO_2 ?
14. What is the pH of a solution made by dissolving 8.5 g of K_2CO_3 and 6.9 g KHCO_3 in 500 mL of water?
15. How many grams of potassium acetate must be added to 2.5 L of 0.250 M acetic acid to prepare a pH = 4.26 buffer?
16. How many grams of ammonium chloride must be added to 0.75 L of 1.2 M ammonia to prepare a pH = 10.18 buffer?
17. How many milliliters of 6.0 M NaOH must be added to 0.50 L of 0.20 M HNO_2 to prepare a pH = 3.86 buffer?
18. How many milliliters of 3.5 M HCl must be added to 3.8 L of 0.18 M K_2HPO_4 to prepare a pH = 7.42 buffer?

EQUILIBRIUM CONSTANTS FOR ACID BASE REACTIONS

19. Use the data in Appendix C to determine the equilibrium constants for the following reactions:
 - a) $\text{NH}_3(\text{aq}) + \text{HCN}(\text{aq}) \rightleftharpoons \text{NH}_4^{1+} + \text{CN}^{1-}$
 - b) $\text{S}^{2-} + \text{HCN}(\text{aq}) \rightleftharpoons \text{HS}^{1-} + \text{CN}^{1-}$
 - c) $\text{F}^{1-} + \text{HCN}(\text{aq}) \rightleftharpoons \text{HF}(\text{aq}) + \text{CN}^{1-}$
20. Use the data in Appendix C to determine the equilibrium constants for the following reactions:
 - a) $\text{NH}_3(\text{aq}) + \text{H}_3\text{O}^{1+} \rightleftharpoons \text{NH}_4^{1+} + \text{H}_2\text{O}$
 - b) $\text{F}^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{HF}(\text{aq}) + \text{OH}^{1-}$
 - c) $\text{HSO}_3^{1-} + \text{HS}^{1-} \rightleftharpoons \text{H}_2\text{S}(\text{aq}) + \text{SO}_3^{2-}$

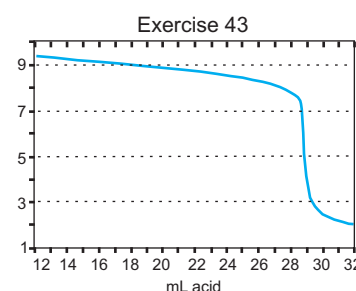
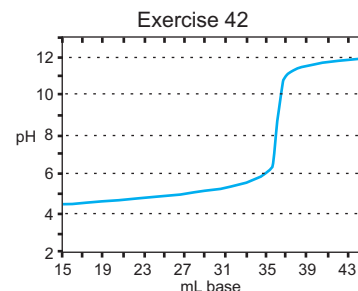
MIXING PROBLEMS

21. What is the sulfite ion concentration in a solution prepared by mixing 25.0 mL of 0.100 M H_2CO_3 and 25.0 mL of 0.100 M K_2SO_3 ?
22. What is the HOCl concentration in a solution prepared by mixing 50.0 mL of 0.160 M KOCl and 50.0 mL of 0.160 M NH_4Cl ?
23. What is the fluoride ion concentration in a solution prepared by mixing 25 mL of 0.16 M HF and 42 mL of 0.086 M KCN?
24. What is the ammonium ion concentration in a solution prepared by mixing 75 mL of 0.34 M ammonia and 85 mL of 0.18 M acetic acid?
25. What is the pH of a solution made by mixing 5.0 mL of 1.2 M HCl and 3.0 mL of 0.88 M HBr?
26. What is the pH of a solution prepared by mixing 39 mL of 0.074 M $\text{Ba}(\text{OH})_2$ and 57 mL of 0.11 M KOH?
27. What is the pH of a solution prepared by mixing 5.00 mL of 1.20 M HCl and 4.60 mL of 0.840 M NaOH?
28. What is the pH of a solution prepared by mixing 38.64 mL of 0.8862 M HCl and 53.66 mL of 0.7500 M NaOH?
29. Calculate the pH change that results when 10. mL of 3.0 M NaOH is added to 500. mL of each of the following solutions:
 - a) pure water
 - b) 0.10 M $\text{CH}_3\text{COO}^{1-}$
 - c) 0.10 M CH_3COOH
 - d) a solution that is 0.10 M in each $\text{CH}_3\text{COO}^{1-}$ and CH_3COOH

30. Calculate the pH change that results when 10. mL of 3.0 M HCl is added to 500. mL of each of the solutions in Exercise 29.
31. Calculate the pH change that results when 10. mL of 6.0 M HCl is added to 750. mL of each of the following solutions:
- pure water
 - 0.10 M NH_4Cl
 - 0.10 M NH_3
 - a solution that is 0.10 M in each NH_4^{1+} and NH_3
32. Calculate the pH change that results when 10. mL of 6.0 M NaOH is added to each of the solutions described in Exercise 31.

TITRATIONS

33. Sketch the titration curve for the titration of 50 mL of 0.1 M HA ($K_a = 10^{-7}$) with 0.1 M NaOH. What are the initial pH, the pH at the midpoint of the titration, and the pH at the equivalence point?
34. Sketch the titration curve for the titration of 50 mL of 0.1 M A^{1-} ($K_b = 10^{-7}$) with 0.1 M HCl. What are the initial pH, the pH at the midpoint of the titration, and the pH at the equivalence point?
35. What are the pH's of the first and second equivalence points in the titration of 25 mL of 0.080 M H_3PO_4 with 0.065 M NaOH?
36. What are the pH's of the two equivalence points in the titration of 25 mL of 0.080 M H_2CO_3 with 0.10 M NaOH?
37. Consider the titration of 35.0 mL of 0.122 M ammonia with 0.0774 M HCl.
- How many mL of HCl are required to reach the equivalence point?
 - What is the pH at the equivalence point? What indicator should be used for this titration?
 - What is the pH of the solution after addition of 15.0 mL of acid?
 - What is the pH of the solution after the addition of 65.0 mL of acid?
38. The CO_2 we breathe reacts with water in our blood to form the weak acid H_2CO_3 . What mole ratio of $\text{H}_2\text{CO}_3/\text{HCO}_3^{1-}$ is required to obtain a pH of 7.40, the pH of blood? Use $K_a = 4.4 \times 10^{-8}$ for H_2CO_3 .
39. 50.0 mL of 0.10 M HCl are required to titrate 10.0 mL of ammonia window cleaner to the end point.
- What is the concentration of ammonia in the window cleaner?
 - What is the pH of the window cleaner if $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$?
 - What is the pH at the equivalence point of the titration?
 - Which indicator in Table 7.4 would be the best to indicate the endpoint?
40. 5.182-g of a solid, weak, monoprotic acid is used to make a 100.0 mL solution. 25.00 mL of the resulting acid solution is then titrated with 0.09685 M NaOH. The pH after the addition of 20.00 mL of the base is 5.58, and the endpoint is reached after the addition of 47.92 mL of the base.
- How many moles of acid were present in the 25.00 mL sample?
 - What is the molar mass of the acid?
 - What is the pK_a of the acid?
41. A benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) sample was analyzed by dissolving 406.2 mg of the sample in 50 mL of water and titrating it with 0.06642 M NaOH.
- What is the percent purity of the benzoic acid if the titration required 38.62 mL of base?
 - What is the pK_a of benzoic acid if the pH of the titration was 4.46 after the addition of 25.00 mL of the base?



42. Use the portion of the titration curve for the titration of 50.00 mL of a weak acid with 0.122 M NaOH shown above left to determine the concentration and pK_a of the weak acid.
43. Use the portion of the titration curve for the titration of 20.00 mL of a weak base with 0.143 M HCl shown above right to determine the concentration and pK_b of the weak base.

COMPOSITION FROM pH

44. What are the concentrations of $\text{C}_6\text{H}_8\text{O}_6$, $\text{C}_6\text{H}_7\text{O}_6^{1-}$, and $\text{C}_6\text{H}_6\text{O}_6^{2-}$ in a solution prepared by adjusting a 0.065 M ascorbic acid solution to the following pH's?
- a) 3.0 b) 5.0 c) 10.0 d) 12.0
45. What are the concentrations of hydrosulfuric acid and the hydrogen sulfate ion in a solution prepared by adjusting a 0.10 M H_2S acid solution to the following pH's?
- a) 5.0 b) 7.0 c) 10.0 d) 13.0
46. To what pH must a 0.15 M ascorbic acid solution be adjusted to obtain the following concentrations?
- a) $[\text{C}_6\text{H}_6\text{O}_6^{2-}] = 0.040 \text{ M}$
 b) $[\text{C}_6\text{H}_7\text{O}_6^{1-}] = 0.15 \text{ M}$
 c) $[\text{C}_6\text{H}_6\text{O}_6^{2-}] = 2.2 \times 10^{-10} \text{ M}$
47. To what pH must a 0.10 M H_2S solution be adjusted to obtain the following sulfide ion concentrations?
- a) $[\text{S}^{2-}] = 0.085 \text{ M}$
 b) $[\text{S}^{2-}] = 1.0 \times 10^{-14} \text{ M}$
 c) $[\text{HS}^{1-}] = 0.10 \text{ M}$
48. NaOH is added to a 0.120 M phosphoric acid solution until the hydrogen phosphate ion concentration is 0.080 M, but the phosphate ion concentration is negligible. What is the pH of the solution?
49. HCl is added to a 0.140 M phosphate ion solution until the dihydrogen phosphate ion concentration is 0.075 M, but the hydrogen phosphate ion concentration is negligible. What is the pH?

MISCELLANEOUS PROBLEMS

50. A tablet of aspirin ($\text{HC}_9\text{H}_7\text{O}_4$) is required to contain 325 mg of aspirin. The quality is analyzed by dissolving one tablet in 50 ml H_2O , then titrating the solution with 0.1000 M NaOH. If 16.05 ml of the NaOH solution are required to reach the endpoint, how many mg of aspirin are actually in the tested sample tablet? Does this product pass your inspection?
51. In molecular biology, phosphate buffers are normally utilized to maintain a physiological pH of 6.8 to 7.4. However for RNA isolation more acidic conditions (pH around 5.8) are often required for optimal enzymatic function.
- a) Explain why an acetate buffer is preferred over a phosphate buffer for RNA isolation.
- b) How many grams of sodium acetate should be dissolved in 500. mL of 0.112 M acetic acid to prepare a pH = 5.8 buffer?
52. Recall from Chapter 2, that the colligative concentration is extremely important in a cell. Thus, both the pH and the concentration of all components are important considerations when preparing a buffer. The concentration of all particles in solution is often termed the *osmolality* or (moles of particles)·kg solvent⁻¹. Using NaH_2PO_4 and Na_2HPO_4 and water, describe how to prepare a buffer with a pH = 7.21 and an osmolality of 300. mmol·kg⁻¹.

CHAPTER 8

Equilibria Containing Metal Ions

8.0 Introduction

8.1 Acid-Base Equilibria

8.2 Dissolution and the Solubility Product

8.3 Precipitation and Separation of Ions

8.4 Complex Ions

8.5 Competing or Simultaneous Equilibria

8.6 Chapter Summary and Objectives

8.7 Exercise

8.0 INTRODUCTION

Three different equilibria must be considered when dealing with aqueous metal ions:

1. Acid-base equilibria: The ions are positively charged, which makes them Lewis acidic (they interact readily with lone pairs of electrons). Consequently, many metal ions react with water in a manner similar to that of weak acids as described in Chapter 6.
2. Complex ion equilibria: Ions formed by the interaction of several Lewis bases and a metal are called **complex ions**, and the Lewis bases that interact with the metal are referred to as **ligands**. The equilibrium between the complex ion and its metal and ligands is another consideration to be made in the treatment of aqueous solutions containing metal ions.
3. Solubility equilibria: Many metal ions form sparingly soluble salts. In fact, water hardness results from the presence of metal ions (Mg^{2+} , Ca^{2+} , and Fe^{2+}) that form insoluble salts. The insoluble salts formed with the fatty acids in soaps leave a residue on washed material and sinks, and those formed with the carbonate ion produce scale in boilers and hot water pipes.

In this chapter, all three of these types of equilibria are considered.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- explain the acidity of some metal ions;
- define dissolution and the K_{sp} expression;
- explain solubility in terms of K_{sp} values;
- apply the common-ion effect to the dissolution process;
- explain the effect of pH on the solubility of acids and bases;
- define the formation reaction and the formation constant for complex ions; and
- explain how complex ion formation and precipitation compete for metal ions.

8.1 ACID-BASE EQUILIBRIA

While metal ions rarely have protons to donate as required by the Brønsted acid definition, they can accept electron pairs to form covalent bonds, so they are Lewis acidic. Consider an aqueous solution of iron(III) nitrate, which is a strong electrolyte that dissociates completely into Fe^{3+} and NO_3^{1-} ions. The solution is acidic even though it contains no protons because the small, highly charged iron(III) ion interacts with the surrounding water molecules in a Lewis acid-base reaction to produce $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, the octahedral ion shown in Figure 8.1. Ions, such as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, that consist of a metal ion bound to several molecules or anions are called **complex ions**, and the bound molecules or anions are referred to as **ligands**. The positive charge of the central metal ion withdraws electron density from the O–H bonds of the water ligands, which weakens them and makes the water ligands stronger acids. Thus, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is a Brønsted acid. The reaction of a hydrated Fe^{3+} ion with water is depicted below and in Figure 8.1.



The above reaction is the acid dissociation reaction of the weak acid $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, which has the following K_a :

$$K_a = \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}][\text{H}_3\text{O}^{1+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]} = 6 \times 10^{-3}$$

Note that the K_a of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is greater than that of acetic acid ($K_a = 1.8 \times 10^{-5}$), so $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is a stronger Brønsted acid than is acetic acid. To summarize, *hydrated metal ions are Brønsted acids because the positive charge on the metal ion removes electron density from the O–H bonds of the water ligands, which weakens the bonds and facilitates the loss of a proton*. The K_a values of several hydrated metal ions are listed in Table 8.1.

8.2 DISSOLUTION AND THE SOLUBILITY-PRODUCT CONSTANT

The process in which a solid dissolves is called **dissolution**, while the process in which it is formed from solution is called **precipitation**. When the rate of dissolution of an ionic solid equals its rate of precipitation, equilibrium between the solid and its ions in solution is established. This type of equilibrium is so common that its equilibrium constant is given a special name and symbol: the **solubility-product constant**, K_{sp} . For example, consider calcium carbonate (limestone), a slightly soluble salt that is responsible for scale in containers of hard water. Its dissolution and subsequent precipitation is also responsible for formation of caves and the stalactites and stalagmites in them.

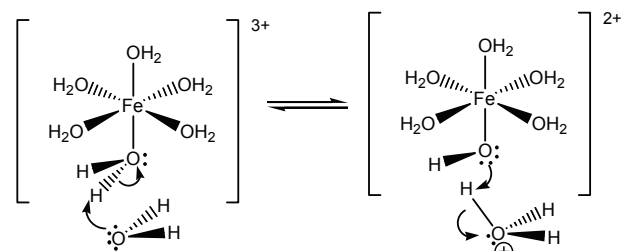
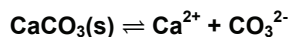


Figure 8.1 Acidity of aqueous Fe^{3+}

Table 8.1 K_a values of selected hydrated metal ions

Ion	K_a
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	6×10^{-3}
$\text{Al}(\text{H}_2\text{O})_6^{3+}$	1×10^{-5}
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	3×10^{-8}
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	1×10^{-9}
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	1×10^{-10}



$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]^*$$

Note that K_{sp} is simply the equilibrium constant for a particular reaction type. Recall that *the activity of a solid is unity, so the solid does not appear in the K_{sp} expression.*

Most slightly soluble salts contain basic anions, which are involved in both acid-base equilibria with water and dissolution equilibria with metal ions, which can lead to a complicated set of equilibria in the case of fairly strong bases such as CO_3^{2-} . Thus, in an aqueous solution of CaCO_3 , not only must its K_{sp} be obeyed, but so too must the K_{b} of the CO_3^{2-} ion. Consequently, our discussions of solubility in water will center on the solubility of neutral or only weakly basic salts such as those of the halides and sulfates. Consider the reaction table for the dissolution of Ag_2SO_4 in water.

	$\text{Ag}_2\text{SO}_4(\text{s})$	\rightleftharpoons	2Ag^{1+}	+	SO_4^{2-}
initial	enough		0		0
Δ	-x		+2x		+x
eq	some		2x		x

x is the **molar solubility** of Ag_2SO_4 in water. The solid does not enter into the equilibrium expression, so the amount of solid remaining at equilibrium is not important, but there must be *enough* initially to assure that *some* solid is present at equilibrium. In a saturated solution of Ag_2SO_4 ,

$$[\text{Ag}^{1+}] = 2x \text{ and } [\text{SO}_4^{2-}] = x$$

Substituting the ion concentrations in terms of the molar solubility of Ag_2SO_4 into the K_{sp} expression, we obtain the following:

$$K_{\text{sp}} = [\text{Ag}^{1+}]^2[\text{SO}_4^{2-}] = (2x)^2(x) = 4x^3$$

$K_{\text{sp}} = 4x^3$ is the form of the solubility-product constant in terms of the molar solubility for any salt in which the cation:anion ratio is 2:1 or 1:2 (*i.e.*, any salt with the general formula M_2X or MX_2). Thus, the solubility-product constant of a compound can be determined from the molar solubility. Conversely, the molar solubility of a salt can be determined from its K_{sp} *if the acid-base reactions between the anion and water can be neglected.*[†] The molar solubility is obtained by solving the K_{sp} expression for x.

$$x = \sqrt[3]{\frac{K_{\text{sp}}}{4}}$$

Example 8.1 and Practice Example 8.1 are examples of using solubility to find K_{sp} , and Example 8.2 demonstrates using of K_{sp} to determine solubility.

* Note that there is no denominator in the K_{sp} expression, so it is simply the product of the ion concentrations, which is the reason it is called the solubility product.

[†] The solubility of a basic salt, one that reacts strongly with water, is discussed in Example 8.2.

Example 8.1

What is the K_{sp} of MgF_2 if its solubility is 7.6 mg in 100. mL of H_2O ?

First, construct the reaction table for the dissolution:

	$MgF_2(s)$	\rightleftharpoons	Mg^{2+}	+	$2F^{-}$	$K_{sp} = [Mg^{2+}][F^{-}]^2$
Initial	enough		0		0	
Δ	-x		+x		+2x	
Eq	some		x		2x	

At equilibrium, $[Mg^{2+}] = x$ and $[F^{-}] = 2x$. Substitution of these ion concentrations into the K_{sp} expression yields

$$K_{sp} = [Mg^{2+}][F^{-}]^2 = (x)(2x)^2 = 4x^3$$

The above expression relates the solubility-product constant of any salt with a cation:anion ratio of 1:2 or 2:1 (MX_2 or M_2X) to its molar solubility. Next, we must determine the molar solubility from the given solubility. We begin by determining the number of moles of MgF_2 that dissolve in 100 mL. $M_m = 62.3 \text{ mg}\cdot\text{mmol}^{-1}$ for MgF_2 .

$$7.6 \text{ mg} \times \frac{1 \text{ mmol}}{62.3 \text{ mg}} = 0.12 \text{ mmol } MgF_2$$

The molar solubility is then determined to be

$$x = [Mg^{2+}] = \frac{0.12 \text{ mmol } MgF_2}{100 \text{ mL}} = 1.2 \times 10^{-3} \text{ M}$$

The molar solubility can then be used directly in the K_{sp} expression in terms of x ,

$$K_{sp} = 4x^3 = 4(1.2 \times 10^{-3})^3 = 7.3 \times 10^{-9}$$

or it can be used to determine the concentrations of the ions,

$$[Mg^{2+}] = x = 1.2 \times 10^{-3}; \quad [F^{-}] = 2x = 2.4 \times 10^{-3},$$

which can then be substituted into the original K_{sp} expression

$$K_{sp} = [Mg^{2+}][F^{-}]^2 = (1.2 \times 10^{-3})(2.4 \times 10^{-3})^2 = 7.3 \times 10^{-9}$$

The two methods are identical. The steps of the second method are simply merged into one step in the first procedure. Also note that the full calculator result for x (1.2199×10^{-3}), not the rounded result, was used in the calculation to reduce rounding errors in the answer (Appendix A.4). If the rounded result is used, the answer is 6.9×10^{-9} .

The solubility-product constants of some slightly soluble salts can be found in Appendix D. Note that the K_{sp} values tabulated in Appendix D are all quite small, so only the solubilities of slightly soluble substances are considered. However, K_{sp} is also defined for materials that are more soluble, but it is seldom applied to them. For example, the K_{sp} of $NaCl$ at $25^\circ C$ is 38, which corresponds to a solubility of $360 \text{ g}\cdot\text{L}^{-1}$.

PRACTICE EXAMPLE 8.1

What is the K_{sp} of $Fe(OH)_2$ if the pH of a saturated solution is 9.07?

Reaction:

The equilibrium concentrations

pOH =

$[OH^{-}] =$

$[Fe^{2+}] =$

Reaction Table

Reaction:

In

Δ

Eq

The solubility-product constant expression

$K_{sp} =$

The value of the solubility-product constant

Example 8.2

a) The K_{sp} of Ag_3PO_4 is 2.6×10^{-18} . What is its predicted molar solubility?

The reaction table for the dissolution is

	$\text{Ag}_3\text{PO}_4 (\text{s})$	\rightleftharpoons	3Ag^{1+}	$+ \text{PO}_4^{3-}$
Initial	enough		0	0
Δ	-x		+3x	+x
Eq	some		3x	x

Determine the expression for the solubility-product constant: $K_{sp} = [\text{Ag}^{1+}]^3[\text{PO}_4^{3-}]$

Substitute the equilibrium concentrations into the expression: $K_{sp} = (3x)^3(x) = 27x^4$

Solve the expression for the solubility: $x = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{2.6 \times 10^{-18}}{27}} = 1.8 \times 10^{-5} \text{ M}$

b) The experimentally determined molar solubility is $1.5 \times 10^{-4} \text{ M}$. Explain.

The difference between the experimental value and that determined from the K_{sp} is due to the fact that PO_4^{3-} is a fairly strong base ($K_b = 0.021$), so much of the phosphate ion produced in the dissolution is converted to HPO_4^{1-} by the reaction with water. The loss of phosphate ion causes more Ag_3PO_4 to dissolve (Le Châtelier's principle). This is why solubilities of basic salts cannot be determined from their solubility products alone.*

The values of the K_{sp} constants are one consideration when determining relative solubilities, but the form of the K_{sp} expression (the multiplier and exponent of the solubility) can also be important if the ion ratios are different. As shown in Table 8.2, the form of the K_{sp} expression depends only upon the cation:anion ratio. If the cation:anion ratios of the salts are the same, then their relative solubilities increase in the order of their K_{sp} 's; but, care must be taken when comparing salts with different ratios.

Example 8.3

List the following salts in order of increasing solubility.

PbCl_2 ($K_{sp} = 1.7 \times 10^{-5}$) AgCl ($K_{sp} = 1.2 \times 10^{-10}$) TlCl ($K_{sp} = 1.9 \times 10^{-4}$)

AgCl and TlCl are both 1:1 salts, and a simple comparison of their K_{sp} values shows that TlCl is much more soluble than AgCl . However, the relative solubilities of TlCl and PbCl_2 cannot be determined by a comparison of their K_{sp} 's because one is a 1:1 salt ($K_{sp} = x^2$) and the other is a 1:2 salt ($K_{sp} = 4x^3$). The two molar solubilities are

$\text{TlCl solubility} = \sqrt{1.9 \times 10^{-4}} = 0.014 \text{ M}$ and $\text{PbCl}_2 \text{ solubility} = \sqrt[3]{\frac{1.7 \times 10^{-5}}{4}} = 0.016 \text{ M}$

Thus, PbCl_2 is slightly more soluble than TlCl even though its K_{sp} is smaller. The solubilities of the three substances are in the order $\text{AgCl} \ll \text{TlCl} < \text{PbCl}_2$.

* The discrepancy does not mean that the K_{sp} is incorrect; it is still obeyed. Rather it is due to the fact that, because PO_4^{3-} also reacts with water, the $[\text{Ag}^{1+}] = 3[\text{PO}_4^{3-}]$ equality predicted from the dissolution chemical equation is no longer valid. Therefore, the assumption that $K_{sp} = 27x^4$ is not valid. We re-examine this problem in Practice Example 8.6.

Table 8.2 K_{sp} expressions in terms of molar solubilities (x) for salts with common cation:anion ratios

Cation:Anion Ratio	K_{sp}
1:1	$(x)(x) = x^2$
1:2 or 2:1	$(x)(2x)^2 = 4x^3$
3:1 or 1:3	$(x)(3x)^3 = 27x^4$
2:3 or 3:2	$(2x)^2(3x)^3 = 108x^5$

The dissolution of a slightly soluble salt is suppressed by the addition of ions that appear in the dissolution equilibrium (common-ion effect). Consider the dissolution of MgF_2 in a solution that already contains Mg^{2+} from another source (a common ion). The reaction table has the following form:

	$\text{MgF}_2(\text{s})$	\rightleftharpoons	Mg^{2+}	+	$2\text{F}^{1-}(\text{aq})$
initial	enough		c_o		0
Δ	-x		+x		+2x
eq	some		$c_o + x$		2x

c_o is the initial molar concentration of Mg^{2+} . The K_{sp} of MgF_2 is 1.7×10^{-5} , so we write

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^{1-}]^2 = (c_o + x)(2x)^2 = 1.7 \times 10^{-5}$$

Solution of the above for x involves a cubic equation. However, if $c_o \gg x$, then $c_o + x$ can be approximated as c_o , and the equation becomes much easier to solve. In Example 8.1, the solubility of MgF_2 in water was found to be 0.0012 M, but the dissolution of MgF_2 is suppressed by the presence of additional Mg^{2+} ions in the solution. Thus, x is less than 0.0012 M, so the approximation that x is negligible with respect to c_o is valid as long as c_o is not very small. We conclude that *the concentration of the common ion is usually unaffected by the dissolution process*, so its equilibrium concentration is equal to its initial concentration. The fact that one of the concentrations is known ($[\text{Mg}^{2+}] = c_o$) simplifies the problem considerably. Solving for $[\text{F}^{1-}]$ in the K_{sp} expression, we obtain the following:

$$[\text{F}^{1-}] = \sqrt{\frac{K_{\text{sp}}}{[\text{Mg}^{2+}]}} = 2x$$

$K_{\text{sp}} = 7.3 \times 10^{-9}$ for MgF_2 . If the concentration of Mg^{2+} ion from the other source is 0.10 M, then the concentration of fluoride ion is

$$[\text{F}^{1-}] = \sqrt{\frac{7.3 \times 10^{-9}}{0.10}} = 2.7 \times 10^{-4} \text{ M} = 2x$$

$[\text{F}^{1-}] = 2x$, so $x = \frac{1}{2}[\text{F}^{1-}]$. Thus, the solubility of magnesium fluoride in a solution that is 0.10 M in Mg^{2+} ion is 1.4×10^{-4} M, which is negligible compared to 0.10 M and our approximation that $c_o + x = c_o$ was valid. Note that, due to the common-ion effect, the solubility of magnesium fluoride is almost ten times less in the presence of 0.10 M Mg^{2+} than it is in pure water.

PRACTICE EXAMPLE 8.2

Indicate the more soluble compound in each pair.

a) PbSO_4 ($K_{\text{sp}} = 2 \times 10^{-8}$) or CaSO_4 ($K_{\text{sp}} = 2 \times 10^{-5}$)

b) BaF_2 ($K_{\text{sp}} = 2 \times 10^{-6}$) or PbF_2 ($K_{\text{sp}} = 4 \times 10^{-8}$)

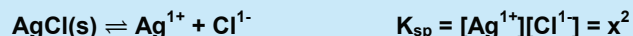
c) BaCrO_4 ($K_{\text{sp}} = 2 \times 10^{-10}$) or Ag_2CrO_4 ($K_{\text{sp}} = 3 \times 10^{-12}$)

d) Ag_3PO_4 ($K_{\text{sp}} = 2 \times 10^{-18}$) or $\text{Mg}_3(\text{PO}_4)_2$ ($K_{\text{sp}} = 5 \times 10^{-24}$)

Example 8.4

a) What is the solubility of AgCl in water?

The K_{sp} for AgCl is 1.8×10^{-10} (Appendix D). The dissolution process is



The solubility of AgCl in water is then determined to be

$$x = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

b) What is the solubility of AgCl in 0.10 M NaCl?

This is a problem of solubility in the presence of a common-ion. The reaction table is

	AgCl(s)	=	Ag¹⁺	+ Cl¹⁻
initial	enough		0	0.10
Δ	-x		+x	+x
eq	some		x	0.10 + x

x must be less than 1.3×10^{-5} M due to the common-ion effect exerted by the chloride ion. Consequently, $[\text{Cl}^{1-}] = 0.10 + x = 0.10$.

The silver ion concentration, which is equal to the solubility in this example, is

$$[\text{Ag}^{1+}] = x = \frac{K_{sp}}{[\text{Cl}^{1-}]} = \frac{1.8 \times 10^{-10}}{0.10} = 1.8 \times 10^{-9} \text{ M}$$

The solubility of silver chloride is ten thousand times less in 0.10 M NaCl than in water because the common ion (Cl^{1-}) suppresses the dissolution process.

PRACTICE EXAMPLE 8.3

What is the solubility of Sn(OH)_2 in a solution buffered at pH = 9.00?

Dissolution reaction:

$$K_{sp} =$$

OH^{1-} produced by the dissolution can be ignored in buffered solutions because the buffer maintains a constant pH.

$$[\text{OH}^{1-}] =$$

$$[\text{Sn}^{2+}] =$$

$$\text{solubility} =$$

What is the solubility of Sn(OH)_2 in a solution buffered at pH = 2.00?

$$[\text{OH}^{1-}] =$$

$$[\text{Sn}^{2+}] =$$

$$\text{solubility} =$$

Note that the solubility is far greater at the lower pH because the hydroxide ion is a strong base that reacts with both Sn^{2+} and H_3O^{1+} (Section 8.5).

8.3 PRECIPITATION AND SEPARATION OF IONS

Our discussion thus far has focused on the amount of a slightly soluble salt that dissolves, but now we consider the ion concentrations required to bring about precipitation. We start by examining the dissolution reaction of magnesium fluoride, but this time we consider the reaction from right to left; that is, we focus on the precipitation of MgF_2 .



Reactions proceed right to left (MgF_2 precipitates) only when the reaction quotient exceeds the equilibrium constant; *i.e.*, when $Q > K$. The reaction quotients for the dissolution of ionic compounds are so common that they are given a special name and symbol: the **ion product**, Q_{ip} . Thus, **precipitation occurs only if $Q_{ip} > K_{sp}$** .

Example 8.5

The pH of an acidified solution that is 0.01 M in Cu^{2+} , Fe^{2+} , Mg^{2+} and Sn^{2+} is increased by adding NaOH. Which hydroxide precipitates at each pH?

Refer to Appendix D to obtain the solubility-product constants in the margin. All of the metal ions are +2, so all of the hydroxides have 1:2 cation:anion ratios. All of the metal ion concentrations are 0.01 M, so a generic ion product can be written as

$$Q_{\text{ip}} = [\text{M}^{2+}][\text{OH}^1]^2 = (0.01)[\text{OH}^1]^2$$

a) pH = 4

The hydroxide ion concentration in the solution is obtained from the pH.

$$\text{pOH} = 14 - \text{pH} = 14 - 4 = 10, \text{ so } [\text{OH}^1] = 10^{-\text{pOH}} = 10^{-10} \text{ M}$$

$$Q_{\text{ip}} = [\text{M}^{2+}][\text{OH}^1]^2 = (0.01)(10^{-10})^2 = 10^{-22}$$

Q_{ip} exceeds the K_{sp} of only $\text{Sn}(\text{OH})_2$. Thus, at pH = 4, only $\text{Sn}(\text{OH})_2$ precipitates, while the other ions remain in solution. The reaction mixture could then be filtered to remove the solid $\text{Sn}(\text{OH})_2$, which could then be re-dissolved in an acidic solution. Thus, two solutions would result: one with Fe^{2+} , Cu^{2+} and Mg^{2+} ions and one with only Sn^{2+} ions. In other words, the Sn^{2+} ions have been separated from the original mixture. To be completely accurate, *most* of the Sn^{2+} ions have been separated. The K_{sp} of $\text{Sn}(\text{OH})_2$ must still be satisfied, so some Sn^{2+} remains in the solution with the other ions. We address this problem in Example 8.8.

b) pH = 6

$$\text{pOH} = 14 - \text{pH} = 14 - 6 = 8, \text{ so } [\text{OH}^1] = 10^{-\text{pOH}} = 10^{-8} \text{ M}$$

$$Q_{\text{ip}} = [\text{M}^{2+}][\text{OH}^1]^2 = (0.01)(10^{-8})^2 = 10^{-18}$$

Sn^{2+} has been removed, so Q_{ip} exceeds the K_{sp} of only $\text{Cu}(\text{OH})_2$. Thus, $\text{Cu}(\text{OH})_2$ precipitates leaving a solution of Fe^{2+} and Mg^{2+} ions. Again, the $\text{Cu}(\text{OH})_2$ could be filtered and re-dissolved to produce three solutions: one with Mg^{2+} and Fe^{2+} ions, one with Cu^{2+} ions, and one with Sn^{2+} ions.

c) pH = 8

Proceeding as above, the ion product for those ions still in solution is

$$Q_{\text{ip}} = [\text{M}^{2+}][\text{OH}^1]^2 = (0.01)(10^{-6})^2 = 10^{-14}$$

which exceeds the K_{sp} of $\text{Fe}(\text{OH})_2$, so $\text{Fe}(\text{OH})_2$ precipitates leaving a solution of Mg^{2+} ions and trace amounts of the other ions as noted in Parts a and b. After a final filtration of $\text{Fe}(\text{OH})_2$ followed by re-dissolving the solid in acid, we end up with four solutions each containing only one of the four ions. This is an example of separations chemistry because the four ions that were together in one solution are now separated into four different solutions.

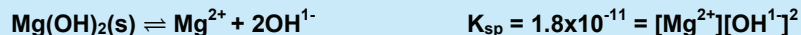
 K_{sp} values for Example 8.5

Hydroxide	K_{sp}
$\text{Sn}(\text{OH})_2$	1.4×10^{-28}
$\text{Cu}(\text{OH})_2$	2.2×10^{-20}
$\text{Fe}(\text{OH})_2$	8.0×10^{-16}
$\text{Mg}(\text{OH})_2$	1.8×10^{-11}

Example 8.6

At what pH does $\text{Mg}(\text{OH})_2$ begin to precipitate from a solution that is 0.01 M in Mg^{2+} ?

We know $[\text{Mg}^{2+}]$ and K_{sp} , so we need only solve the K_{sp} expression for $[\text{OH}^{1-}]$.



Solving for the hydroxide ion concentration and substituting the known K_{sp} and $[\text{Mg}^{2+}]$, we obtain the following:

$$[\text{OH}^{1-}] = \sqrt{\frac{K_{\text{sp}}}{[\text{Mg}^{2+}]}} = \sqrt{\frac{1.8 \times 10^{-11}}{0.01}} = 4 \times 10^{-5} \text{ M}$$

Converting $[\text{OH}^{1-}]$ to pH, we obtain the answer:

$$\text{pOH} = -\log(4 \times 10^{-5}) = 4.4; \text{ pH} = 14.0 - 4.4 = 9.6$$

$\text{Mg}(\text{OH})_2$ begins to precipitate when the pH reaches 9.6.

The four ions in Example 8.5 were separated from solution, but some of each metal ion remains in solution after each precipitation because the equilibrium between the metal and hydroxide ions is maintained even after precipitation. Increasing the hydroxide ion concentration shifts the equilibrium to the left, but it does not eliminate all of the metal ions. Thus, after $\text{Sn}(\text{OH})_2$ is precipitated, the following equilibrium is still maintained:



Solving the K_{sp} expression for the equilibrium concentration of Sn^{2+} , we obtain

$$[\text{Sn}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^{1-}]^2}$$

If we want to separate the tin(II) ions from the other ions, then we want to minimize this concentration and maximize the amount that precipitates; *i.e.*, a good separation is one in which the Sn^{2+} ion concentration is very low after the precipitation. To reduce the tin(II) concentration, we simply need to add more hydroxide, but care must be taken not to increase the pH so high that the hydroxides of other metal ions begin to precipitate as well. Example 8.7 demonstrates how to determine the concentration of a remaining ion, and Example 8.8 shows how to optimize a separation by precipitating the maximum amount of one substance without precipitating another.

PRACTICE EXAMPLE 8.4

Identify any precipitates that result when 5.0 mL of 0.010 M HCl is added to 20. mL of a solution in which $[\text{Ti}^{1+}] = 0.15 \text{ M}$ and $[\text{Pb}^{2+}] = 0.20 \text{ M}$.

$$K_{\text{sp}} \text{ of } \text{TiCl} = 1.9 \times 10^{-4} \quad K_{\text{sp}} \text{ of } \text{PbCl}_2 = 1.7 \times 10^{-5}$$

Concentrations of ions after mixing but before precipitation occurs

$$[\text{Ti}^{1+}] =$$

$$[\text{Pb}^{2+}] =$$

$$[\text{Cl}^{1-}] =$$

Ion products

TiCl

$$Q_{\text{ip}} =$$

PbCl_2

$$Q_{\text{ip}} =$$

Precipitates that form:

Example 8.7

What is the concentration of Sn^{2+} ions remaining after precipitation of $\text{Sn}(\text{OH})_2$ at pH = 4.0?

We are given $K_{\text{sp}} = 1.4 \times 10^{-28}$ and $[\text{OH}^{1-}] = 1 \times 10^{-10} \text{ M}$ and asked for $[\text{Sn}^{2+}]$.

$$[\text{Sn}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^{1-}]^2} = \frac{1.4 \times 10^{-28}}{(1 \times 10^{-10})^2} = 1 \times 10^{-8} \text{ M} = 0.01 \text{ } \mu\text{M}$$

The concentration of the Sn^{2+} remaining after the precipitation is about one hundred millionth molar! The concentration of Sn^{2+} in solution went from 0.01 M to 0.01 μM , so 99.9999% of the Sn^{2+} was separated from solution.

Example 8.8

A solution is 0.010 M each in Sn^{2+} and Fe^{2+} . At what pH would optimum be achieved?

The K_{sp} values are $\text{Fe}(\text{OH})_2 = 8 \times 10^{-16}$ and $\text{Sn}(\text{OH})_2 = 1 \times 10^{-28}$. The K_{sp} of $\text{Sn}(\text{OH})_2$ is by far the smaller, so it will precipitate well before the $\text{Fe}(\text{OH})_2$. The $[\text{OH}^{1-}]$ required to begin precipitation for each is:

$$\text{Fe}^{2+}: [\text{OH}^{1-}] = \sqrt{\frac{K_{\text{sp}}}{[\text{Fe}^{2+}]}} = \sqrt{\frac{8 \times 10^{-16}}{0.010}} = 3 \times 10^{-7} \text{ M and}$$

$$\text{Sn}^{2+}: [\text{OH}^{1-}] = \sqrt{\frac{K_{\text{sp}}}{[\text{Sn}^{2+}]}} = \sqrt{\frac{1 \times 10^{-28}}{0.010}} = 1 \times 10^{-13} \text{ M}$$

Optimum separation requires that $[\text{Sn}^{2+}]$ be as low as possible after precipitation, so we make $[\text{OH}^{1-}]$ as high as possible but well below $3 \times 10^{-7} \text{ M}$ to insure that $\text{Fe}(\text{OH})_2$ does not precipitate. We choose a hydroxide ion concentration of $1 \times 10^{-7} \text{ M}$, which is well above that required to precipitate $\text{Sn}(\text{OH})_2$ but only $1/3$ that required to precipitate $\text{Fe}(\text{OH})_2$. At pH = 7.0,

$$[\text{Sn}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^{1-}]^2} = \frac{1 \times 10^{-28}}{(1 \times 10^{-7})^2} = 1 \times 10^{-14} \text{ M}$$

Thus, only $10^{-10}\%$ of the original Sn^{2+} remains in solution! The Q_{ip} of $\text{Fe}(\text{OH})_2$ is $(0.010)(1.0 \times 10^{-7})^2 = 1.0 \times 10^{-16}$, which does not exceed its K_{sp} , so ~100% of Sn^{2+} precipitates with no precipitation of $\text{Fe}(\text{OH})_2$. This is a good separation.

Example 8.9

What mass of Ag_2CrO_4 is formed when 50. mL of 0.10 M K_2CrO_4 and 50. mL of 0.10 M AgNO_3 are mixed?

The net equation for the precipitation: $2\text{Ag}^{1+} + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4(\text{s})$

The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} , so the equilibrium constant for the precipitation is large ($K_{\text{sp}}^{-1} \sim 10^{12}$). Thus, this reaction goes essentially to completion. We next determine the limiting reactant. Initially, there are

$$50. \text{ mL solution} \times \frac{0.10 \text{ mmol Ag}^{1+}}{\text{mL solution}} = 5.0 \text{ mmol Ag}^{1+} \text{ ions}$$

$$50. \text{ mL solution} \times \frac{0.10 \text{ mmol CrO}_4^{2-}}{\text{mL solution}} = 5.0 \text{ mmol CrO}_4^{2-} \text{ ions}$$

Two moles of silver ions are required for every one mole of chromate ion, but there are equal numbers of moles of each reactant initially. Consequently, silver ion is the limiting reactant, and the reaction table for the precipitation has the following form:

	2Ag^{1+}	$+ \text{CrO}_4^{2-}$	\rightarrow	$\text{Ag}_2\text{CrO}_4(\text{s})$
initial	5.0	5.0		0 mmol
Δ	-5.0	-2.5		+2.5 mmol
final	0	2.5		2.5 mmol

The silver ion concentration is not zero at equilibrium because silver chromate is slightly soluble. The reaction table for the dissolution of Ag_2CrO_4 in the presence of the excess chromate ion is discussed in Example 8.10. However, the numbers of moles of all other species present at equilibrium are given in the above table. The mass of Ag_2CrO_4 ($M_{\text{m}} = 332 \text{ g} \cdot \text{mol}^{-1} = 332 \text{ mg} \cdot \text{mmol}^{-1}$) that forms is

$$2.5 \text{ mmol} \times \frac{332 \text{ mg}}{\text{mmol}} = 8.3 \times 10^2 \text{ mg} = 0.83 \text{ g}$$

Example 8.10

What are the concentrations of the ions in the solution produced in Example 8.9?

In a reaction as extensive as the precipitation of Ag_2CrO_4 , the amount of product formed can be determined from stoichiometry without using equilibrium considerations (Example 8.9). However, Ag_2CrO_4 is slightly soluble, and we now determine how much of the solid dissolves. First, determine the concentration of the chromate ion after precipitation. The resulting solution has a total volume of 100. mL (assuming additive volumes), and contains 2.5 mmol CrO_4^{2-} , so the concentration of the chromate ion is

$$[\text{CrO}_4^{2-}] = \frac{2.5 \text{ mmol}}{100. \text{ mL}} = 0.025 \text{ M}$$

PRACTICE EXAMPLE 8.5

What is the concentration of lead ions in a solution formed by mixing 24 mL of 0.10 M $\text{Pb}(\text{NO}_3)_2$ and 50. mL of 0.12 M KF ?

K_{sp} of $\text{PbF}_2 =$ _____ from Appendix D

mmoles of $\text{Pb}^{2+} =$

mmoles of $\text{F}^{1-} =$

Limiting Reactant

mmol PbF_2 from Pb^{2+}

mmol PbF_2 from F^{1-}

limiting reactant is _____

Reaction Table for the precipitation

Reaction:

Initial

Δ

Final

Total volume =

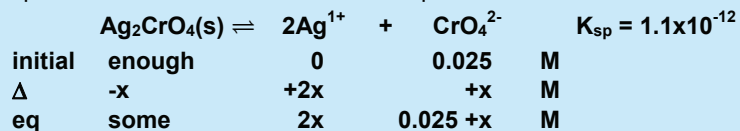
Fluoride ion concentration in final solution

$[\text{F}^{1-}] =$ _____ M

$[\text{Pb}^{2+}]$ from K_{sp} and excess F^{1-} ion concentration:

$[\text{Pb}^{2+}] =$ _____ M

Next, carry out the dissolution of the precipitated Ag_2CrO_4 in the presence of excess CrO_4^{2-} . The initial line of the reaction table for the dissolution is based on the final line of the precipitation reaction table shown in Example 8.9.



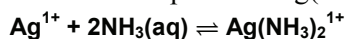
Thus, $K_{\text{sp}} = 1.1 \times 10^{-12} = [\text{Ag}^{1+}]^2[\text{CrO}_4^{2-}] = (2x)^2(0.025+x)$. However, x is expected to be negligible compared to 0.025 because K_{sp} is very small and there is a common-ion effect due to the excess reactant. Consequently, $[\text{CrO}_4^{2-}] = 0.025 \text{ M}$. Using this assumption, we can solve for $[\text{Ag}^{1+}]$ directly.

$$[\text{Ag}^{1+}] = \sqrt{\frac{K_{\text{sp}}}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{1.1 \times 10^{-12}}{0.025}} = 6.6 \times 10^{-6} \text{ M} = 6.6 \mu\text{M}$$

The assumption is valid because the amount that dissolves is negligible compared to the initial chromate ion concentration.

8.4 COMPLEX IONS

Complex ions are ions in which a central metal ion is surrounded by molecular or anionic ligands. For example, the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion discussed in Section 8.1 is a complex ion. The ligands and the metal are in equilibrium in much the same way that the protons and anion of a polyprotic acid are in equilibrium. That is, there is a series of equilibria in which the ligands are added or removed one at a time. However, we will consider only the overall process in which all of the ligands are added or removed in one step. The equilibrium constant governing the one-step formation of the complex ion from the metal ion and the ligands is called the **formation constant** and given the symbol K_f . Table 8.3 contains the formation constants at 25 °C for some common complex ions. As an example, consider formation of the complex ion $\text{Ag}(\text{NH}_3)_2^{1+}$.



The equilibrium constant for the above is the formation constant of the $\text{Ag}(\text{NH}_3)_2^{1+}$ ion.

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^{1+}]}{[\text{Ag}^{1+}][\text{NH}_3]^2} = 1.7 \times 10^7$$

Biochemists prefer the reverse of the formation reaction, so tables of **dissociation constants**, K_d , are also available, but the K_d of an ion is merely the reciprocal of its K_f . K_d is used in Example 8.11 because the reaction deals with the dissociation of the ion.

Table 8.3 Selected formation constants at 25 °C

Complex Ion	K_f	Formation Reaction
$\text{Ag}(\text{NH}_3)_2^{1+}$	1.7×10^7	$\text{Ag}^{1+} + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^{1+}$
$\text{Ag}(\text{CN})_2^{1-}$	3.0×10^{20}	$\text{Ag}^{1+} + 2\text{CN}^{1-} \rightleftharpoons \text{Ag}(\text{CN})_2$
$\text{Cu}(\text{NH}_3)_4^{2+}$	4.8×10^{12}	$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$
$\text{Fe}(\text{CN})_6^{4-}$	1.0×10^{35}	$\text{Fe}^{2+} + 6\text{CN}^{1-} \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{42}	$\text{Fe}^{3+} + 6\text{CN}^{1-} \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}$
$\text{Ni}(\text{NH}_3)_6^{2+}$	5.6×10^8	$\text{Ni}^{2+} + 6\text{NH}_3 \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}$
$\text{Zn}(\text{OH})_4^{2-}$	2.8×10^{15}	$\text{Zn}^{2+} + 4\text{OH}^{1-} \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}$

Example 8.11

What is the concentration of free Cu^{2+} in a 0.26-M solution of $\text{Cu}(\text{NH}_3)_4^{2+}$?

Construct the reaction table for the dissociation of the complex ion. The dissociation constant (K_d) is the reciprocal of the formation constant ($K_f = 4.8 \times 10^{12}$).

	$\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$	\rightleftharpoons	$\text{Cu}^{2+}(\text{aq})$	$+$	$4\text{NH}_3(\text{aq})$	$K_d = 2.1 \times 10^{-13}$
initial	0.26		0		0	
Δ	-x		x		4x	
eq	0.26 - x		x		4x	

$K \ll 1$, so assume that x can be ignored in the subtraction to obtain

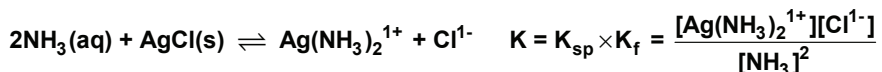
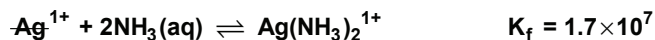
$$K_d = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[\text{Cu}(\text{NH}_3)_4^{2+}]} = \frac{(x)(4x)^4}{0.26 - x} = \frac{256x^5}{0.26} = 2.1 \times 10^{-13}$$

Solve the above for x and verify that x is negligible compared to 0.26 M.

$$x = [\text{Cu}^{2+}] = \sqrt[5]{\frac{(0.26)(2.1 \times 10^{-13})}{256}} = 7.3 \times 10^{-4} \text{ M}$$

8.5 COMPETING OR SIMULTANEOUS EQUILIBRIA

The reaction between silver and chloride ions to form AgCl is a Lewis acid-base reaction between a Lewis acid (Ag^{1+}) and a Lewis base (Cl^{1-}). The formation of $\text{Ag}(\text{NH}_3)_2^{1+}$ ions is also a Lewis acid-base reaction in which NH_3 is the base. Thus, when AgCl is added to an NH_3 solution, there is competition between Cl^{1-} and NH_3 for silver ions. Consequently, some Ag^{1+} ions are pulled into solution as the complex ion, which has the effect of making the AgCl more soluble in ammonia than in water. The effect can be quantified by considering the dissolution of AgCl and the formation of $\text{Ag}(\text{NH}_3)_2^{1+}$ simultaneously.



Summing the chemical equations for the dissolution and formation reactions produces the chemical equation for the dissolution of AgCl in ammonia. Consequently, its equilibrium constant is the product of the equilibrium constants of the two reactions that add to produce it. The solubility of AgCl in ammonia is explored in Example 8.12.

Example 8.12**What is the solubility of AgCl in 1.0 M NH₃?**

The reaction table for the dissolution of AgCl in 1.0 M ammonia is

	2NH₃(aq)	+	AgCl(s)	⇌	Ag(NH₃)₂¹⁺(aq)	+	Cl¹⁻(aq)
initial	1.0		enough		0		0
Δ	-2x		-x		+x		+x
eq	1.0 - 2x		some		x		x

The value of the equilibrium constant is $K = K_{sp}K_f = (1.8 \times 10^{-10})(1.7 \times 10^7) = 3.1 \times 10^{-3}$

$$K = 3.1 \times 10^{-3} = \frac{[\text{Ag}(\text{NH}_3)_2^{1+}][\text{Cl}^{1-}]}{[\text{NH}_3]^2} = \frac{x^2}{(1.0 - 2x)^2}$$

which is most easily solved by taking the square root of both sides.

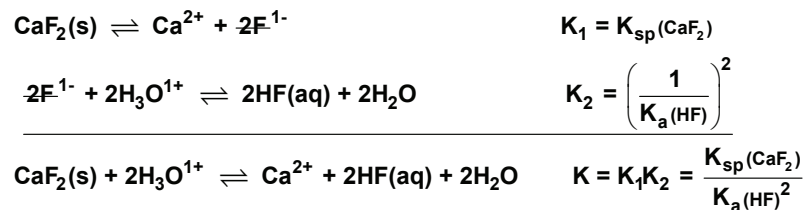
$$\sqrt{3.1 \times 10^{-3}} = 0.056 = \frac{x}{1.0 - 2x}$$

Multiplication of both sides by 1.0 - 2x yields 0.056 - 0.11x = x. Solving for x:

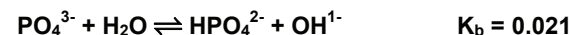
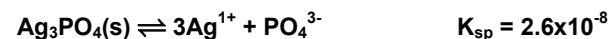
$$x = \frac{0.056}{1.11} = 0.050 \text{ M} = [\text{Ag}(\text{NH}_3)_2^{1+}] = [\text{Cl}^{1-}]$$

The solubility of AgCl in 1.0 M NH₃ is 0.050 M, which is nearly 4,000 times more soluble than in pure water. (1.3×10^{-5} M Example 8.4)

Ligands are Lewis bases, so when a ligand is in solution with two Lewis acids, the acids compete for the ligand, and the competition results in an equilibrium that is related to the equilibria between the ligand and each of the two acids. For example, fluoride ion is a Lewis base that reacts with Ca²⁺ to produce CaF₂, a slightly soluble salt, and with H₃O¹⁺ to produce HF. Thus, when CaF₂ is added to a solution of a strong acid, both the Ca²⁺ and the H₃O¹⁺ ions compete for the fluoride ions. Consequently, some F¹⁻ ions are pulled into solution as HF molecules. One Ca²⁺ ion goes into solution for each two F¹⁻ ions as some of the CaF₂ dissolves, making CaF₂ more soluble in acid than in water. The process, which is characterized by the K_{sp} reaction of CaF₂ and the reverse of the K_a reaction of 2HF, is described below.

**PRACTICE EXAMPLE 8.6**

In Example 8.2, we showed that the solubility of Ag₃PO₄ is over eight times greater than predicted from its K_{sp}. We attributed this to the fact that PO₄³⁻ reacts with both Ag¹⁺ and H₂O; *i.e.*, there are competing equilibria. Let us revisit that solubility as a competing equilibrium problem. Assume the following competing equations:



What is the chemical equation for dissolving Ag₃PO₄ in water that accounts for the competing equilibria, and what is its equilibrium constant?

$$K = \quad = \underline{\hspace{2cm}}$$

What is the solubility of Ag₃PO₄ in a solution buffered at pH = 9.00, where all phosphate is in the form of HPO₄²⁻ (Figure 7.8)?

Reaction Table:

In

Δ

Eq

K =

$$[\text{HPO}_4^{2-}] = x = \underline{\hspace{2cm}} \text{ M}$$

How does this compare to the experimental solubility of Ag₃PO₄ (1.5×10^{-4} M)? Compare that to the solubility predicted using K_{sp} alone (1.8×10^{-5} M).

Example 8.13

What is the solubility of CaF_2 in a solution buffered at $\text{pH} = 2.00$?

The solution is buffered, so the hydronium concentration is constant.

$$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 10^{-2.00} = 0.010 \text{ M}$$

The solution is buffered, so we assume that the hydronium ion concentration change is negligible. The reaction table for the dissolution is then constructed as follows:

	$\text{CaF}_2(\text{s})$	+	$2\text{H}_3\text{O}^{1+}$	\rightleftharpoons	Ca^{2+}	+	$2\text{HF}(\text{aq})$	+	$2\text{H}_2\text{O}$
in	enough		0.010		0		0		
Δ	-x		0		+x		+2x		
eq.	some		0.010		x		2x		

Look up the K_{sp} of CaF_2 and the K_{a} of HF to determine the value of the equilibrium constant as discussed in the text.

$$K = \frac{K_{\text{sp}}}{K_{\text{a}}^2} = \frac{3.9 \times 10^{-11}}{(7.2 \times 10^{-4})^2} = 7.5 \times 10^{-5}$$

Setup the equilibrium constant expression and solve for x.

$$7.5 \times 10^{-5} = \frac{[\text{Ca}^{2+}][\text{HF}]^2}{[\text{H}_3\text{O}^{1+}]^2} = \frac{(x)(2x)^2}{(0.010)^2}$$

$$4x^3 = 7.5 \times 10^{-9}; \quad x = \sqrt[3]{\frac{7.5 \times 10^{-9}}{4}} = 1.2 \times 10^{-3} \text{ M}$$

CaF_2 is about 20 times more soluble at $\text{pH} = 2$ than at $\text{pH} = 7$.

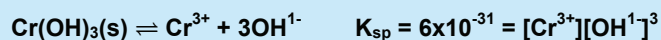
The equilibrium constant for the dissolution of a basic salt in acid involves the K_{a} of the weak acid in the denominator, so it gets larger as the base gets stronger (the K_{a} of its conjugate acid gets smaller). Thus, the degree to which the solubility of a basic salt is enhanced in acid increases as the base strength of the anion increases. We conclude that *slightly soluble salts are more soluble in basic solution (OH^{1-} , CN^{1-} , NH_3) if the Lewis acidic metal ion forms a complex ion with the base (Example 8.12), and they are more soluble in acidic solution if the ligand is a base that can react with the acid (Example 8.13).*

Some anions form a slightly soluble salt and a complex ion with the same cation. In these cases, a precipitate forms with the addition of the anion to a solution of the cation only to dissolve as the complex ion with further addition of the anion. Example 8.14 treats an example of this behavior.

Example 8.14

A precipitate of $\text{Cr}(\text{OH})_3$ ($K_{\text{sp}} = 6 \times 10^{-31}$) is produced as hydroxide ion is added slowly to an acidified solution that is 0.04 M in Cr^{3+} . However, the precipitate dissolves as the $\text{Cr}(\text{OH})_4^{1-}$ ion ($K_{\text{f}} = 8 \times 10^{29}$) with the addition of more base. Assume that the volume of added base is negligible and determine the pH at which precipitate first forms and the pH at which it completely disappears.

Use the K_{sp} to treat the precipitation.

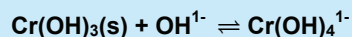


Solve the K_{sp} for the hydroxide ion concentration and substitute the known values:

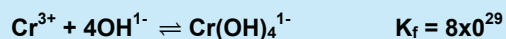
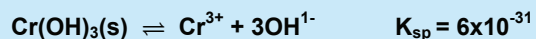
$$[\text{OH}^{1-}] = \sqrt[3]{\frac{K_{\text{sp}}}{[\text{Cr}^{3+}]}} = \sqrt[3]{\frac{6 \times 10^{-31}}{0.04}} = 2 \times 10^{-10} \text{ M}$$

$$\text{pOH} = -\log(2 \times 10^{-10}) = 9.6 \quad \& \quad \text{pH} = 14.0 - 9.6 = 4.4$$

$\text{Cr}(\text{OH})_3$ forms at pH = 4.4. It is dissolved in excess base by the following reaction.



The above chemical equation is the sum of the dissolution reaction for $\text{Cr}(\text{OH})_3$ and the formation reaction for $\text{Cr}(\text{OH})_4^{1-}$.



$$\text{so its equilibrium constant is } K = K_{\text{sp}}K_{\text{f}} = (6 \times 10^{-31})(8 \times 10^{29}) = 0.5 = \frac{[\text{Cr}(\text{OH})_4^{1-}]}{[\text{OH}^{1-}]}$$

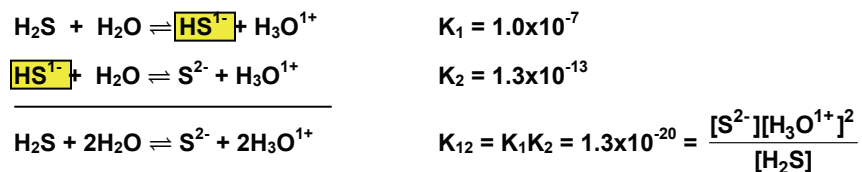
When all of the solid dissolves, $[\text{Cr}(\text{OH})_4^{1-}] = 0.04 \text{ M}$, so we can solve the above expression for $[\text{OH}^{1-}]$.

$$[\text{OH}^{1-}] = \frac{[\text{Cr}(\text{OH})_4^{1-}]}{K} = \frac{0.04}{0.5} = 0.08 \text{ M}$$

$$\text{pOH} = -\log(0.08) = 1.1 \quad \& \quad \text{pH} = 14.0 - 1.1 = 12.9$$

Thus, solid begins to form at a pH = 4.4, but it is completely gone again at a pH = 12.9.

Polyprotic acids also have simultaneous equilibria to consider and their chemical equations can also be added to produce a third chemical equation that does not include the concentration of the intermediate ion. In Chapter 7, we examined the case of H_2S where the HS^{1-} ion is eliminated by the addition of the two dissociations.



If $[\text{H}_2\text{S}]$ is known, K_{12} allows us to determine the pH required for a given $[\text{S}^{2-}]$ or to determine $[\text{S}^{2-}]$ from a given pH. H_2S is a gas, and its solubility in water at 25 °C is 0.10 M, thus a solution with a desired sulfide ion concentration can be prepared by buffering a solution to a predetermined pH and then saturating it with H_2S . Both $[\text{H}_2\text{S}]$ and pH are known, so the sulfide ion concentration can be determined.

Example 8.15

- a) To what pH should the solution that is 0.010 M in each Fe^{2+} and Mn^{2+} be saturated with H_2S to achieve an optimum separation of the ions?

The ions will precipitate as their sulfides, so we first get their K_{sp} 's from Appendix D.

$$K_{\text{sp}}(\text{MnS}) = 5.6 \times 10^{-16} \quad K_{\text{sp}}(\text{FeS}) = 6.3 \times 10^{-18}$$

FeS is less soluble, so it is the sulfide that precipitates first. To achieve optimum separation, we want to minimize the $[\text{Fe}^{2+}]$ remaining in solution after the addition of S^{2-} ion. To do this, we must maximize $[\text{S}^{2-}]$, but it cannot exceed the concentration where MnS precipitates. The minimum sulfide ion concentration required to precipitate 0.010 M Mn^{2+} is determined as follows:

$$[\text{S}^{2-}] = \frac{K_{\text{sp}}}{[\text{Mn}^{2+}]} = \frac{5.6 \times 10^{-16}}{0.010} = 5.6 \times 10^{-14} \text{ M}$$

The above sulfide ion concentration minimizes the $[\text{Fe}^{2+}]$ remaining in solution without precipitation of any MnS . We use this concentration and the fact that a saturated solution of H_2S is 0.10 M in the K_{12} expression for H_2S to determine the required $[\text{H}_3\text{O}^{1+}]$ and pH.

$$[\text{H}_3\text{O}^{1+}] = \sqrt{\frac{K_{12}[\text{H}_2\text{S}]}{[\text{S}^{2-}]}} = \sqrt{\frac{(1.3 \times 10^{-20})(0.10)}{5.6 \times 10^{-14}}} = 1.5 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.82$$

If $\text{pH} > 3.82$ when the solution is saturated with H_2S , MnS will precipitate. Thus, a $\text{pH} < 3.82$ is required. An optimum separation would occur at $\text{pH} \sim 3.80$. The solution would be buffered at $\text{pH} = 3.80$ and then H_2S gas would be bubbled into the solution until saturation. The FeS that is produced would be filtered from solution leaving a solution that was still 0.01 M in Mn^{2+} , but the concentration of Fe^{2+} would be greatly reduced.

b) What are the concentrations of the metal ions in solution after precipitation?

Use the K_{12} expression to determine $[S^{2-}]$ at pH = 3.80

$$[S^{2-}] = \frac{K_{12}[H_2S]}{[H_3O^{1+}]^2} = \frac{(1.3 \times 10^{-20})(0.10)}{(10^{-3.80})^2} = 5.2 \times 10^{-14} \text{ M}$$

Determine Q_{ip} for the above $[S^{2-}]$ and the given metal ion concentrations.

$$Q_{ip} = [M^{2+}][S^{2-}] = (0.010)(5.2 \times 10^{-14}) = 5.2 \times 10^{-16}$$

$Q_{ip} < K_{sp}$ for MnS ($5.2 \times 10^{-16} < 5.6 \times 10^{-16}$), so MnS does not precipitate: $[Mn^{2+}] = 0.010 \text{ M}$.

FeS does precipitate and the metal ion concentration is determined from its K_{sp} and the sulfide ion concentration.

$$[Fe^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{6.3 \times 10^{-18}}{5.2 \times 10^{-14}} = 1.2 \times 10^{-4} \text{ M}$$

$(1.2 \times 10^{-4} / 0.010) \times 100\% = 1.2\%$ of the iron is still in solution, so this is not a very good separation.

8.6 CHAPTER SUMMARY AND OBJECTIVES

Metal ions are Lewis acids, and the Brønsted acidity of metal ions results from the protons of the water molecules that are bound to the metal. The positive charge of the metal ion withdraws electron density from the O–H bonds and weakens them. The weaker O–H bonds make the water ligands stronger acids.

The equilibrium constant for the dissolution of a slightly soluble salt is called the solubility-product constant, K_{sp} . The molar solubility of the soluble salt can be determined from the value of the salt's K_{sp} when the anion is neutral or only slightly basic. The form of the K_{sp} in terms of the molar solubility depends only on the cation:anion ratio. The solubility of a salt decreases in the presence of a common ion due to the common-ion effect.

Precipitation of a slightly soluble salt occurs when the ion product exceeds the solubility-product constant of the salt. By careful variation of the anion concentration in a solution of several different metal ions, the ion product of one salt at a time can be made to exceed its solubility-product constant and selective precipitation can be achieved. The ions in a mixture can be separated from one another by this procedure.

The equilibrium constant for the reaction in which a complex ion is formed from the metal and the ligands is called the formation constant, K_f . Formation constants are

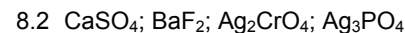
typically quite large and the ligands of a complex ion can compete with the anions of insoluble salts for the metal ion. As a result, the solubility of a slightly soluble salt can be enhanced substantially in the presence of a ligand with which the metal forms a complex ion. The equilibrium constant of the dissolution of the salt in the presence of the ligand is obtained by combining the formation and solubility-product constants.

After studying the material presented in this chapter, you should be able to:

1. explain the acidity of metal ions and write the acid-dissociation reaction associated with the acidity (Section 8.1);
2. write the dissolution reaction of a slightly soluble salt (Section 8.2);
3. write the expression for the solubility-product constant, K_{sp} , of a given salt (Section 8.2);
4. calculate the solubility of an ionic compound given its K_{sp} value, and *vice versa* (Section 8.2);
5. calculate the solubility of an ionic compound in the presence of one of its ions (Section 8.2);
6. predict whether a precipitation will occur given the concentrations of the ions and the K_{sp} of the salt (Section 8.3);
7. determine the appropriate anion concentration to achieve maximum separation of two ions by the selective precipitation of one (Section 8.3);
8. write the formation reaction for a given complex ion (Section 8.4);
9. write the formation constant expression for a given complex ion (Section 8.4);
10. calculate the solubility of a slightly soluble salt in the presence of a substance that forms a complex ion with the metal (Section 8.5);
11. write the reaction for the dissolution of a basic salt in acid (Section 8.5);
12. determine the pH at which a solution should be saturated with H_2S to separate two cations in solution as their sulfides (Section 8.5); and
13. determine the equilibrium constant for the dissolution of a basic salt in acid (Section 8.5).

Answers to Practice Examples

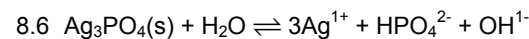
8.1 $K_{sp} = 8.1 \times 10^{-16}$



8.3 1.4×10^{-18} M at pH = 9.00; 1.4×10^{-4} M at pH = 2.00

8.4 $TiCl$ precipitates

8.5 $[Pb^{2+}] = 1.4 \times 10^{-4}$ M



$$K = (2.6 \times 10^{-18})(0.021) = 4.5 \times 10^{-20}$$

$$[Ag^{1+}] = 3x; [HPO_4^{2-}] = x; [OH^{1-}] = 10^{-5.00} = 1.0 \times 10^{-5}$$

$$K = (3x)^3(x)(1.0 \times 10^{-5}) = 4.5 \times 10^{-20}$$

$x = 1.2 \times 10^{-4}$ M, which is a much better approximation of the solubility than using K_{sp} alone. While Ag_3PO_4 is a basic salt, the pH of a saturated solution will differ somewhat from pH = 9 as assumed here.

8.7 EXERCISES

ACID-BASE EQUILIBRIA

1. Explain why $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is a stronger acid than $\text{Fe}(\text{H}_2\text{O})_6^{2+}$.
2. What is the conjugate base of $\text{Al}(\text{H}_2\text{O})_6^{3+}$?
3. Write the chemical equation that explains the acidity of an aqueous CuSO_4 solution and calculate the pH of a 0.20 M CuSO_4 solution.
4. Write the chemical equation that explains the acidity of an aqueous NiSO_4 solution and calculate the pH of a 0.10 M NiSO_4 solution.

DISSOLUTION AND THE SOLUBILITY-PRODUCT CONSTANT

Refer to Appendix D for solubility product constants for the remaining exercises. Assume that all solutions are at 25 °C.

5. Write the chemical equation and the K_{sp} expression for the dissolution process of each of the following substances:
 - a) CoS
 - b) HgI_2
 - c) $\text{Al}(\text{OH})_3$
6. Write the chemical equation and the K_{sp} expression for the dissolution process of each of the following substances:
 - a) $\text{Ba}_3(\text{PO}_4)_2$
 - b) MgNH_4PO_4
 - c) Ag_2S
7. Express the K_{sp} expression of each of the compounds in Exercise 5 in terms of its molar solubility (x).
8. Express the K_{sp} expression of each of the compounds in Exercise 6 in terms of its molar solubility (x).
9. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities:
 - a) AgI
 - b) CaF_2
10. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities:
 - a) PbBr_2
 - b) BaSO_4
11. The solubility of mercury(I) chloride is $0.0020 \text{ g}\cdot\text{L}^{-1}$. What is the K_{sp} of Hg_2Cl_2 ? Note: mercury(I) exists as Hg_2^{2+} ions.
12. The solubility of lithium phosphate is $0.39 \text{ g}\cdot\text{L}^{-1}$. What is the K_{sp} of lithium phosphate? Neglect the reaction of PO_4^{3-} with water.
13. The Au^{3+} concentration in a saturated solution of gold(III) chloride is $33 \mu\text{M}$. What is the solubility-product constant of AuCl_3 ?
14. What is the molar solubility of silver chromate? What is the concentration of silver ions in a saturated solution of silver chromate?
15. What is the pH of saturated barium hydroxide?
16. Calculate the pH of a saturated solution of zinc hydroxide.
17. A 386-mg sample of PbCl_2 is washed with 10.0 mL of 0.10 M HCl . What is the maximum fraction of PbCl_2 that can dissolve in the wash?
18. What is the molar solubility of calcium fluoride in each of the following?
 - a) water
 - b) 0.15 M KF
 - c) 0.20 M $\text{Ca}(\text{NO}_3)_2$
19. What is the molar solubility of lead(II) sulfate in:
 - a) water
 - b) 0.20 M MgSO_4
 - c) 0.11 M $\text{Pb}(\text{NO}_3)_2$
20. What is the molar solubility of $\text{Fe}(\text{OH})_3$ in a solution buffered at pH = 5.00? What is the solubility at pH = 8.00?

PRECIPITATION AND SEPARATION OF IONS

21. Rank the following sulfides in order of decreasing solubility:

CdS	CoS	CuS	FeS	MnS
--------------	--------------	--------------	--------------	--------------
22. Rank the following sulfides in order of decreasing solubility:

CuS	Cu_2S	Ag_2S	SnS	ZnS
--------------	-----------------------	-----------------------	--------------	--------------
23. Would a precipitate form in a solution that contained the following concentrations?
 - a) 0.01 M NaCl and 0.02 M $\text{Pb}(\text{NO}_3)_2$
 - b) 1.0 mM AgNO_3 and 1 μM NaCl
 - c) 5.0 mM KI and 2.0 mM $\text{Pb}(\text{NO}_3)_2$
24. The Co^{2+} and Cu^{2+} ions in a solution that is 0.01 M each are to be separated by precipitation of CuS .
 - a) What sulfide ion concentration (to one significant figure) should be used to obtain optimum separation?
 - b) What is the $[\text{Cu}^{2+}]$ after precipitation at this sulfide ion concentration?
25. Construct the reaction table for mixing 20.0 mL of 0.124 M $\text{Ca}(\text{NO}_3)_2$ and 30.0 mL of 0.0852 M KF .
 - a) What mass of precipitate forms?
 - b) What is the concentration of the excess reactant at equilibrium?
 - c) What is the concentration of the limiting reactant at equilibrium?

26. Construct the reaction table for mixing 55 mL of 0.10 M AgNO_3 and 75 mL of 0.20 M K_2CrO_4 .
- What mass of precipitate forms?
 - What is the concentration of the excess reactant at equilibrium?
 - What is the concentration of the limiting reactant at equilibrium?
27. Construct the reaction table for mixing 35.0 mL of 0.175 M AgNO_3 and 25.0 mL of 0.200 M KI .
- What mass of AgI forms?
 - What is the concentration of the excess reactant at equilibrium?
 - What is the concentration of the limiting reactant at equilibrium?
28. To what pH (to 0.1 pH unit) should a solution that is 0.020 M each in Ca^{2+} and Cd^{2+} ions be adjusted in order to best separate ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the pH is adjusted to this value?
29. To what pH (to 0.1 pH unit) should a solution that is 0.030 M in Pb^{2+} and 0.030 M in Mg^{2+} be buffered in order to obtain maximum separation of the ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the solution is buffered at this pH?
30. An acidic solution is 5 mM in each of the following metal ions: Co^{2+} , Ba^{2+} , Cu^{2+} and Zn^{2+} .
- Which of the metals precipitate as their hydroxides at pH = 6.00?
 - Which of the metals precipitate as their hydroxides at pH = 8.00?
 - At what pH does $\text{Ba}(\text{OH})_2$ begin to precipitate?
31. Indicate whether or not a precipitate would form when the following solutions are mixed:
- 5.0 mL of 0.10 M HCl and 5.0 mL of 1.0 mM $\text{Pb}(\text{NO}_3)_2$
 - 5.0 mL of 0.10 M KOH and 5.0 mL of 0.10 mM $\text{Mn}(\text{NO}_3)_2$
 - 5.0 mL of 0.10 M Na_2SO_4 and 5.0 mL of 0.10 mM $\text{Ba}(\text{NO}_3)_2$
32. What $[\text{I}^-]$ is needed to start precipitation of AgI from a saturated solution of AgCl ?
33. Solid NaCl is added to a solution that is 0.10 M in Pb^{2+} and 0.10 M in Ag^{1+} .
- Which compound precipitates first?
 - What is the concentration of the first ion precipitated when the second ion starts to precipitate?

COMPLEX IONS

Refer to Table 8.3 for formation constants

34. What is the concentration of free Cu^{2+} in a solution made by mixing 25.0 mL of 1.00 M CuSO_4 and 1.00 L of 0.500 M NH_3 ?
35. What is the concentration of free Ni^{2+} in a solution made by mixing 10.0 mL of 0.652 M NiSO_4 and 475 mL of 2.00 M NH_3 ?
36. What is the free silver ion concentration in a 0.24 M $\text{Ag}(\text{NH}_3)_2^{1+}$ solution?
37. What is the free cyanide ion concentration in a 0.10 M $\text{Fe}(\text{CN})_6^{3-}$ solution?

COMPETING EQUILIBRIA

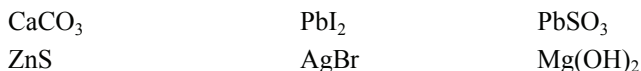
38. Use the data in Table 8.3 and Appendix D to determine the equilibrium constants for the following reactions.
- $\text{AgCN}(\text{s}) + \text{CN}^{1-} \rightleftharpoons \text{Ag}(\text{CN})_2^{1-}$
 - $\text{CuS}(\text{s}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+} + \text{S}^{2-}$
39. Use the data in Table 8.3 and Appendix D to determine the equilibrium constants for the following reactions.
- $\text{Fe}(\text{OH})_2(\text{s}) + 6\text{CN}^{1-} \rightleftharpoons \text{Fe}(\text{CN})_6^{4-} + 2\text{OH}^{1-}$
 - $\text{Ag}_2\text{S}(\text{s}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons 2\text{Ag}(\text{NH}_3)_2^{1+} + \text{S}^{2-}$
40. Consider the dissolution of CaF_2 in hydrochloric acid.
- Write the reaction for the dissolution.
 - What is the equilibrium constant for the reaction?
41. Consider the dissolution of $\text{Al}(\text{OH})_3$ in hydrochloric acid.
- Write the reaction for the dissolution.
 - What is the equilibrium constant for the reaction?
42. The pH of a solution that is 0.05 M in Zn^{2+} is slowly raised.
- At what pH does $\text{Zn}(\text{OH})_2$ ($K_{\text{sp}} = 4.5 \times 10^{-17}$) begin to precipitate?
 - Refer to Table 8.3 and determine the equilibrium constant for the reaction: $\text{Zn}(\text{OH})_2(\text{s}) + 2\text{OH}^{1-}(\text{aq}) \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}(\text{aq})$
 - At what pH does the solid $\text{Zn}(\text{OH})_2$ dissolve again?
43. At what pH should a solution be saturated with H_2S to separate 0.020 M Pb^{2+} and Zn^{2+} ? What are the concentrations of the ions after separation?
44. At what pH should a solution be saturated with H_2S to separate 0.010 M Co^{2+} and Fe^{2+} ? What are the concentrations of the ions after separation?

MISCELLANEOUS PROBLEMS

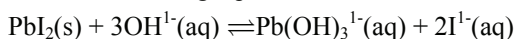
45. Indicate whether each of the following salts produces an acidic, a neutral, or a basic solution in water.



46. For which of the following compounds does solubility increase as the pH of the solution is lowered?



47. Consider the following equilibrium:



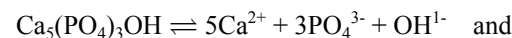
Use LeChâtelier's Principle to predict the effect on the solubility of PbI_2 of each of the following:

- H^+ (H_3O^+) ions are added.
 - The concentration of I^- is decreased.
 - The amount of PbI_2 is increased.
 - The pH of the solution is increased.
48. To image the upper gastrointestinal (GI) tract for medical evaluation of intestinal disorders, a suspension of BaSO_4 is ingested. The heavy element Ba absorbs X-rays so that the soft tissue of the intestine becomes visible to X-ray imaging. In order to minimize the physiological absorption of Ba, which is toxic, the suspension is frequently prepared using a Na_2SO_4 solution. Calculate the difference in the Ba^{2+} solubility in a solution of pure water and a solution of 0.10 M Na_2SO_4 . (This concentration has approximately the same osmotic balance as cellular fluids.) The K_{sp} of BaSO_4 is 1.1×10^{-10} .
49. In a foundry that produces plumbing fittings, the brass components are cleaned with nitric acid, which dissolves and oxidizes the copper and zinc of brass resulting in a solution of Cu^{2+} and Zn^{2+} . Given that K_{sp} of $\text{Cu}(\text{OH})_2$ is 2.2×10^{-20} and K_{sp} of $\text{Zn}(\text{OH})_2$ is 4.5×10^{-17} , determine the pH to which the effluent must be adjusted to precipitate the copper and zinc hydroxides such that the levels of Cu and Zn in the water are below the federal clean water standards of 50. ppm? Are the solubilities of these two species sufficiently different such that the copper and zinc could be separated during this neutralization process? Assume the density of the water sample is $1.00 \text{ g}\cdot\text{cm}^{-3}$.

50. Kidney stones are caused by the precipitation of either calcium oxalate, $\text{Ca}(\text{C}_2\text{O}_4)$, or calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, in the kidneys. If the normal concentration of Ca^{2+} in the kidneys is 2.5 mM, at what concentration of oxalate ion will kidney stones begin to form? K_{sp} of $\text{Ca}(\text{C}_2\text{O}_4) = 2.3 \times 10^{-9}$.

51. Explain why the solubility of PbF_2 increases with the addition of HNO_3 , but the solubility of PbCl_2 is unaffected.

52. The compound hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, forms the hard enamel layer that coats our teeth. Drinking fluorinated water, or brushing with fluorinated tooth paste, replaces some of the OH^- ions with F^- . The two dissolution reactions



have comparable equilibrium constants. Which of the two materials, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ or $\text{Ca}_5(\text{PO}_4)_3\text{F}$, is predicted to be more resistant to the weak acids formed during food digestion? (Hint: What effect do the relative base strengths of the hydroxide and fluoride ions have?)

53. A sample of drinking water was found to contain 500 ppm of Fe^{3+} , which is well above clean water levels. How much phosphate ion must be added to 1000 L of the water supply in order to precipitate excess iron from the solution so that the final Fe^{3+} concentration is less than 50. ppm? Assume the density of the water sample is $1.00 \text{ g}\cdot\text{cm}^{-3}$.

CHAPTER 9

Electrochemistry

<i>9.0 Introduction</i>	<i>9.5 The Electrolytic Cell</i>
<i>9.1 Review of Redox Processes</i>	<i>9.6 Predicting the Products of Electrolysis</i>
<i>9.2 Balancing Redox Reactions</i>	<i>9.7 Stoichiometry of Electrochemistry</i>
<i>9.3 Free Energy and Electrochemical Cells</i>	<i>9.8 Chapter Summary and Objectives</i>
<i>9.4 The Effect of Concentration on Cell Potential</i>	<i>9.9 Exercises</i>

9.0 INTRODUCTION

Electron transfer, or redox, reactions form one of the broadest and most important classes of reactions in chemistry. All batteries and reactions involving oxygen, such as combustion and corrosion, are redox reactions. Photosynthesis, respiration, and the breakdown of food are biological processes that involve sequences of electron transfer reactions to transport and utilize energy from the sun. In this chapter, we review some of the topics introduced in Chapter 11 of CAMS, and extend our study of electrochemistry to include the effect of concentration on cell potentials and electrolysis - using an external power supply to plate one metal on another or to carry out redox reactions that are not spontaneous.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- show how to determine the free energy of a redox reaction from its cell potential;
- show the relationship between the standard cell potential and the equilibrium constant of a redox reaction;
- show how to calculate the voltage of a cell at nonstandard conditions;
- explain how an electrolytic cell works;
- show how to predict the products of the electrolysis of a mixture; and
- explain the relationships between current, time, and mass during an electrolysis.

9.1 A REVIEW OF REDOX PROCESSES*

During a redox reaction, electrons are transferred from an electron donor to an electron acceptor. **Donors** lose electrons in a process known as **oxidation**, while the **acceptors** gain electrons in a process known as **reduction**. An acceptor cannot be reduced unless a donor is oxidized because electron transfer requires both a source and a destination for the transferred electrons. Thus, the reduction of an acceptor causes the oxidation of a donor, so acceptors are called **oxidizing agents** or **oxidants**. Similarly, oxidation of the donor causes the reduction of an acceptor, so donors are called **reducing agents** or **reductants**. Reductants lose electrons to become oxidants, and oxidants gain electrons to become reductants. A reducing agent and the oxidizing agent that it becomes when it is oxidized form a **redox couple**.

There are many similarities between Brønsted acid-base reactions and electron transfer reactions. In acid-base reactions, protons are transferred from a proton donor (acid) to a proton acceptor (base), while in redox reactions, electrons are transferred from an electron donor to an electron acceptor. In an acid-base reaction, the reacting acid and the produced base are called a conjugate acid-base pair, and in a redox reaction, the reacting donor and produced acceptor are called a redox couple. Acid-base reactions are extensive when the reacting acid and base are stronger than the produced acid and base, and redox reactions are extensive when the reacting oxidizing and reducing agents are stronger than the produced oxidizing and reducing agents. For example, consider Figure 9.1, which represents the electron transfer from an isolated iron atom to an isolated copper(II) ion to produce iron(II) ions and copper atoms. The electrons are on Fe initially, so it is the donor (reducing agent or reductant). The produced Fe^{2+} has empty redox orbitals, so it can function as an acceptor (oxidizing agent or oxidant). Thus, Fe is a donor, and Fe^{2+} is the produced acceptor, so Fe/Fe^{2+} is a redox couple. The acceptor orbitals on Cu^{2+} are empty, but they are occupied in Cu. Thus, Cu^{2+} is the initial acceptor and Cu is the produced donor, so Cu/Cu^{2+} is also a redox couple. The electrons are at higher energy on the donor (Fe) than on the acceptor (Cu), so the electron transfer is downhill in energy, exothermic, and spontaneous. The electron transfer from Cu to Fe^{2+} is uphill in energy, endothermic, and NOT spontaneous.

We have considered electron transfer between isolated atoms and ions because the picture is far more complicated when metals and solutions are involved. Consider all that must occur when a piece of iron reacts with copper(II) ions in aqueous solution. Metallic

* See Chapter 11 of CAMS for a more thorough introduction into redox reactions.

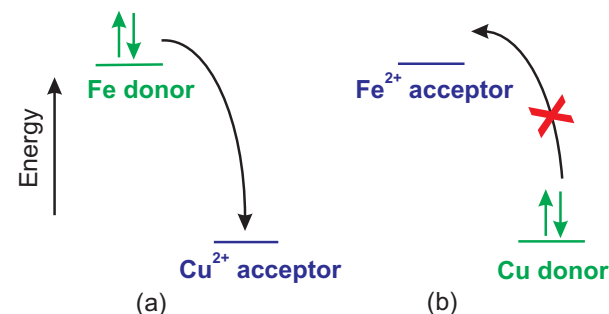


Figure 9.1 Electrons transfer extensively to lower energy

- (a) The energy of the donor orbital on Fe is greater than that of the acceptor orbital of Cu^{2+} , so the electron transfer from an isolated Fe atom to an isolated Cu^{2+} ion is extensive, $\text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}$.
- (b) The energy of the produced donor orbital on Cu is lower than that of the produced acceptor orbital of Fe^{2+} , so the reverse electron transfer is not extensive.

bonds must be broken in the iron to produce an iron atom, the iron atom must lose two electrons to form Fe^{2+} , a cavity must be created in the water to accommodate the ion, and the Fe^{2+} ion must enter the cavity and be hydrated. Similar processes must occur in the reverse direction when the Cu^{2+} ion is reduced to copper metal. Thus, the situation in aqueous redox reactions is far more complicated. If the energy difference between the donor and acceptor orbitals is not large, then these other factors can dominate the energy of the redox process. Consequently, the simple tendency of electrons to move from high-energy orbitals into orbitals at lower energy is not sufficient if the orbital energies are not very different. As in all processes carried out at constant temperature and pressure, it is the free energy change, ΔG , that is the driving force behind redox reactions.

In an electrochemical cell like the one shown in Figure 9.2, the oxidation and reduction processes are separated into two half-cells, and the reactions that take place in them are called **half-reactions**. The half-cell in which oxidation of the donor occurs is called the **anode**, and the half-cell where reduction of the acceptor occurs is known as the **cathode**. The anode and cathode are connected by a liquid junction (KCl salt bridge in Figure 9.2), which prevents mixing of the two solutions but allows the free movement of ions (charge) between the two compartments. An iron atom loses two electrons (is oxidized to Fe^{2+}) in the anode compartment as a copper(II) ion gains two electrons (is reduced to Cu) in the cathode compartment. The result is that two electrons are transferred through the circuit from an iron atom to a copper(II) ion. The resulting cell is a complete electrical circuit consisting of three types of charge movement:

- electron movement through the electrodes and the external circuitry,
- electron transfer at the two electrode surfaces, and
- ion migration through the two electrolyte solutions.

The **cell potential** is the potential difference between the anode and the cathode.

$$\mathcal{E} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}}$$

Eq. 9.1a

where $\mathcal{E}_{\text{cathode}}$ and $\mathcal{E}_{\text{anode}}$ are known as the **half-cell potentials**. In a redox reaction, electrons must flow from the anode (donor) to the cathode (acceptor), but electrons are also negatively charged, so they also seek the more positive potential. Thus, electrons transfer spontaneously to the cathode if it is at the higher potential, but they must be forced to transfer if the cathode is at the lower potential. A **galvanic cell** is a cell in which $\mathcal{E}_{\text{cathode}} > \mathcal{E}_{\text{anode}}$ ($\mathcal{E} > 0$), so redox reactions in galvanic cells are spontaneous ($\Delta G < 0$). The released free energy in a galvanic cell can be used to do work. Thus, *galvanic cells convert*

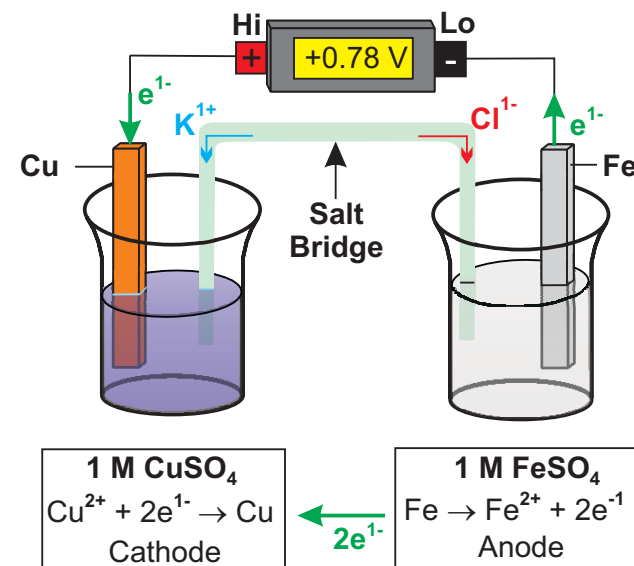


Figure 9.2 A galvanic cell constructed from the Fe/Fe^{2+} and the Cu/Cu^{2+} half-reactions

The two half-cells are connected by a liquid junction, which is a salt bridge in the above experiment. Cu^{2+} is reduced in the cathode while Fe is oxidized in the anode.

chemical potential energy into electrical potential energy. All batteries are galvanic cells. The cell potential of the electrochemical cell shown in Figure 9.2 is +0.78 V, so it is a galvanic cell, and the electron transfer from Fe to Cu^{2+} is spontaneous.

An **electrolytic cell** is a cell in which $\mathcal{E}_{\text{cathode}} < \mathcal{E}_{\text{anode}}$ ($\mathcal{E} < 0$), so $\Delta G > 0$ and the redox electrons must be forced to move to the more negative potential with an external power supply. Thus, *electrolytic cells convert electrical potential energy into chemical potential energy.* Recharging a battery and producing hydrogen and oxygen from water are two examples of the utility of electrolytic cells.

The criterion for spontaneous electron transfer is $\mathcal{E}_{\text{cathode}} > \mathcal{E}_{\text{anode}}$. Therefore, tables of half-cell potentials could be used to predict spontaneity in electron transfer reactions. However, the potential of only half of a cell cannot be measured, so absolute half-cell potentials cannot be determined. To solve this problem, chemists chose the *standard hydrogen electrode* (SHE) as the reference half-cell. The half-cell potential of the SHE is assigned a value of exactly zero. A SHE is represented as



By convention, the cell potential is measured by connecting the 'lo' or (-) lead of the voltmeter to the SHE. This convention *assumes* that the SHE is the oxidation and the half-cell being measured is the *reduction*. Under these conditions, the potential of the cell formed from the SHE and any half-cell at standard conditions is known as the **standard reduction potential** of the half-reaction.* Consider that, if the anode of the cell shown in Figure 9.1 had been a SHE instead of an Fe/Fe²⁺ half-cell, the cell potential would have been 0.34 V, the standard reduction potential of the Cu/Cu²⁺ couple. If the Fe/Fe²⁺ half-cell is attached to the 'hi' (+) side and the SHE to the 'lo' (-) side, the potential would be -0.44 V, the standard reduction potential of the Fe/Fe²⁺ couple.

The standard reduction potential of a redox couple is a measure of the electrical potential of the electron in the couple. Therefore, the standard cell potential can be determined from tabulated standard reduction potentials (Appendix E) and Equation 9.1b.

$$\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} \quad \text{Eq. 9.1b}$$

$\mathcal{E}^{\circ}_{\text{cathode}}$ is the standard reduction potential of the redox couple in the cathode and $\mathcal{E}^{\circ}_{\text{anode}}$ is the standard reduction potential of the redox couple in the anode. For example, consider the reaction between Cu^{2+} and Fe in Figure 9.2. $\mathcal{E}^{\circ}_{\text{cathode}} = 0.34 \text{ V}$ (the standard reduction potential of the Cu/Cu²⁺ couple) and $\mathcal{E}^{\circ}_{\text{anode}} = -0.44 \text{ V}$ (the standard reduction potential of the Fe/Fe²⁺ couple). Using Equation 9.1b, we determine that $\mathcal{E}^{\circ} = 0.34 - (-0.44) = +0.78 \text{ V}$.

* If the leads are reversed, the sign of the potential changes, and the cell potential is known as the oxidation potential of the half-reaction. The change in sign results because the leads have been reversed, not because the reaction has been reversed. We consider only reduction potentials in this text.

\mathcal{E}° is positive (the reaction is extensive) when $\mathcal{E}^\circ_{\text{cathode}}$ is high and $\mathcal{E}^\circ_{\text{anode}}$ is low or negative. Therefore, *good oxidizing agents have high standard reduction potentials and good reducing agents have low or negative standard reduction potentials.*

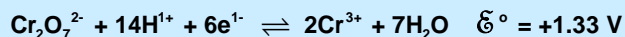
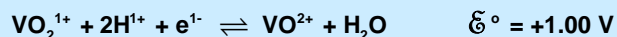
9.2 BALANCING REDOX REACTIONS

Redox reactions can be difficult to balance because the loss and gain of redox electrons must also be balanced, but there are two methods that simplify the task: the *half-reaction method*, which is readily applied to ionic equations; and the *oxidation state change method*, which is useful when balancing chemical equations that do not involve ions. Balancing redox chemical equations with these methods is something chemists do occasionally, but not frequently, so these tools are presented in Appendix F but not here.

In this chapter, balanced redox reactions are constructed from tabulated half-reactions. The given oxidation and reduction half-reactions are each multiplied by an integer that assures that the number of electrons gained in the reduction equals the number lost in the oxidation. We will refer to the number of electrons gained and lost in the balanced chemical equation as the **number of electrons transferred** and give it the symbol **n**. $n = 2$ for the reaction $\text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}$, so the reaction is said to be a *two-electron transfer*. The standard reduction potential of a half-reaction is a measure of the electrical potential of the redox electron. As such, reduction potentials are not changed when a reaction is reversed or multiplied by a constant. Example 9.1 demonstrates this fact and reviews the procedure for balancing redox equations.

Example 9.1

Given the following standard reduction half-reactions and their potentials,



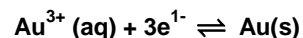
write the balanced equation for the extensive process and determine the number of electrons transferred and the standard cell potential.

As is usually the case, both half-reactions are given as reductions, but one half-reaction must be an oxidation. Thus, one of the two half-reactions must be reversed to become the oxidation. The question asks for the spontaneous process, which means that $\mathcal{E}^\circ_{\text{cathode}}$ must be greater than $\mathcal{E}^\circ_{\text{anode}}$. Consequently, the first half-reaction is the oxidation in a galvanic cell, so we write



PRACTICE EXAMPLE 9.1

Given the following half-reactions,



write the overall reaction for the oxidation of gold by permanganate ion.

Reverse one reduction half-reaction to make it an oxidation.

The lowest common multiple of electrons gained and lost is ____.

Rewrite the two half-reactions so that the correct number of electrons is gained or lost and then sum them to produce the overall reaction.

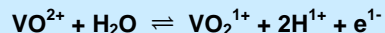
What is the standard cell potential if the standard reduction potentials of Au^{3+} and acidified MnO_4^{1-} are 1.50 and 1.51 V, respectively?

$$\mathcal{E}^\circ = \quad = \quad \text{V}$$

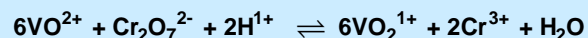
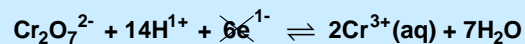
Although $\mathcal{E}^\circ_{\text{anode}}$ is the standard reduction potential of the couple involved in the oxidation half-reaction, there is no change in sign. The cell potential is

$$\mathcal{E}^\circ = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}} = 1.33 - 1.00 = 0.33 \text{ V}$$

The oxidation half-reaction is



The number of electrons gained must equal the number of electrons lost, but each VO^{2+} gives up only one electron, while each $\text{Cr}_2\text{O}_7^{2-}$ requires six. Therefore, the VO^{2+} half-reaction must be multiplied by six, but multiplying the half-reaction by six does not change the potential of the half-reaction ($\mathcal{E}^\circ_{\text{anode}}$). The two half-reactions are each written as six-electron processes and summed to yield the overall redox reaction.



Note that the six electrons lost in the oxidation half-reaction are cancelled by the six electrons gained in the reduction half-reaction, so no electrons appear in the net equation. This reaction is a six-electron transfer reaction. The 14H^{1+} required for the reduction and the 12H^{1+} produced in the oxidation sum to a net 2H^{1+} required. Similarly, the $6\text{H}_2\text{O}$ required for the oxidation and the $7\text{H}_2\text{O}$ produced in the reduction result in a net production of $1\text{H}_2\text{O}$ molecule. *The net equation for the overall reaction must never show the same substance on both sides of the reaction, and it must never show any electrons.*

9.3 FREE ENERGY AND ELECTROCHEMICAL CELLS

The heat released during the exothermic process that occurs when Fe is placed in a solution of CuSO_4 simply warms the solution. However, that energy can be harnessed to do work by separating the reactants and forcing the electrons through an external circuit. The metal electrodes placed in each half-cell are the keys. Remember that electrons move freely in the delocalized orbitals of the conduction bands in metals, and this mobility is responsible for the electrical conductivity of the metal.* The combination of electrical conductivity and redox chemical reactions is the field known as **electrochemistry**.

Electron transfer reactions in electrochemical cells are known as **electrochemical reactions**. Electrochemical reactions occur at the surfaces of the two electrodes in the cell as electrons are injected into the external circuit at the anode as the donor is oxidized and withdrawn from the circuit at the cathode as the acceptor is reduced. Electrodes that take

* See Section 8.6 of CAMS for a discussion of band theory.

part in the electrochemical reactions are said to be **active electrodes**. Both the copper and iron electrodes in Figure 9.2 are active electrodes. However, there are many instances where neither member of a redox couple is a conducting solid, but an electrode is still required to serve as the interface between the reaction and the circuit. In these cases, an inert metal is normally used as a passive or inactive electrode. **Passive** electrodes do not participate in the reaction; they simply serve as a conducting surface through which electrons are injected into either the circuit or the reaction. A passive electrode must be constructed from a metal that will not oxidize in the cell; *i.e.*, the metal must have a very positive reduction potential. Some common passive electrodes are Ag, Au, Pt, C, and Hg.

Electrochemical cells are often represented in the following abbreviated form:

anode electrode | anode compartment || cathode compartment | cathode electrode

The single vertical lines represent the phase change between the solid electrode and the solution. The double vertical lines in the middle represent the liquid junction or salt bridge. This order is easily remembered if you remember your ABC's (**A**node | **B**ridge | **C**athode). As an example, the cell shown in Figure 9.2 is abbreviated



and the cell in which the SHE is the anode and copper is the cathode is

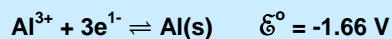


where a platinum wire serves as a *passive* electrode for the standard hydrogen electrode. Note that the order in which the substances appear in the solution of the cell is arbitrary. We know that H_2 is oxidized to H^{1+} because it is the anode, not because H_2 is written first.

Example 9.2

- a) Write the abbreviated form of the standard galvanic cell produced by combining Al/Al^{3+} and Sn/Sn^{2+} couples, determine the standard cell potential, write the overall cell reaction, and determine the number of electrons transferred.

First, we need to know which half-reaction occurs spontaneously at the anode and which occurs at the cathode. We refer to Appendix K to obtain the following standard reduction potentials.



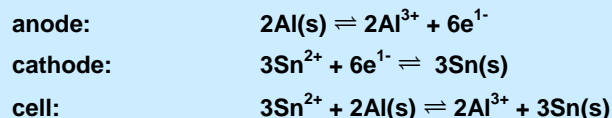
$\mathcal{E}^{\circ}_{\text{cathode}} > \mathcal{E}^{\circ}_{\text{anode}}$ for a galvanic cell, so the Sn/Sn^{2+} couple is the cathode, and the Al/Al^{3+}

couple is the anode. The abbreviated form of the standard cell is

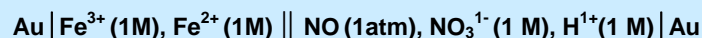


The cell potential is $\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = -0.14 - (-1.66) = 1.52 \text{ V}$

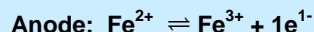
The anode half-reaction involves a three-electron transfer while the cathode half-reaction involves a two-electron transfer. The lowest common multiple of three and two is six electrons, so this is a six-electron transfer. Multiplying the anode half-reaction by two and the cathode half-reaction by three, we obtain the following:



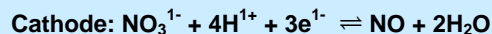
b) Determine the cell reaction and cell potential at 25 °C for the following:



Au is a passive electrode in each cell. All activities are unity, so the cell potential is the standard cell potential. The anode compartment contains the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple ($\mathcal{E}^{\circ} = +0.77 \text{ V}$). The anode half-reaction is the oxidation of Fe^{2+} .

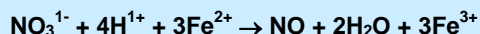


The cathode compartment contains NO_3^{-} , H^{1+} , and NO , so the half-reaction must be the reduction of nitric acid ($\mathcal{E}^{\circ} = +0.96\text{V}$).



The cell potential is $\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = 0.96 - 0.77 = 0.19 \text{ V}$

The anode half-reaction must be multiplied by three to produce a three-electron oxidation, which cancels the electrons in the three-electron reduction of nitric acid. Summing the two half-reactions, we obtain the chemical equation for this three- electron transfer reaction.



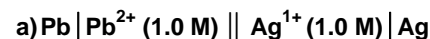
Recall from Chapter 4 that the maximum amount of work that can be obtained from a process is the amount of free energy released during the process. Thus, the amount of work that can be done by the transferred electrons in a spontaneous redox reaction is

$$\text{work done by electrons} = -\Delta G \quad \text{Eq. 9.2}$$

The work done by the transferred electrons is expressed in terms of their *charge* and the *electrical potential difference*, \mathcal{E} , through which they transfer. The charge is equal to the

PRACTICE EXAMPLE 9.2

Use the data in Appendix E to determine the cell potentials at 25 °C, the number of electrons transferred, and the cell reactions for the following cells:



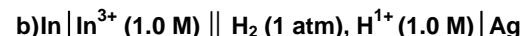
cell potential:

$$\mathcal{E}^{\circ} = \text{_____ V}$$

electrons transferred:

$$n = \text{_____}$$

cell reaction:



cell potential:

$$\mathcal{E}^{\circ} = \text{_____ V}$$

electrons transferred:

$$n = \text{_____}$$

cell reaction:

number of moles of electrons transferred times the charge carried by a mole of electrons. The absolute value of the charge of one mole of electrons is called the **faraday** and given the symbol \mathcal{F} .^{*} The faraday is Avogadro's number times the absolute value of the charge on a single electron:

$$\mathcal{F} = (6.02214 \times 10^{23} \text{ electrons} \cdot \text{mol}^{-1})(1.60218 \times 10^{-19} \text{ C} \cdot \text{electron}^{-1}) = 9.6485 \times 10^4 \text{ C} \cdot \text{mol}^{-1}$$

Equation 9.3 expresses the work that can be done by the transfer of n moles of electrons through an electrical potential \mathcal{E} .

$$\text{work done by electrons} = n\mathcal{F}\mathcal{E} \quad \text{Eq. 9.3}$$

\mathcal{E} is expressed in terms of joules-coulomb⁻¹, which is the **volt** (1V = 1J·C⁻¹). Combining Equations 9.2 and 9.3, we obtain Equation 9.4a,

$$\Delta G = -n\mathcal{F}\mathcal{E} \quad \text{Eq. 9.4a}$$

Equation 9.4a is extended to standard cells in Equation 9.4b.

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ \quad \text{Eq. 9.4b}$$

Equation 9.4a shows the relationship between the free energy change of a redox reaction and the electrical potential difference between the anode and cathode. *A positive cell potential means that $\Delta G < 0$ and the process is spontaneous. A negative cell potential means that $\Delta G > 0$ and the reaction is spontaneous in the reverse reaction.*

Example 9.3

Determine the standard free energy change for $3\text{Sn}^{2+} + 2\text{Al} \rightleftharpoons 3\text{Sn} + 2\text{Al}^{3+}$

This is a six-electron transfer with $\mathcal{E}^\circ = 1.52 \text{ V}$ (See Example 9.2). We substitute these values into Equation 9.4b to obtain

$$\Delta G^\circ = -n\mathcal{F}\mathcal{E}^\circ = -(6 \text{ mol electrons})(9.65 \times 10^4 \text{ C} \cdot \text{mol electrons}^{-1})(1.52 \text{ J} \cdot \text{C}^{-1})$$

$$\Delta G^\circ = -8.80 \times 10^5 \text{ J} = -880 \text{ kJ}$$

9.4 THE EFFECT OF CONCENTRATION ON CELL POTENTIAL

The cell potential is a measure of the chemical free energy of a redox reaction, so we can apply the relationships regarding the reaction quotient, the equilibrium constant, and the free energy of reaction to electrochemical processes. We start by recalling that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

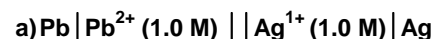
Substitute the expressions for ΔG and ΔG° from Equations 9.4a and 9.4b to obtain

$$-n\mathcal{F}\mathcal{E} = -n\mathcal{F}\mathcal{E}^\circ + RT \ln Q$$

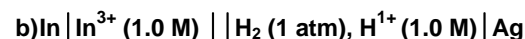
* Electrons carry a negative charge, so the charge carried by a mole of electrons is $-\mathcal{F}$.

PRACTICE EXAMPLE 9.3

Use the results of Practice Example 9.2 to determine the free energy of the following cells:



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



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

Divide by $-n\mathcal{F}$ to obtain the expression for the cell potential as a function of the standard cell potential and the reaction quotient:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln Q = \mathcal{E}^\circ - \frac{2.3026RT}{n\mathcal{F}} \log Q$$

The preceding expression was obtained by using the fact that $\ln x = 2.3026 \log x$. The above expression is called the **Nernst equation**. At 25 °C,

$$\frac{2.3026RT}{n\mathcal{F}} = \frac{(2.3026)(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})}{n(96,485 \text{ C} \cdot \text{mol}^{-1})} = \frac{0.05916}{n} \text{ J} \cdot \text{C}^{-1} = \frac{0.05916}{n} \text{ V}$$

Substitution of the above constant into the Nernst equation yields the common expression of the Nernst equation at 25 °C given in Equation 9.5.

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592}{n} \log Q \quad \text{at 25 } ^\circ\text{C}$$

Note that Q is the thermodynamic reaction quotient, so it is defined in terms of activities. Thus, gases enter the expression as their partial pressures in atmospheres, solutes as molar concentrations, and solids and liquids as unity. Examination of Equation 9.5 reveals that any change to the cell that increases the reaction quotient decreases the cell potential, while any change that decreases Q increases the cell potential. Alternatively, $\Delta G = -n\mathcal{F}\mathcal{E}$, so anything that makes ΔG more negative increases the cell potential. Thus, *increasing the activity of a reactant or decreasing the activity of a product increases the cell potential, while decreasing a reactant activity or increasing a product activity decreases the cell potential.*

The same conclusion about cell potentials can be drawn by the application of LeChâtelier's principle (Section 5.2). The cell potential is considered to be a product of the reaction just as heat is considered to be a product in an exothermic reaction. Thus, adding more reactant or removing a product increases the cell potential, while removing a reactant or adding a product decreases the cell potential.

Example 9.4

Use Le Châtelier's principle to predict the effect that each of the following actions would have on the cell potential of the following cell: $\text{Pt} | \text{H}_2, \text{H}^{1+} || \text{Cu}^{2+} | \text{Cu}$.

The cell reaction is $\text{H}_2 + \text{Cu}^{2+} \rightarrow 2\text{H}^{1+} + \text{Cu} + \text{volts}$. 'Volts' is used to represent the cell potential, which is a product of a spontaneous redox reaction.

i. increasing the partial pressure of H_2

H_2 is a reactant, so increasing its partial pressure drives the reaction to the right, which increases volts (cell potential).

ii. adding NH_3 to the cathode compartment

NH_3 forms a complex ion with copper, $\text{Cu}(\text{NH}_3)_4^{2+}$, which reduces $[\text{Cu}^{2+}]$, a reactant. The effect is to shift the equilibrium to the left to replace some of the Cu^{2+} , which reduces the amounts on the right, including the cell potential.

iii. adding NH_3 to the anode compartment

Ammonia is also a Brønsted base, so it reacts with acid to decrease $[\text{H}^{1+}]$. H^{1+} is a product, so the effect is a shift in the equilibrium to the right to make more H^{1+} . The shift increases the number of volts, i.e., the cell potential.

iv. using a larger Cu electrode

Adding a solid does not affect its activity, so it does not change Q or affect the cell potential.

v. adding water to the cathode

Adding water to a compartment dilutes the solution. Thus, $[\text{Cu}^{2+}]$ decreases, which forces the equilibrium to shift to the left causing the cell potential to drop.

At equilibrium, $\Delta G = 0$, so $\xi = 0$. Thus, a battery dies because the redox processes have reached equilibrium. Applying these equilibrium conditions and the fact that $Q = K$ at equilibrium to the Nernst equation at 25 °C, we obtain

$$0 = \xi^\circ - \frac{0.05916}{n} \log K$$

which can be solved for either ξ° or $\log K$.

$$\xi^\circ = \frac{0.0592}{n} \log K$$

$$\log K = \frac{n\xi^\circ}{0.0592} = 16.9n\xi^\circ \text{ or } K = 10^{16.9n\xi^\circ}$$

A large, positive value of ξ° implies a large equilibrium constant, so we conclude that *the more positive the standard cell potential, the more extensive is the electron transfer.*

PRACTICE EXAMPLE 9.4

Predict the effect of each of the following on the cell potential of the following cell.



Enlarging the lead electrode,

Increase no change decrease

Adding KCl solution to the anode to precipitate PbCl_2 ,

Increase no change decrease

Adding KCl solution to the cathode to precipitate AgCl ,

Increase no change decrease

Evaporating water from the cathode compartment,

Increase no change decrease

Dissolving solid $\text{Pb}(\text{NO}_3)_2$ in the anode compartment,

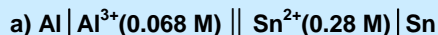
Increase no change decrease

Adding some silver wire to the cathode compartment.

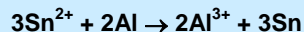
Increase no change decrease

Example 9.5

Determine ΔG , ΔG° , Q , K , and ξ for the following cells at 298 K:



From Example 9.2a: $\xi^\circ = 1.52 \text{ V}$ and $n = 6$. The cell reaction is:



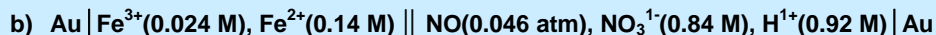
$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Sn}^{2+}]^3} = \frac{(0.068)^2}{(0.28)^3} = 0.21$$

$$\xi = 1.52 - \frac{0.0592}{6} \log(0.21) = 1.53 \text{ V}$$

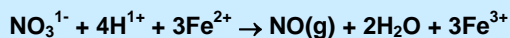
$$\log K = 16.9n\xi^\circ = 16.9(6)(1.52) = 154 \quad K = 10^{154}$$

$$\Delta G^\circ = -nF\xi^\circ_{\text{anode}} = -(6 \text{ mol})(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(1.52 \text{ J} \cdot \text{C}^{-1}) = -8.80 \times 10^5 \text{ J} = -880 \text{ kJ}$$

$$\Delta G = -nF\xi_{\text{anode}} = -(6 \text{ mol})(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(1.53 \text{ J} \cdot \text{C}^{-1}) = -8.86 \times 10^5 \text{ J} = -886 \text{ kJ}$$



From Example 9.2b: $\xi^\circ = 0.19 \text{ V}$ and $n = 3$. The cell reaction is



NO is a gas, so its activity equals its partial pressure in atm.

$$Q = \frac{P_{\text{NO}}[\text{Fe}^{3+}]^3}{[\text{NO}_3^-][\text{H}^+]^4[\text{Fe}^{2+}]^3} = \frac{(0.046)(0.024)^3}{(0.84)(0.92)^4(0.14)^3} = 3.9 \times 10^{-4}$$

$$\xi = 0.19 - \frac{0.0592}{3} \log(3.9 \times 10^{-4}) = 0.26 \text{ V}$$

$$\log K = 16.9n\xi^\circ = 16.9(3)(0.19) = 9.6 \quad K = 10^{9.6} = 4 \times 10^9$$

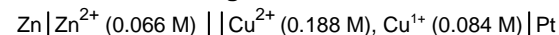
$$\Delta G^\circ = -nF\xi^\circ = -(3 \text{ mol})(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.19 \text{ J} \cdot \text{C}^{-1}) = -5.5 \times 10^4 \text{ J} = -55 \text{ kJ}$$

$$\Delta G = -nF\xi = -(3 \text{ mol})(9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})(0.26 \text{ J} \cdot \text{C}^{-1}) = -7.5 \times 10^4 \text{ J} = -75 \text{ kJ}$$

As an electrochemical cell discharges, reactants are consumed and products are formed; *i.e.*, Q increases. The increase in Q results in a drop in the cell potential, which eventually reaches zero at equilibrium. It is important to remember that a change in one activity as a result of reaction must be accompanied by stoichiometric changes in all other activities. Thus, a combination of stoichiometry and the Nernst equation can be used to predict the cell potential after a given amount of reaction. The process is described in Example 9.6.

Practice example 9.5

Consider the following cell at 298 K:



The cell reaction

The standard cell potential

$$E^\circ = \text{_____ V}$$

The reaction quotient

$$Q = \text{_____}$$

The cell potential

$$E = \text{_____ V}$$

The equilibrium constant

$$K = \text{_____}$$

The standard free energy

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

The free energy

$$\Delta G = \text{_____ kJ}$$

Example 9.6

What is the cell potential of the following cell after the Sn^{2+} concentration has dropped to 0.01 M? $\text{Al} \mid \text{Al}^{3+}(1.00 \text{ M}) \parallel \text{Sn}^{2+}(1.00 \text{ M}) \mid \text{Sn}$

Construct a reaction table for the cell discharge. The initial concentrations of the two ions are each 1.00 M, and the final concentration of the Sn^{2+} ion is 0.01 M. We, therefore, begin with the following entries in the reaction table.

	3Sn^{2+}	$+ 2\text{Al(s)}$	\rightarrow	3Sn(s)	$+ 2\text{Al}^{3+}$	
Initial	1.00			1.00		M
Δ						
Final	0.01					M

Clearly, the tin ion concentration drops by 0.99 M, so we use the reaction stoichiometry to determine the change in the aluminum-ion concentration.

$$\frac{0.99 \text{ mol Sn}^{2+} \text{ reacts}}{\text{L}} \times \frac{2 \text{ mol Al}^{3+} \text{ forms}}{3 \text{ mol Sn}^{2+} \text{ reacts}} = \frac{0.66 \text{ mol Al}^{3+} \text{ forms}}{\text{L}}$$

The Reaction Table can now be completed.

	3Sn^{2+}	$+ 2\text{Al(s)}$	\rightarrow	3Sn(s)	$+ 2\text{Al}^{3+}(\text{aq})$	
Initial	1.00			1.00		M
Δ	-0.99			+0.66		M
Final	0.01			1.66		M

The reaction quotient is $\frac{[\text{Al}^{3+}]^2}{[\text{Sn}^{2+}]^3} = \frac{(1.66)^2}{(0.01)^3} = 2.8 \times 10^6$

We found that $n = 6$ and $\mathcal{E}^\circ = 1.52 \text{ V}$ in Example 9.5, so the cell potential at 25°C as determined with the Nernst equation is

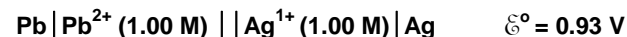
$$\mathcal{E} = 1.52 - \frac{0.0592}{6} \log(2.8 \times 10^6) = 1.46 \text{ V}$$

Note that the cell potential dropped by only 0.06 V from the initial conditions even though 99% of the Sn^{2+} was consumed. The small change in \mathcal{E} is due to the fact that the cell potential drops as $\log Q$, which is why batteries maintain a relatively constant cell potential throughout most of their life.

Standard cell potentials are referenced against other electrodes, frequently the standard hydrogen electrode (SHE). However, the SHE is not commonly used in the laboratory because it is cumbersome and dangerous due to the need for H_2 . In addition, it is not always easy to prepare a solution at standard conditions. Consequently, standard reduction potentials relative to SHE are frequently determined at non-standard conditions and referenced against a half-cell other than the SHE. Example 9.7 converts an experimental cell potential to the standard reduction potential versus the SHE.

PRACTICE EXAMPLE 9.6

Determine the cell potential of the following cell when the Ag^{1+} ion concentration has dropped to 0.04 V.



Reaction table:

the reaction quotient:

$$Q = \underline{\hspace{2cm}}$$

the cell potential:

$$\mathcal{E} = \underline{\hspace{2cm}} \text{ V}$$

Example 9.7

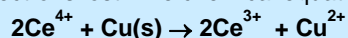
Determine the standard reduction potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple from the cell potential of the following cell at 25 °C.



Step 1. Write the balanced chemical equation for the cell reaction. Cu is oxidized in the anode and Ce^{4+} is reduced in the cathode, so the half-reactions are



The cathode half-reaction must be multiplied by two in order for electrons gained to equal electrons lost. The chemical equation for this two-electron transfer is



Step 2. Determine the reaction quotient

$$Q = \frac{[\text{Ce}^{3+}]^2 [\text{Cu}^{2+}]}{[\text{Ce}^{4+}]^2} = \frac{(0.020)^2 (0.043)}{(0.142)^2} = 8.5 \times 10^{-4}$$

Step 3. Determine the standard cell potential. Solve the Nernst equation for the standard cell potential and substitute the known quantities.

$$\mathcal{E}^{\circ}_{\text{cell}} = \mathcal{E}_{\text{cell}} + \frac{0.0592}{n} \log Q = 1.36 + \frac{0.0592}{2} \log (8.5 \times 10^{-4}) = 1.27 \text{ V}$$

Step 4. Determine the standard reduction potential. The $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple is the cathode, so express the standard cell potential in terms of the standard reduction potentials ($\mathcal{E}^{\circ}_{\text{anode}} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}}$), and solve for $\mathcal{E}^{\circ}_{\text{cathode}}$. The standard reduction potential of Cu^{2+}/Cu from Appendix K is +0.34 V.

$$1.27 \text{ V} = \mathcal{E}^{\circ}_{\text{cathode}} - 0.34, \text{ so } \mathcal{E}^{\circ}_{\text{cathode}} = 1.27 + 0.34 = 1.61 \text{ V.}$$

The $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple is 1.61 V more positive than the SHE.

PRACTICE EXAMPLE 9.7

The following cell has a cell potential of 0.58 V at 25 °C.



What is the cell reaction?

What is the value of the reaction quotient?

$$Q = \underline{\hspace{2cm}}$$

What is the standard cell potential?

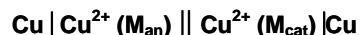
$$\mathcal{E}^{\circ}_{\text{cell}} = \underline{\hspace{2cm}} \text{ V}$$

What is the standard reduction potential for the Cu^{1+}/Cu couple?

$$\mathcal{E}^{\circ}_{\text{Pb}} = \underline{\hspace{2cm}} \quad (\text{from Appendix E})$$

$$\mathcal{E}^{\circ}_{\text{Cu}} = \underline{\hspace{2cm}}$$

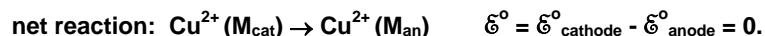
An electrochemical cell is used to harness the free energy of spontaneous electron transfer reactions by separating the reactants into separate half-cells, but it can also be used to harness the free energy that drives the mixing of two solutions of different concentrations to one solution of an intermediate concentration by separating the two solutions. Such cells are called **concentration cells**. Consider the following concentration cell:



M_{an} is the molarity of Cu^{2+} in the anode and M_{cat} is the molarity of Cu^{2+} in the cathode. The two half-reactions are identical except for the concentrations of the metal ions, so they have the same standard half-cell potential ($\mathcal{E}^{\circ}_{\text{cathode}} = \mathcal{E}^{\circ}_{\text{anode}}$).



The metal atoms and electrons cancel in the sum of half-reactions, so the net equation is



Apply the Nernst equation to the net reaction to obtain

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.0592}{n} \log Q = 0 - \frac{0.0592}{2} \log \left(\frac{M_{\text{an}}}{M_{\text{cat}}} \right)$$

Use the fact that $-\log(x/y) = +\log(y/x)$ to arrive at Equation 9.8, which shows the cell potential that develops when solutions differing only in the concentration of the ions are placed into an electrochemical cell.

$$\mathcal{E} = \frac{0.0592}{2} \log \left(\frac{M_{\text{cat}}}{M_{\text{an}}} \right) \quad \text{Eq. 9.8}$$

Note that the process is spontaneous only if $M_{\text{cat}} > M_{\text{an}}$, *i.e.*, the copper ion concentration must be greater in the cathode. As the reaction proceeds, $[\text{Cu}^{2+}]$ decreases in the cathode as the ions are reduced to copper metal, which deposits on the electrode. Simultaneously, $[\text{Cu}^{2+}]$ increases in the anode as the copper atoms in the electrode are oxidized to Cu^{2+} ions in solution. Thus, *the mass of the anode decreases and the concentration of Cu^{2+} ions in the anode increases, while the mass of the cathode increases and the concentration of Cu^{2+} ions in the cathode decreases.* The cell potential drops as the concentration of copper(II) ions in the two half-cells get closer, and goes to zero when they are equal.

Example 9.8

Determine the cell potential of the following: $\text{Zn} | \text{Zn}^{2+} (0.068 \text{ M}) || \text{Zn}^{2+} (0.84 \text{ M}) | \text{Zn}$

Use Equation 9.8 and the given concentrations.

$$\mathcal{E} = \frac{0.0592}{2} \log \left(\frac{0.84}{0.068} \right) = 0.032 \text{ V} = 32 \text{ mV}$$

What is $[\text{Zn}^{2+}]$ in a concentration cell constructed with the unknown solution in the anode and 1.00 M in Zn^{2+} if the cathode has a cell potential of 0.088 V?

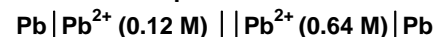
The unknown solution is in the anode, so solve Equation 9.8 for M_{an} .

$$\log \left(\frac{M_{\text{cat}}}{M_{\text{an}}} \right) = \frac{2\mathcal{E}}{0.0592} = 33.8\mathcal{E} = 33.8(0.088) = 2.97; M_{\text{cat}} = 1.00 \text{ M}$$

$$\frac{1.00}{M_{\text{an}}} = 10^{2.97} = 933; M_{\text{an}} = \frac{1.00 \text{ M}}{933} = 1.07 \times 10^{-3} \text{ M} = 1.07 \text{ mM}$$

PRACTICE EXAMPLE 9.8

What is the cell potential of the following concentration cell?



$$\mathcal{E}_{\text{cell}} = \text{_____ mV}$$

An **ion selective electrode** consists of a reference electrode and a membrane that can be penetrated by only the selected ion. When the electrode is immersed into a solution containing that ion, an equilibrium is established between the ions within the membrane and those in the bulk solution. The counter ions cannot enter the membrane, so a charge separation develops between the membrane and the bulk solution, which creates an electrical potential difference that is a function of the concentration of the selected ion.* Thus, the concentration of the ion in a solution can be determined by immersing the ion selective electrode into the solution, along with another reference electrode to complete the circuit, and measuring the resulting potential difference. A **pH meter** consists of a voltmeter that has been calibrated in pH units, an ion selective electrode that contains a membrane that allows only H^{1+} ions to enter, and another reference electrode. When the ion selective electrode is placed into a solution, H^{1+} ions move to establish an equilibrium between the bulk solution and the membrane, which creates the cell potential that is read by the voltmeter. Example 9.9 presents a less elegant pH meter, but one that demonstrates the utility of the Nernst equation.

* For example, if an ion selective electrode for Na^{1+} ions is dipped into a solution of NaCl, the Na^{1+} ions penetrate the membrane, but the Cl^{1-} ions cannot. Consequently, the membrane develops a positive charge and the bulk solution a negative charge. The charge separation produces an electrical potential difference across the boundary between the membrane and the solution.

PRACTICE EXAMPLE 9.9

Determine the pH of the solution in the anode compartment of the following cell if the cell potential is 0.53 V.



The two half-reactions (Refer to Appendix E):

Anode:

Cathode:

The standard reduction potentials from Appendix E

$$\mathcal{E}^{\circ}_{\text{cathode}} = \text{_____ V} \quad \mathcal{E}^{\circ}_{\text{anode}} = \text{_____ V}$$

$$\text{The standard cell potential: } \mathcal{E}^{\circ} = \text{_____ V}$$

The cell reaction:

The number of electrons transferred: $n = \text{_____}$

The reaction quotient: $Q =$

Nernst Equation for this cell:

The Nernst Equation in terms of the pH:

Solve for pH.

Example 9.9

a) Express the potential of the following cell, as a function of the pH of the acidic solution. $\text{Pt} \mid \text{H}_2(1 \text{ atm}), \text{H}^{1+}(x \text{ M}) \parallel \text{Cu}^{2+}(1 \text{ M}) \mid \text{Cu}$

The two half-reactions are



The standard reduction potentials are $\mathcal{E}^{\circ}_{\text{anode}} = 0.00 \text{ V}$ and $\mathcal{E}^{\circ}_{\text{cathode}} = 0.34 \text{ V}$

The overall cell reaction is $\text{Cu}^{2+} + \text{H}_2(\text{g}) \rightarrow 2\text{H}^{1+} + \text{Cu}(\text{s})$

and the standard cell potential is $\mathcal{E}^{\circ} = \mathcal{E}^{\circ}_{\text{cathode}} - \mathcal{E}^{\circ}_{\text{anode}} = 0.34 - 0.00 = 0.34 \text{ V}$

The Nernst equation as it applies to this cell is $\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.0592}{2} \log \left(\frac{[\text{H}^{1+}]^2}{P_{\text{H}_2} [\text{Cu}^{2+}]} \right)$

The reaction involves a two-electron transfer ($n=2$), the partial pressure of hydrogen is maintained at 1 atm, and the concentration of Cu^{2+} is maintained at 1 M. We may, therefore, simplify the Nernst equation to the following:

$$\mathcal{E} = 0.34 - \frac{0.0592}{n} \log [\text{H}^{1+}]^2$$

Substitution of $\log [\text{H}^{1+}]^2 = 2 \log [\text{H}^{1+}]$ and $-\log [\text{H}^{1+}] = \text{pH}$, yields:

$$\mathcal{E} = 0.34 + 0.0592 \text{ pH} \quad \text{or} \quad \text{pH} = 16.9 (\mathcal{E} - 0.34)$$

b) What are the pH and the hydronium ion concentrations in the cell when the cell potential is 0.56 V?

Solving the preceding expression for the pH when the cell potential is 0.56 V,

$$\text{pH} = 16.9(0.56 - 0.34) = 3.7 \rightarrow [\text{H}^{1+}] = 10^{-3.7} = 2 \times 10^{-4} \text{ M}$$

9.5 THE ELECTROLYTIC CELL

A second technological side of electrochemistry is based on the use of external electrical circuits to control the redox chemistry itself, including the ability to force electrons “uphill” in energy. Many examples are around us: recharging batteries, electroplating, recovering elemental metals from ores, and making chemicals. Electrolytic cells, the topic of this section, are used for all of these processes.

Molten salts and aqueous solutions of electrolytes conduct electricity when a sufficient voltage is applied across two electrodes immersed in them because the ions (electrolytes) are mobile and migrate toward the electrodes. This type of conduction is called **electrolytic conduction**, and it occurs in electrolytic cells. For the sake of simplicity, the following discussion focuses on electrolytic conduction in molten salts.

Electrolytic conduction occurs when electrons flow between the metallic electrodes and the electrolytes in the melt. Electrodes are metallic conductors, so they contain partially filled bands. The energy level of the highest energy electrons in the band is called the **Fermi level**. Thus, metal orbitals above the Fermi level are unfilled and can accept electrons while metal orbitals below the Fermi level are occupied and can donate electrons. Figure 9.3 shows the effect of an applied voltage on two electrodes in a sodium chloride melt. As the voltage across the two electrodes is increased, one electrode becomes positively charged, which lowers its Fermi level as electrons are removed from it, and the other electrode becomes negatively charged, which raises its Fermi level as electrons are added to it. The energy difference between the two Fermi levels is directly proportional to the applied voltage. Cations migrate toward the negative electrode and anions migrate toward the positive electrode.* At a sufficiently high applied voltage (Figure 9.4), the electrons at the Fermi level of the negative electrode are higher in energy than the empty orbitals on the sodium ions, and the unfilled orbitals at the Fermi level in the positive electrode are lower in energy than the highest energy electrons on the chloride ions. At this point, electrons flow through the circuit as sodium ions are reduced at the negative electrode (cathode) and chloride ions are oxidized at the positive electrode (anode). The

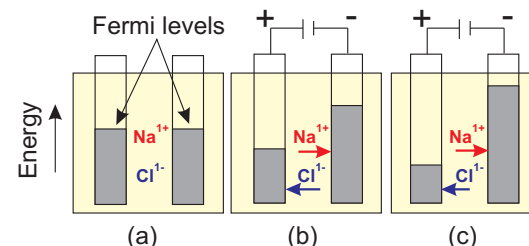


Figure 9.3 Effect of applied voltage on the Fermi levels of two identical electrodes

a) If no voltage is applied, the two Fermi levels are at the same energy. b) An applied voltage increases the energy difference between the two Fermi levels and causes ion migration. Cations migrate toward the negative electrode, and the anions migrate toward the positive electrode. c) Increasing the applied voltage increases the energy difference between the two Fermi levels.

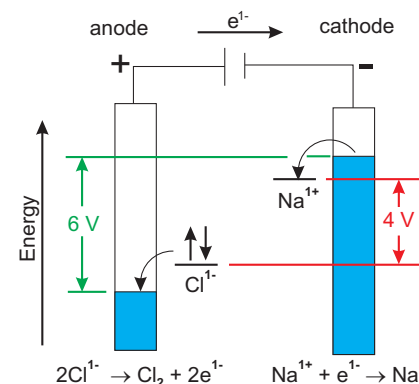


Figure 9.4 Electrolysis of NaCl

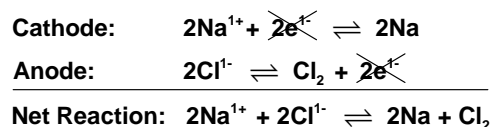
An applied voltage of 6V exceeds the 4V difference between the two half-reactions. As a result, the Fermi level of the anode is lower in energy than the filled orbitals on the chloride ion, while the Fermi level of the cathode is higher in energy than the empty orbital on the sodium ion. Electrons flow through the circuit as the redox reactions take place.

* The negative electrode is the cathode and the positive electrode is the anode. The origin of the names anion and cation lies in the fact that anions are ions that migrate to the anode, while cations are ions that migrate to the cathode.

net reaction, $2\text{Na}^{1+} + 2\text{Cl}^{1-} \rightarrow 2\text{Na} + \text{Cl}_2$, is referred to as the electrolysis of NaCl.

Electrolysis is the process in which a power supply is used to drive an electron transfer uphill in free energy. The external supply forces electrons to move from a higher (more positive) potential (+) at the anode to a lower (more negative) potential (-) at the cathode. Forcing the electrons to move in this direction requires energy, which is stored in the higher free energy of the products. Thus, an electrolytic cell converts electrical potential energy into chemical potential energy.

The voltage at which electrolysis of NaCl begins depends upon the potential difference between the two half-reactions. The half-reactions and the net reaction are



$\mathcal{E}^{\circ}_{\text{cathode}} = -2.71 \text{ V}$ and $\mathcal{E}^{\circ}_{\text{anode}} = 1.36 \text{ V}$, so $\mathcal{E}^{\circ} = -2.71 - 1.36 = -4.07 \text{ V}$. The negative value of \mathcal{E}° indicates that this reaction does not proceed spontaneously to measurable amounts of product. However, it can be driven by the application of a sufficiently high voltage. A voltage greater than 4.07 V must be applied to *electrolyze* NaCl.* Figure 9.4 represents the situation in which a 6-volt battery is connected to the electrodes immersed in molten sodium chloride. The applied voltage is greater than the 4-volt difference between the two half-reactions, so sodium chloride is *electrolyzed* to sodium metal and chlorine gas.

The electrolysis of NaCl demonstrates two uses of electrolysis: electroplating metals and chemical synthesis (making compounds). In the electrolysis of NaCl, the cathode is plated with sodium metal, but if CrCl_3 had been used instead, the electrode would have been *chrome plated*. Industrial electrolysis is the major source of chlorine gas and sodium metal.

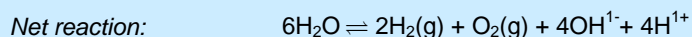
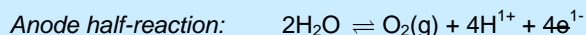
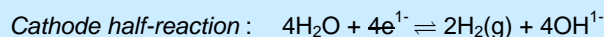
Molecules, like atoms, have empty orbitals that are higher in energy than the filled orbitals. The empty orbitals can accept electrons, and the filled orbitals can donate electrons. However, either process can lead to the decomposition of the molecule. Consider the case where two inert electrodes connected to a voltage supply are placed in water. When the voltage is sufficient, electrons can be injected into water at the cathode, reducing it to H_2 , and removed from water at the anode, oxidizing it to O_2 . Example 9.10 treats this important example of electrolysis.

* It should be noted that the standard reduction potentials in Appendix E are for the aqueous reactions at 25 °C, not for the reactions in a melt above 800 °C. However, the aqueous numbers are used here for the sake of discussion.

Example 9.10

How many 1.5 V batteries would be required to prepare molecular hydrogen and molecular oxygen by the electrolysis of water?

The pertinent reactions are



The cathode reaction has been multiplied by two in order to cancel electrons. The $4\text{OH}^{1-} + 4\text{H}^{1+}$ on the right side combine to form $4\text{H}_2\text{O}$, which cancel four of the water molecules on the left. Thus, the net electrolysis of water is written as



The non-spontaneous process ($\mathcal{E} < 0$) can be driven by the application of a voltage exceeding 1.23 V. Thus, only one 1.5 V battery is predicted.

* The standard cell potential for the cathode reaction is for a cell in which $[\text{OH}^{1-}] = 1 \text{ M}$, its standard state, and that for the anode is for the cell in which $[\text{H}^{1+}] = 1 \text{ M}$. However, the solution is pure water, so $[\text{OH}^{1-}] = [\text{H}^{1+}] = 10^{-7} \text{ M}$. Thus, the pH = 7 potentials, not the standard potentials from Appendix E are used.

In Example 9.10, it was determined that a single 1.5 V battery is sufficient to electrolyze water, but, in fact, the rates of the two half-reactions are negligible at such a potential because the activation energies[†] of the two half-reactions are so high. To obtain reasonable reaction rates, the applied potential must be about 1 V higher than the predicted value. The amount by which the potential must be increased above the predicted value to obtain a reasonable rate of reaction is called the **overpotential**. The overpotential for each of the water half-reactions is about a 0.5 volt. Overpotentials can be very difficult to predict because they depend not only upon the reaction, but also upon the electrode and the ions in solution.

† Recall from Section 9.9 of CAMS that the activation energy is the energy required to reach the transition state. For example, the reaction between hydrogen and oxygen is spontaneous, but no reaction occurs in a balloon filled with both gases until a flame or spark is used to initiate the reaction. The energy in the flame or spark is used to overcome the activation energy for the reaction.

9.6 PREDICTING THE PRODUCTS OF ELECTROLYSIS

When electrolysis is carried out on a mixture, the predominant products are from those components of the mixture that are most easily oxidized and reduced. Thus, the electrolysis reaction is usually between the strongest oxidant and the strongest reductant in the mixture. Stated somewhat differently, the species that is reduced at the cathode is the one with the most positive (least negative) reduction potential, and the species that is oxidized at the anode is the one with the most negative (least positive) reduction potential. However, the situation is more complicated when the predicted reactions have high overpotentials. In these cases, reaction of the best oxidizing or reducing agent may be

negligibly slow at the predicted potential, so weaker oxidizing and reducing agents with smaller overpotentials may react if the potential is increased. Many electrolysis experiments are performed in water, and water's large overpotential can also make predictions difficult. This is the case in the electrolysis of seawater, where chloride ion is oxidized to chlorine gas even though its reduction potential (1.36 V) is more positive than that for the oxidation of water to oxygen gas (0.82 V at pH=7).

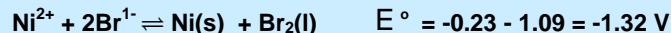
Example 9.11

a) What are the predicted products in the electrolysis of a molten mixture of FeCl_2 and NiBr_2 ?

The mixture contains Fe^{2+} , Cl^{1-} , Ni^{2+} and Br^{1-} ions, so the choices for reduction are Fe^{2+} and Ni^{2+} , while those for oxidation are Cl^{1-} and Br^{1-} . The half-reactions in the appropriate compartment along with their standard reduction potentials are

Cathode	$\mathcal{E}^\circ_{\text{cathode}}$	Anode	$\mathcal{E}^\circ_{\text{anode}}$
$\text{Fe}^{2+} + 2\text{e}^{1-} \rightleftharpoons \text{Fe(s)}$	-0.44 V	$2\text{Br}^{1-} \rightleftharpoons \text{Br}_2(\text{l}) + 2\text{e}^{1-}$	+1.09 V
$\text{Ni}^{2+} + 2\text{e}^{1-} \rightleftharpoons \text{Ni(s)}$	-0.23 V	$2\text{Cl}^{1-} \rightleftharpoons \text{Cl}_2(\text{g}) + 2\text{e}^{1-}$	+1.36 V

The cathode reaction is the one with the more positive reduction potential (more easily reduced), so metallic nickel is formed at the cathode. The anode reaction is the one with the more negative or least positive reduction potential (more easily oxidized), so bromine forms at the anode. Summing the two half-reactions we obtain



An applied voltage greater than 1.32 V would be required.

b) What are the predicted products in the electrolysis of aqueous KI?

As discussed in Section 9.4, water can be both oxidized and reduced, so it is possible reactant at both electrodes. The possible anode and cathode reactions are

Cathode	$\mathcal{E}^\circ_{\text{cathode}}$	Anode	$\mathcal{E}^\circ_{\text{anode}}$
$\text{K}^{1+} + \text{e}^{1-} \rightleftharpoons \text{K(s)}$	-2.92V	$2\text{I}^{1-} \rightleftharpoons \text{I}_2(\text{s}) + 2\text{e}^{1-}$	+0.54 V
$2\text{H}_2\text{O} + 2\text{e}^{1-} \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^{1-}$	-0.41V	$2\text{H}_2\text{O} \rightleftharpoons \text{O}_2(\text{g}) + 4\text{H}^{1+} + 4\text{e}^{1-}$	+0.82 V

Water is easier to reduce than potassium, so H_2 is formed at the cathode, and I^{1-} is more easily oxidized than water so I_2 forms at the anode.

PRACTICE EXAMPLE 9.10

Predict the products of the electrolysis of a 1-M CuSO_4 solution.

Possible cathode reactions and their standard reduction potentials:

Product formed at Cathode:

Possible anode reactions and their standard reduction potentials:

Product formed at anode:

9.7 STOICHIOMETRY OF ELECTROCHEMISTRY

By the 1830's, Michael Faraday had discovered that the amount of electricity produced or consumed when a chemical reaction was harnessed to an electrical current using an electrochemical cell corresponded directly to the amount of chemical reactant involved. In this section, we discuss these quantitative aspects of the electrochemical cell.

The electron is a reactant or a product in each of the half-reactions and is, therefore, an integral part of the cell stoichiometry. However, we do not determine the mass or volume of electrons involved as we would with other reactants and products. Instead, we determine the charge that is passed during the reaction. The charge can be measured directly and easily with an instrument called a *coulometer*. The number of moles of electrons that are transferred can then be determined by using the fact that the charge on one mole of electrons is one faraday (\mathcal{F}), which is 96,500 C. Thus, we can either determine the number of electrons (or amount of charge) that is required to produce a given amount of material, or the amount of material that is produced from the charge that is passed during the electrochemical reaction. Example 9.12 demonstrates the latter.

Example 9.12

How much copper is produced by passing 2.00×10^4 C through a solution of Cu^{2+} ?

This is a stoichiometry problem in which we are given the charge that flows through the circuit during the reaction.

1. Convert the charge passed into the number of moles of electrons transferred:

$$2.00 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^{-}}{96,500 \text{ C}} = 0.207 \text{ mol e}^{-}$$

2. Determine the stoichiometric ratio that relates moles of electrons transferred to moles of copper being formed.

The half reaction is $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$, so the stoichiometric ratio is $\frac{1 \text{ mol Cu}}{2 \text{ mol e}^{-}}$

3. Determine the number of moles of copper that are formed:

$$0.207 \text{ mol e}^{-} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^{-}} = 0.104 \text{ mol Cu}$$

4. Determine the mass of the copper produced:

$$0.104 \text{ mol Cu} \times \frac{63.5 \text{ g Cu}}{\text{mol Cu}} = 6.58 \text{ g Cu}$$

Alternatively, all of the above steps can be combined into one step using the factor label method to help us with the order.

$$2.00 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^{-}}{96,500 \text{ C}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^{-}} \times \frac{63.5 \text{ g Cu}}{\text{mol Cu}} = 6.58 \text{ g Cu}$$

Electrical current is the rate at which charge flows through the circuit. It is given the symbol i and has units of amperes (A or amps). One ampere is one coulomb per second ($1\text{A} = 1\text{C}\cdot\text{s}^{-1}$). The charge in coulombs that flows during an electrochemical experiment carried out at a fixed current of i amperes for t seconds is given by Equation 9.9.

$$\text{charge} = i \cdot t \quad \text{Eq. 9.9}$$

Example 9.13 is an example of how Equation 9.9 can be used.

Example 9.13

How long should a 5.0 A current be passed through a solution of $\text{Ni}(\text{NO}_3)_2$ in order to nickel plate a bathroom fixture with 0.85 g of nickel?

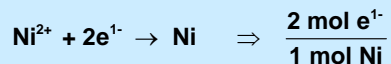
1. Determine the number of moles of nickel to be deposited.

$$0.85 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.7 \text{ g Ni}} = 0.014 \text{ mol Ni}$$

Note that the result of the calculation is given more precisely as 0.01448, which will be used in subsequent calculations to minimize round-off error.

2. Determine the stoichiometric ratio between the nickel formed and the electrons transferred.

Nickel is reduced from +2 in $\text{Ni}(\text{NO}_3)_2$ to zero in the metal.



3. Determine the number of moles of electrons that must be passed.

$$0.014 \text{ mol Ni} \times \frac{2 \text{ mol e}^{-}}{\text{mol Ni}} = 0.029 \text{ mol e}^{-}$$

4. Convert moles of electrons to Coulombs of charge.

$$0.029 \text{ mol e}^{-} \times \frac{96,500 \text{ C}}{\text{mol e}^{-}} = 2.8 \times 10^3 \text{ C}$$

PRACTICE EXAMPLE 9.11

What mass of gold would be plated on an earring by passing a current of 10 mA through a solution of AuCl_3 for 1.5 hours?

Half-reaction:

atomic mass of Au =

Coulombs of charge passed:

moles of electrons passed:

moles of gold metal formed:

5. Determine how long it takes to pass that charge at the given current.

$$t = \frac{\text{charge}}{i} = 2.8 \times 10^3 \text{ C} \times \frac{1 \text{ s}}{5 \text{ C}} = 5.6 \times 10^2 \text{ s} = 9.3 \text{ min}$$

Or, in one step using the factor label method to dictate the order,

$$0.85 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.7 \text{ g Ni}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Ni}} \times \frac{96,500 \text{ C}}{1 \text{ mol e}^-} \times \frac{1 \text{ s}}{5 \text{ C}} = 5.6 \times 10^2 \text{ s} = 9.3 \text{ min}$$

PRACTICE EXAMPLE 9.12

For how many minutes should water be electrolyzed with 2.56 A to produce 25.0 mL of H₂ at 1.00 atm and 298 K?

moles of H₂:

n = _____ mmol H₂

half-reaction:

time required:

_____ minutes

9.8 CHAPTER SUMMARY AND OBJECTIVES

Electrochemistry is the marriage of the conductivity of metals and redox reactions. In an electrochemical cell, electron transfer occurs at the surfaces of two electrodes: the anode and the cathode. Electrochemical cells are often abbreviated as

anode electrode | anode compartment || cathode compartment | cathode electrode.

The free energy of an electron-transfer reaction is related to the cell potential by the expression, $\Delta G = -n\mathcal{F}\mathcal{E}$. Galvanic cells are cells for which $\Delta G < 0$, and the electron transfer is spontaneous; the decrease in free energy is the maximum work that can be derived from the cell. Electrolytic cells involve electron-transfer reactions for which $\Delta G > 0$ and are not spontaneous; the increase in free energy must be supplied by an external power supply to drive the reaction ‘uphill’ in free energy.

The Nernst equation relates a cell’s potential to the reaction quotient,

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592}{n} \log Q \quad \text{at } 25^\circ \text{C}$$

\mathcal{E}° is the standard cell potential at 25 °C, and n is the number of electrons transferred in the balanced chemical equation. At equilibrium, the free energy is zero as is the cell potential, which leads to the relationship between the standard cell potential and the equilibrium constant for a redox reaction, $\log K = 16.9 n\mathcal{E}^\circ$.

An external power supply can lower the Fermi level of the anode and raise the Fermi level of the cathode to the point that a non-spontaneous electron transfer takes place. The resulting non-spontaneous electron-transfer reaction is called electrolysis. The applied voltage must be sufficient to overcome the negative cell potential determined for the reaction. The anode reaction in the electrolysis of a mixture involves that species that is most easily oxidized, while the cathode reaction involves that species most easily reduced.

The amount of substance consumed or produced in an electrochemical cell depends on the number of electrons that flow through the cell during the experiment. The number of electrons is usually given in terms of the charge passing through the cell. The charge of one mole of electrons is 96,500 C. Although the flow of charge can be determined directly, it is often obtained by current/time measurements. Current is the rate of flow of the charge and is measured in amperes. One ampere is one coulomb per second. Thus, the charge passed during an experiment carried out at constant current is the product of the current in amperes and the time in seconds.

After studying the material presented in this chapter you should be able to:

1. determine the anode and cathode reactions of the spontaneous cell given the standard reduction potentials of the two half-reactions (Section 9.3);
2. express an electrochemical cell in the abbreviated form (Section 9.3);
3. determine the free energy of a redox reaction from its cell potential, and *vice versa* (Section 9.3);
4. determine the cell potential of a redox reaction given the standard cell potential and the concentrations of all reactants and products (Section 9.4);
5. determine the cell potential after some reaction from an initial potential and the amount of reaction (Section 9.4);
6. determine the standard reduction potential of one couple from a cell potential and the standard reduction potential of the other couple (Section 9.4);
7. describe a concentration cell and determine its cell potential (Section 9.4);
8. determine the concentration of a reactant or product in an electrochemical cell from the cell potential and the concentrations of the other products and reactants (Section 9.4);
9. describe how an electrolytic cell works (Section 9.5);
10. determine the minimum voltage that must be applied in an electrolytic cell (Section 9.5);
11. predict the products of the electrolysis of a mixture (Section 9.6);
12. determine the mass of product given the amount of charge that has flowed through the cell (Section 9.7);
13. determine the number of coulombs of charge that are passed through a circuit given the current and the length of time the current flowed (Section 9.7);
14. determine the mass of product given the current and the length of time the current flowed (Section 9.7); and
15. determine how long a given current must be applied in order to produce a given amount of product (Section 9.7).

ANSWERS TO PRACTICE EXAMPLES

- 9.1 $5\text{Au} + 3\text{MnO}_4^{1-} + 24\text{H}^{1+} \rightarrow 5\text{Au}^{3+} + 3\text{Mn}^{2+} + 12\text{H}_2\text{O}$
 $\mathcal{E}^\circ = 0.01 \text{ V}$
- 9.2 a) $\text{Pb} + 2\text{Ag}^{1+} \rightarrow \text{Pb}^{2+} + 2\text{Ag}$ $n=2$ $\mathcal{E}^\circ = 0.93 \text{ V}$
 b) $2\text{In} + 6\text{H}^{1+} \rightarrow 2\text{In}^{3+} + 3\text{H}_2$ $n=6$ $\mathcal{E}^\circ = 0.34 \text{ V}$
- 9.3 a) $-1.8 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$ b) $-2.0 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$
- 9.4 no change, increase, decrease, increase, decrease, no change
- 9.5 $\text{Zn} + 2\text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + 2\text{Cu}^{1+}$ $\mathcal{E}^\circ = 0.92 \text{ V}$
 $Q = 0.013$; $\mathcal{E} = 0.98 \text{ V}$; $K = 1.2 \times 10^{31}$;
 $\Delta G^\circ = -1.8 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$; $\Delta G = -1.9 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$
- 9.6 $Q = 9 \times 10^2$; $\mathcal{E} = 0.84 \text{ V}$
- 9.7 $Q = 300$; $\mathcal{E}^\circ_{\text{cell}} = 0.65 \text{ V}$; $\mathcal{E}^\circ_{\text{Cu}} = 0.52 \text{ V}$
- 9.8 $\mathcal{E}_{\text{cell}} = 22 \text{ mV}$
- 9.9 $\text{H}_2(\text{g}) + 2\text{AgCl}(\text{s}) \rightarrow 2\text{H}^{1+}(\text{aq}) + 2\text{Ag}(\text{s}) + 2\text{Cl}^{1-}(\text{aq})$
 $\mathcal{E}^\circ = 0.22 \text{ V}$; $\text{pH} = 16.9(\mathcal{E} - 0.22) = 5.2$
- 9.10 Cathode: Cu Anode: O_2
- 9.11 54 C; 0.56 mmol e^{1-} ; 0.19 mmol Au ; 37 mg Au
- 9.12 $n = PV/RT = 1.02 \text{ mmol H}_2$ ($R = 0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
 $2\text{H}_2\text{O} + 2\text{e}^{1-} \rightarrow \text{H}_2 + 2\text{OH}^{1-}$; 1.28 min

9.9 EXERCISES

GENERAL

1. What is a passive electrode? What quality in a metal is required to serve as a passive electrode? Give three examples of metals that would make good passive electrodes.
2. Use Equation 9.3 to define the volt.
3. Distinguish between a galvanic and an electrolytic cell. Which type of cell would be used to nickel plate a faucet? Which type of cell can act as a battery?

In Exercises 4 - 7, construct galvanic cells from the given couples and answer the following questions about each cell:

- a) What is the anode half-reaction?
 - b) What is the cathode half-reaction?
 - c) What is the cell reaction?
 - d) What are the oxidizing and reducing agents?
 - e) How many electrons are transferred in the cell reaction?
 - f) What is the abbreviated form of the cell? Use a Pt wire as a passive electrode where needed.
 - g) What is the cell potential?
4. Pb/Pb²⁺ (1.0 M) and Ag/Ag¹⁺ (1.0 M) - See instructions above.
 5. Sn/Sn²⁺ (1.0 M) and Zn/Zn²⁺ (1.0 M) - See instructions above.
 6. Fe²⁺ (1.0 M)/Fe³⁺ (1.0 M) and Al/Al³⁺ (1.0 M) - See instructions above.
 7. Au/Au³⁺ (1.0 M) and ClO₄¹⁻ (1.0 M)/ClO₃¹⁻ (1.0 M) - See instructions above.

THERMODYNAMICS AND ELECTROCHEMICAL CELLS

8. Refer to Appendix E and determine ΔG° for the following reactions.
 - a) $2\text{Fe}^{3+} + \text{Pb(s)} \rightarrow 2\text{Fe}^{2+} + \text{Pb}^{2+}$
 - b) $\text{H}_2(\text{g}) + \text{Cu}^{2+} \rightarrow \text{Cu(s)} + 2\text{H}^{1+}$
 - c) $\text{Hg}^{2+} + 2\text{Ag(s)} \rightarrow \text{Hg(l)} + 2\text{Ag}^{1+}$
 - d) $2\text{ClO}_2^{1-} \rightarrow \text{ClO}^{1-} + \text{ClO}_3^{1-}$
 - e) $\text{Ag}_2\text{O(s)} + \text{PbO(s)} \rightarrow 2\text{Ag(s)} + \text{PbO}_2(\text{s})$

9. Refer to Appendix E and determine ΔG° for the following reactions.

- a) $2\text{I}^{1-} + \text{Cl}_2(\text{g}) \rightarrow \text{I}_2(\text{s}) + 2\text{Cl}^{1-}$
- b) $2\text{NO(g)} + \text{H}_2\text{O} + 3\text{VO}_2^{1+} \rightarrow 2\text{NO}_3^{1-} + 3\text{VO}^{2+} + 2\text{H}^{1+}$
- c) $\text{H}_2\text{O}_2 + \text{ClO}^{1-} \rightarrow \text{H}_2\text{O} + \text{ClO}_2^{1-}$
- d) $\text{ClO}_4^{1-} + \text{CH}_3\text{OH(aq)} \rightarrow \text{ClO}_3^{1-} + \text{HCHO} + \text{H}_2\text{O}$
- e) $2\text{Au(s)} + 3\text{Br}_2(\text{l}) \rightarrow 2\text{Au}^{3+} + 6\text{Br}^{1-}$

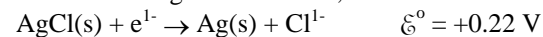
10. Determine equilibrium constants for the following reactions.

- a) $\text{BrO}^{1-} + \text{H}_2\text{O} + 2\text{Fe}^{2+} \rightleftharpoons 2\text{Fe}^{3+} + \text{Br}^{1-} + 2\text{OH}^{1-}$
- b) $\text{O}_3(\text{g}) + 2\text{Cl}^{1-} + 2\text{H}^{1+} \rightleftharpoons \text{O}_2(\text{g}) + \text{Cl}_2(\text{g}) + \text{H}_2\text{O}$

11. Determine the equilibrium constants for the following reactions.

- a) $\text{Pb(s)} + \text{Sn}^{2+} \rightleftharpoons \text{Pb}^{2+} + \text{Sn(s)}$
- b) $\text{Zn(s)} + \text{HCHO(aq)} + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH(aq)} + \text{Zn}^{2+} + 2\text{OH}^{1-}$

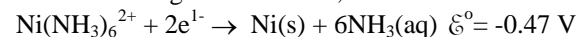
12. Given the following half-reactions,



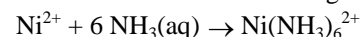
Construct a cell with the following cell reaction: $\text{AgCl(s)} \rightarrow \text{Ag}^{1+} + \text{Cl}^{1-}$

- a) What is the standard cell potential?
- b) What is the value of ΔG° for the reaction?
- c) What is the equilibrium constant as determined from the cell potential?
- d) What is this equilibrium constant called?

13. Given the following half-reactions,



Construct a cell with the following cell reaction:



- a) What is the standard cell potential?
- b) What is the value of ΔG° for the reaction?
- c) What is the equilibrium constant as determined from the cell potential?
- d) What is this equilibrium constant called?

14. Consider the following cell: $\text{Pb(s)} \mid \text{Pb}^{2+} \parallel \text{Ag}^{1+} \mid \text{Ag(s)}$

- a) In which direction do the electrons flow, $\text{Pb} \rightarrow \text{Ag}$ or $\text{Ag} \rightarrow \text{Pb}$?
- b) What is the electrical sign of the anode?
- c) In which direction do the anions flow through the liquid junction (bridge), anode \rightarrow cathode or cathode \rightarrow anode?

15. Write the cell reaction and the equilibrium constant expression for and determine the cell potentials at 25 °C of the following electrochemical cells.

- $\text{Cr} \mid \text{Cr}^{3+} (0.060 \text{ M}) \parallel \text{Ag}^{1+} (0.68 \text{ M}) \mid \text{Ag}$
- $\text{Pt} \mid \text{Sn}^{4+} (0.041 \text{ M}), \text{Sn}^{2+} (0.12 \text{ M}) \parallel \text{Cu}^{2+} (0.84 \text{ M}), \text{Cu}^{1+} (0.0084 \text{ M}) \mid \text{Ag}$
- $\text{Ti} \mid \text{Ti}^{2+} (0.0020 \text{ M}) \parallel \text{Au}^{3+} (1.0 \text{ M}) \mid \text{Au}$

16. Write the cell reaction and the equilibrium constant expression for and determine the cell potentials at 25 °C of the following electrochemical cells.

- $\text{Cr} \mid \text{Cr}^{3+} (0.060 \text{ M}) \parallel \text{Ag}^{1+} (0.68 \text{ M}) \mid \text{Ag}$
- $\text{Cu} \mid \text{Cu}^{2+} (0.0073 \text{ M}) \parallel \text{Cr}^{3+} (0.11 \text{ M}), \text{Cr}_2\text{O}_7^{2-} (0.046 \text{ M}), \text{H}^{1+} (1.0 \text{ M}) \mid \text{Au}$
- $\text{Pt} \mid \text{H}_2 (1.0 \text{ atm}), \text{H}^{1+} (3.5 \text{ mM}) \parallel \text{Hg}^{2+} (0.060 \text{ M}) \mid \text{Hg}$

THE EFFECT OF CONCENTRATION ON CELL POTENTIAL

17. Consider the following cell: $\text{Pb(s)} \mid \text{Pb}^{2+} \parallel \text{Ag}^{1+} \mid \text{Ag(s)}$. What effect would each of the following have on the cell potential?

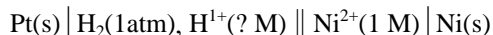
- enlarging the lead electrode
- dissolving KCl in the anode
- dissolving KCl in the cathode
- adding water to the cathode
- reducing the volume of the solution in the anode

18. Consider the following reaction taking place in an electrochemical cell:
 $2\text{Cr}^{2+} + \text{HClO(aq)} + \text{H}^{1+} \rightarrow 2\text{Cr}^{3+} + \text{Cl}^{1-} + \text{H}_2\text{O}$

Predict the effect of the following changes on the cell voltage.

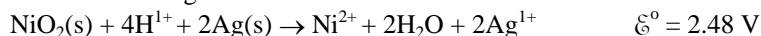
- increasing $[\text{HClO}]$ in the cathode
- increasing pH of the cell solution of the cathode
- increasing size of the inert electrodes
- adding KCl solution to the cathode

19. The following cell has a potential of 0.27 V at 25 °C:



What is the pH of the solution in the anode compartment?

20. For the following reaction:



What is the pH of the solution if $\xi = 2.10 \text{ V}$ and $[\text{Ag}^{1+}] = [\text{Ni}^{2+}] = 0.015 \text{ M}$?

21. Calculate ξ° , ξ and ΔG for the reaction: $3\text{Cu}^{2+} + 2\text{Al(s)} \rightarrow 2\text{Al}^{3+} + 3\text{Cu(s)}$ when $[\text{Cu}^{2+}] = 0.010 \text{ M}$ and $[\text{Al}^{3+}] = 0.0085 \text{ M}$.

22. Calculate ΔG for the reaction: $\text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu(s)}$ when $[\text{Cu}^{2+}] = 0.010 \text{ M}$ and $[\text{Zn}^{2+}] = 0.080 \text{ M}$.

23. Consider the following concentration cell: $\text{Cu} \mid \text{Cu}^{2+} (M_1) \parallel \text{Cu}^{2+} (M_2) \mid \text{Cu}$, where M_1 and M_2 are the molar concentrations.

- Write the two half-reactions and the net cell reaction.
- Explain why $\xi^\circ = 0$ for a concentration cell.
- Write the expression for the Nernst equation for the cell at 25 °C.
- What must be true about the relative values of M_1 and M_2 if the cell is to function as a galvanic cell?
- What is the final concentration in the cell when equilibrium is reached?
- What happens to the mass of the electrode in the compartment on the left of the abbreviated cell?

24. Determine the cell potential and the equilibrium concentrations of the following concentration cell: $\text{Cu} \mid \text{Cu}^{2+} (0.020 \text{ M}) \parallel \text{Cu}^{2+} (2.0 \text{ M}) \mid \text{Cu}$

25. Determine the cell potential and the equilibrium concentrations of the following concentration cell: $\text{Ag} \mid \text{Ag}^{1+} (0.28 \text{ mM}) \parallel \text{Ag}^{1+} (1.88 \text{ M}) \mid \text{Ag}$

26. Assume that each of the solutions in the half-cells in Exercise 24 has a volume of 100. mL and determine the mass change that the electrode in the anode must undergo to reach equilibrium.

27. Assume that each of the solutions in the half-cells in Exercise 25 has a volume of 150. mL and determine the mass change that the electrode in the cathode must undergo to reach equilibrium.

THE ELECTROLYTIC CELL

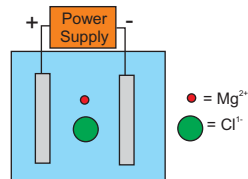
28. What is a Fermi level? What happens to the Fermi level of an electrode when electrons are withdrawn from it by a power supply?

29. One of the advantages of electrochemistry is that we have control of the free energy of the electrons. Explain how we have that control and how it can be used.

30. What is a faraday?

31. How many moles of electrons are required to produce a charge of 1.0 C?

32. What is overpotential? How is it important in the electrolysis of aqueous solutions?
33. Consider the diagram of an electrolytic cell shown below.



- a) Toward which electrode, (+) or (-), do the magnesium ions migrate?
- b) What is the electrical sign of the anode? How does this compare to a galvanic cell?
- c) In which direction do the electrons flow, anode \rightarrow cathode or cathode \rightarrow anode? How does this compare to a galvanic cell?
34. Consider the following cell:
 $\text{Cr} \mid \text{Cr}^{3+}(1.00 \text{ M}) \parallel \text{Ni}^{2+}(1.00 \text{ M}) \mid \text{Ni} \quad \mathcal{E}^\circ = 0.68 \text{ V}.$
- a) How many milligrams of metallic nickel would be plated on the cathode if a current of 0.11 A is drawn for 1.5 hrs?
- b) What is the Cr^{3+} concentration when the Ni^{2+} concentration has dropped to 10^{-4} M ? What is the cell potential at this point?
35. What is the standard reduction potential of the X^{2+}/X couple given that the cell potential of the following cell is 0.44 V?
- $$\text{X} \mid \text{X}^{2+}(0.044 \text{ M}) \parallel \text{Ag}^{1+}(0.27 \text{ M}) \mid \text{Ag}$$
36. What is the standard reduction potential of Y^{3+} given that the cell potential of the following cell is 1.32 V?
- $$\text{Zn} \mid \text{Zn}^{2+}(0.14 \text{ M}) \parallel \text{Y}^{3+}(1.2 \text{ M}) \mid \text{Y}$$

PREDICTING THE PRODUCTS OF ELECTROLYSIS

37. Ignore overpotential effects and write the anode and cathode reactions occurring in the electrolysis of aqueous solutions of the following substances?
- a) FeSO_4 b) NiF_2 c) HI d) AgNO_3
38. Ignore overpotential effects and predict the products formed at the electrodes in the electrolysis of the following:
- a) $\text{HF}(\text{aq})$ b) $\text{BaCl}_2(\text{l})$ c) $\text{KI}(\text{aq})$ d) $\text{KOH}(\text{aq})$

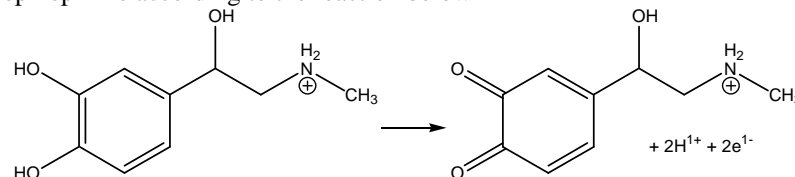
QUANTITATIVE ASPECTS OF ELECTROCHEMISTRY

39. How many Coulombs are required to reduce 3.0 moles of nitrate ion to ammonia?
40. How long would a solution of $\text{Cr}_2(\text{SO}_4)_3$ have to be electrolyzed with a current of 3.0 A in order to deposit 10. g of Cr?
41. A Nicad battery involves the following cell reaction:

$$\text{NiO}_2(\text{s}) + \text{Cd}(\text{s}) + 2 \text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$$
 How many grams of NiO_2 are required in a Nicad battery rated at 1.0 A-hr? A rating of one A-hr means that the battery has enough reactant to support drawing 1 ampere of current for one hour.
42. A current of 0.600 A deposits 1.33 g of a certain metal in 1.00 hour. Assume a two-electron reduction to determine the atomic mass and identity of the metal.
43. Determine the concentration of Ni^{2+} in a solution if 90.5 C is required to reduce all of the Ni^{2+} in 25.0 mL of the solution.

MISCELLANEOUS

44. Epinephrine (epp-uh-nef'-frin) is one of an important class of organic molecules known as catecholamines (cat-uh-cole'-amines), which function in living organisms as chemical messengers. Epinephrine is stored inside biological cells in extremely tiny sacs known as vesicles until they are secreted when a chemical signal is received, causing rupture of the vesicle and release of the contents, a process known as exocytosis. Electrochemical detection of epinephrine released from vesicles can be performed using inert microscopic carbon electrodes, which oxidize epinephrine according to the reaction below



- a) If $1.1 \times 10^{-12} \text{ C}$ of charge resulted from the oxidation of all the epinephrine released from a spherical vesicle of 300. nm diameter, how many epinephrine molecules were in the vesicle?
- b) Calculate the molarity of epinephrine in the vesicle prior to its release. The volume of a sphere is $\frac{4}{3} \pi r^3$, $1 \text{ nm} = 10^{-9} \text{ m}$, and $1 \text{ L} = 1 \text{ dm}^3$.

45. Electrochemical machining is a process in which a metal can be removed (etched) selectively by making it the anode in an electrolytic cell. It is essentially the reverse of metal electroplating and can be thought of as externally enforced corrosion. Electrochemical machining is used in the aerospace and automobile industries for shaping metal parts, and electrochemical *micromachining* is seeing increased use in the microelectronics industry for creating intricate wiring patterns on microcircuit boards. Consider a 35 μm thick uniform copper foil layer of 5.0 cm x 5.0 cm square geometry on a circuit board.
- Write the electrochemical half-reaction for this process and its standard reduction potential.
 - How many Coulombs of charge should be passed to remove 74 % of the volume of the copper foil? The density of copper is $9.0 \text{ g}\cdot\text{cm}^{-3}$.
 - Approximately how many layers of copper atoms are there in a 35 μm thick foil? The radius of a copper atom is 1.3 \AA .
46. The world's aluminum is electrolytically extracted from the mineral bauxite, which is predominately hydrated aluminum oxide. This is a high-temperature process (1030 $^{\circ}\text{C}$) in which bauxite is first converted into molten cryolite (Na_3AlF_6), which is then electrolytically reduced to molten aluminum metal. Although the mechanism is very complicated, the overall reaction is:
- $$2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2$$
- Whereas the calculated thermodynamic cell potential for this reaction is -1.2 V, the actual cell potential in an industrial cell is -4.3 V.
- Calculate the energy required, in $\text{kJ}\cdot\text{mol}^{-1}$, to industrially produce one ton of aluminum.
 - What fraction of this energy is wasted in the process?
 - Suggest a possible reason for the large disparity between the thermodynamic cell potential and the actual cell potential.

Chapter 10

Chemical Kinetics

10.0	Introduction
10.1	Reaction Rates
10.2	Rate Laws
10.3	Determining Rate Laws
10.4	Reaction Mechanisms and Rate Laws

10.5	Effect of Temperature on Reaction Rates
10.6	Catalysis
10.7	Chapter Summary and Objectives
10.8	Exercises

10.0 INTRODUCTION

To this point in our study of chemistry, we have been concerned only with the composition of equilibrium mixtures, not the length of time required to obtain equilibrium. However, the time required is also an important consideration. If a reaction proceeds too slowly, it will not be useful no matter how large the equilibrium constant, and if a reaction proceeds too rapidly, it may not be possible to control it. Thermodynamics allows us to predict the extent of a reaction, but it tells us nothing about the speed of the reaction or about how it occurs. These latter two considerations are the domain of **kinetics**, the study of the rates and mechanisms of chemical reactions.

Consider the decomposition of 0.020 M HI at 700 °C; $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$. The concentrations of both reactants and products are shown in Figure 10.1a as a function of time. The concentration of HI decreases for about 10,000 seconds (about three hours) and then levels off at 0.015 M. During that time, the concentrations of H_2 and I_2 each rise from zero to about 0.0025 M. Once the concentrations are no longer changing, the system has reached equilibrium. Thus, approximately three hours are required to obtain an equilibrium mixture at this temperature. $\Delta n_{\text{g}} = 0$ for the reaction, so the equilibrium constant can be determined from the equilibrium concentrations,

$$K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(0.0025)(0.0025)}{(0.015)^2} = 0.028$$

Now, consider the same reaction, but proceeding in the reverse direction. The concentrations of reactants and products during the reaction in which HI is formed by reaction of 0.010 M H_2 and 0.010 M I_2 at 700 °C are shown in Figure 10.1b. The HI concentration rises from 0 to 0.015 M while the I_2 and H_2 concentrations each start at 0.010 M and drop to their equilibrium value of 0.0025 M. These are the same concentrations obtained in Figure 10.1a. *The equilibrium concentrations are the same regardless of the direction from which the equilibrium is approached.*

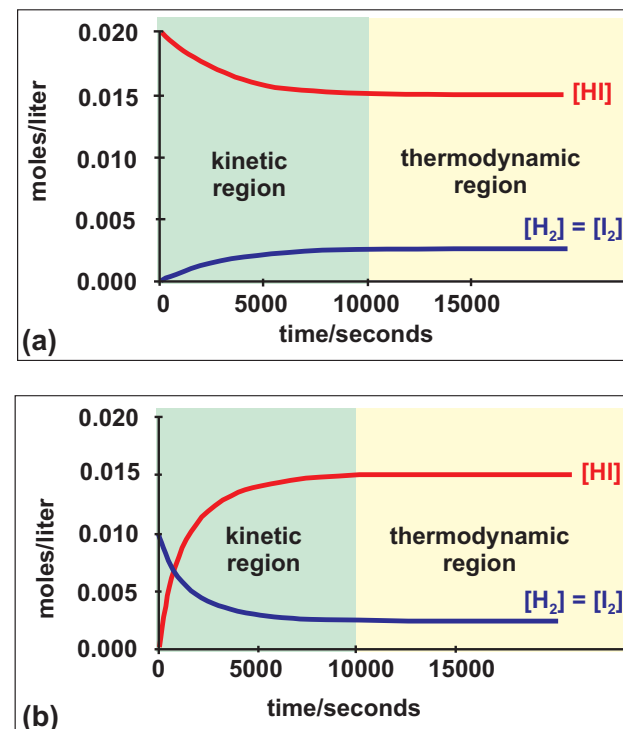


Figure 10.1 Variation of concentration of H_2 , I_2 , and HI during the (a) decomposition of 0.02 M HI and (b) formation of HI from 0.010 M H_2 and 0.010 M I_2

The reaction is in the kinetic region as long as concentrations are changing. Once there is no net change in concentrations, equilibrium is established, and the reaction is in the thermodynamic region.

There are two regions in the graphs shown in Figure 10.1. In one region (approximately the first 10,000 s), the concentrations change with time; this region is called the **kinetic region** because it is the region to which kinetics applies. In the other region (after $\sim 10,000$ s), the concentrations no longer change because the system has reached equilibrium; this region is called the **thermodynamic region** because the composition and energy changes predicted from thermodynamics apply to it. Thus far, we have concerned ourselves only with the thermodynamic region, but this chapter is devoted to the kinetic region. Kinetic considerations give us not only an understanding of how concentrations vary with time, but they also give us insight into the reaction mechanism.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- define reaction rates, rate constants and the order of a reactant;
- differentiate between the order of a reactant and the order of a reaction;
- describe the rate law and show how it is determined and used;
- extend the rate law to concentration versus time;
- show how reactant orders and rate constants are determined experimentally;
- define elementary reactions and molecularity;
- show how the experimental rate law can lead to a reaction mechanism; and
- define the activation energy and show how it can be determined from rate constant versus temperature data.

10.1 REACTION RATES

Rates are changes in one quantity with respect to another. For example, speed is the rate of change of position with respect to time. The *average* speed is determined by dividing the distance traveled (the change in position) by the time required to travel it. Thus, a person traveling 300 km in 4 hours has an average speed of $75 \text{ km} \cdot \text{hour}^{-1}$ (~ 50 mph).

$$\frac{\text{change in position}}{\text{time required}} = \frac{\Delta x}{\Delta t} = \frac{300 \text{ km}}{4 \text{ hours}} = 75 \text{ km} \cdot \text{hour}^{-1}$$

However, it is unlikely that the person traveled at a constant speed of $75 \text{ km} \cdot \text{hour}^{-1}$ for the entire trip. The *instantaneous* speed (the speed given by the speedometer at any instant) for such a trip would usually vary from 0 to over $100 \text{ km} \cdot \text{hour}^{-1}$.

Reaction rates are measured as changes in concentration with respect to time. They are the most important of the kinetic parameters. The concentration of HI *versus* time at

700 °C in the reaction of 0.010 M H₂ and 0.010 M I₂ is shown in more detail in Figure 10.2a. Note that the concentration of HI has increased from 0 to about 0.014 M in 5000 seconds, so the average rate of change of HI concentration during this interval was

$$\frac{\Delta[\text{HI}]}{\Delta t} = \frac{0.014 \text{ M}}{5000 \text{ s}} = 2.8 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$$

However, the rate at which the HI forms is not constant throughout the reaction. For example, the concentration of HI had reached 0.010 M after only 2000 seconds, which yields an average rate of $5.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ over the first 2000 seconds. In fact, the rate at which the concentration of HI increases slows during the reaction and eventually reaches zero when equilibrium is established.

It is not the *average* rate of change of HI concentration but its *instantaneous* rate of change (*i.e.*, the rate at which the concentration of HI is changing at a given time) that is important. The instantaneous rate at a given time equals the slope of the tangent to the concentration versus time curve at that instant. Figure 10.2a shows the variation of the HI concentration with time, and Figure 10.2b shows the variation of the H₂ and I₂ concentrations with time. The slopes of the tangents at 665 seconds are $6.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ for HI and $-3.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ for H₂ and I₂. The slope of the tangent, and therefore the rate of change of concentration with respect to time, is positive for HI and negative for H₂ and I₂ because HI is being formed in the reaction while the H₂ and I₂ are disappearing. Consequently, a positive rate is read as a **rate of formation**, and a negative rate is read as a rate of disappearance. Thus, the rate of formation of HI at 665 seconds is $6.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$, while the rate of disappearance of H₂ and I₂ at 665 seconds is $3.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$. Note that both numbers are positive; the sign is implied by the use of *formation* or *disappearance*.

Rates of formation and disappearance are related by the stoichiometry of the chemical equation. As an example, consider the following reaction table:

	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow$		$2\text{HI}(\text{g})$	
in	c	c	c'	M
Δ	$-\Delta x$	$-\Delta x$	$+2\Delta x$	M
final	$c - \Delta x$	$c - \Delta x$	$c' + 2\Delta x$	M

The entries on the Δ line are the concentration changes during some time interval Δt . Thus, the rate at which a reactant disappears or a product forms during the interval equals its concentration change divided by the time interval. However, each concentration change on the Δ line is related to the stoichiometry of the reaction. Thus, *rates of formation and/or disappearance are all related by the stoichiometry of the reaction*. The coefficient

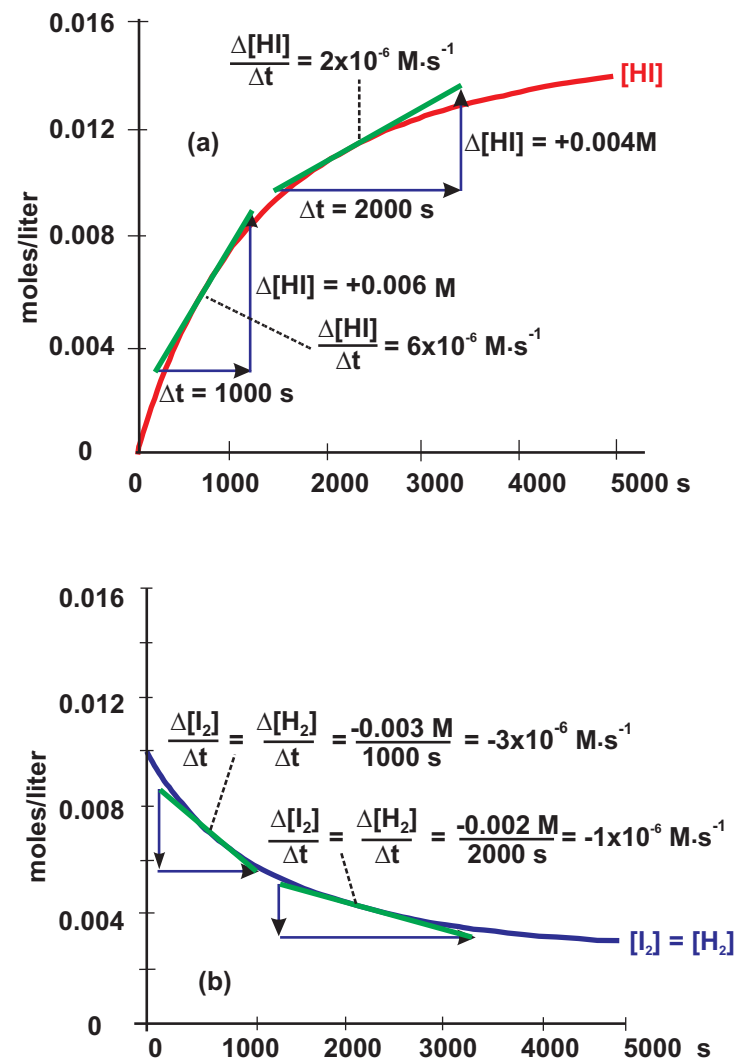


Figure 10.2 Rates of Reaction

a) The rate of change in the concentration of HI 665 seconds into the reaction is $6.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$, but after 2130 seconds, the rate has dropped to $2.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$.

b) The rates of change of the concentrations of H₂ and I₂ are equal to one another and, at the same times as used in Part a to determine the rate of change of the HI concentration, they are determined to be $-3.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ and $-1.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$, respectively. Thus, they are opposite in sign and one-half the rate of change of the HI concentration at any time.

of HI is twice that of either H_2 or I_2 , so the rate of formation of HI at any instant is exactly twice the rate of disappearance of H_2 or I_2 . Thus, the rates of appearance and/or disappearance of the various substances in a chemical reaction can be different, but the reaction still has a unique reaction rate. The **rate of reaction** is defined as $\Delta x/\Delta t$, where Δx is the amount of a substance whose coefficient in the chemical equation is unity would react during a time interval Δt .

$$\frac{\Delta x}{\Delta t} = \frac{\text{rate of formation of product}}{\text{coefficient of product}} = \frac{\text{rate of disappearance of reactant}}{\text{coefficient of reactant}} \quad \text{Eq. 10.1}$$

If the rate of appearance of HI is $6.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ at some time, then the rate of reaction is $3.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ because the coefficient of HI in the chemical equation is two.

Example 10.1

At some time during the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, the rate of formation of ammonia is $0.024 \text{ M} \cdot \text{s}^{-1}$. What is the rate of the reaction and what are the rates of disappearance of each of the reactants at this time?

Using Equation 10.1, we determine the rate of the reaction to be

$$\frac{\Delta x}{\Delta t} = \frac{\text{rate of formation of } \text{NH}_3}{\text{coefficient of } \text{NH}_3} = \frac{0.024 \text{ M} \cdot \text{s}^{-1}}{2} = 0.012 \text{ M} \cdot \text{s}^{-1}$$

Rearranging Equation 10.1 we obtain

$$\text{rate of disappearance of reactant} = (\text{coefficient of reactant})(\text{rate of reaction})$$

Consequently, the rate of disappearance of N_2 is $(1)(0.012 \text{ M} \cdot \text{s}^{-1}) = 0.012 \text{ M} \cdot \text{s}^{-1}$ and the rate of disappearance of H_2 is $3(0.012 \text{ M} \cdot \text{s}^{-1}) = 0.036 \text{ M} \cdot \text{s}^{-1}$.

10.2 RATE LAWS

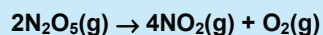
Experimentally, we observe that the rate of a reaction depends upon both the concentrations of the reactants and the temperature. The manner in which the rate varies at a given temperature is expressed by the **rate law** for the reaction. Rate laws can be very complicated, but they often take the form of a constant times the concentrations of the *reactants* each raised to some exponent; for example, $\text{rate} = k[\text{A}]^a[\text{B}]^b$. The constant, which is a function of temperature, is called the **rate constant** for the reaction. The exponent of a reactant concentration is referred to as the **reactant order**, and the sum of all exponents is called the **reaction order**. Consider the following examples:

- a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ $\text{Rate} = k_a[\text{H}_2][\text{I}_2]$
 b) $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ $\text{Rate} = k_b[\text{HI}]^2$
 c) $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ $\text{Rate} = k_c[\text{N}_2\text{O}_5]$

Reaction **a**, which is first order in H_2 and first order in I_2 , is a second-order reaction. Reaction **b**, which is second order in HI , is second order. *It is important to recognize that the exponents are not necessarily the stoichiometric coefficients in the balanced equation and must be determined experimentally.* Thus, Reaction **c**, which is first order in N_2O_5 , is a first-order reaction even though the stoichiometric coefficient of N_2O_5 is two. The rate constants k_a and k_b are called second-order rate constants, while k_c is a first-order rate constant. The reaction rate has units of concentration per unit time, but the units of the rate constant depend on the reaction order.

Example 10.2

- a) The rate of decomposition of 0.10 M N_2O_5 at 298 K is $0.022 \text{ M} \cdot \text{min}^{-1}$. What is the first-order rate constant for the decomposition at 298 K?



The reaction is first order, so the rate law is

$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]$$

The minus sign is used to show that the N_2O_5 is disappearing, and the $1/2$ indicates that the coefficient of N_2O_5 in the balanced equation is two. Thus, the rate of reaction is one-half the rate of disappearance of N_2O_5 .

$$\text{rate} = 1/2(0.022) = 0.011 \text{ M} \cdot \text{min}^{-1} = k[\text{N}_2\text{O}_5]$$

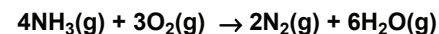
Solving for the first-order rate constant, we obtain

$$k = \frac{\text{rate}}{[\text{N}_2\text{O}_5]} = \frac{0.011 \text{ M} \cdot \text{min}^{-1}}{0.10 \text{ M}} = 0.11 \text{ min}^{-1}$$

Note that the rate constant for a reaction at a specific temperature is frequently called a specific rate constant. Thus, the specific rate constant for the decomposition of N_2O_5 at 298 K is 0.11 min^{-1} .

PRACTICE EXAMPLE 10.1

At some time during the following reaction, N_2 was being formed at a rate of $0.32 \text{ M} \cdot \text{s}^{-1}$.



What is the rate of disappearance of NH_3 at that time?

What is the rate of disappearance of O_2 at that time?

What is the rate of formation of water at that time?

b) What is the rate of formation of NO_2 at 298 K when the concentration of N_2O_5 is 0.042 M?

Determine the rate of reaction at this concentration by using the rate law and the specific rate constant obtained in Part a.

$$\text{reaction rate} = k[\text{N}_2\text{O}_5] = (0.11 \text{ min}^{-1})(0.042 \text{ M}) = 4.6 \times 10^{-3} \text{ M} \cdot \text{min}^{-1}$$

The coefficient of NO_2 in the balanced equation is four, so the rate of formation of NO_2 is four times the reaction rate.

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 4(\text{reaction rate}) = 4(4.6 \times 10^{-3}) = 1.8 \times 10^{-2} \text{ M} \cdot \text{min}^{-1}$$

10.3 DETERMINING RATE LAWS

The rate law is an expression that relates the rate of the reaction to the concentrations of the reactants. We present two methods for determining the rate of a reaction as a function of reactant concentrations: the method of initial rates and concentration versus time behavior.

THE METHOD OF INITIAL RATES

In the method of initial rates, the *average* rate of the reaction is determined at the beginning of the reaction. However, in order to assure that the average rate is close to the instantaneous rate, the time interval must be small enough that only a small fraction of the reactants has been consumed. This method has the advantage that the concentrations are initial concentrations, which means that they are easily determined and adjusted. In addition, because the concentrations of the products at the beginning of the reaction are zero, the reverse reaction can be ignored. This is a real advantage when studying the kinetics of reactions where forward and reverse reactions can compete with one another when the product concentrations become appreciable.

At least one experiment must be performed for each unknown that is to be determined. This usually means one experiment for the rate constant and one for each reactant order. Consider the generic reaction, $\text{A} + \text{B} \rightarrow \text{products}$. The general rate law for the reaction has the form $R = k[\text{A}]^a[\text{B}]^b$, so a minimum of three rates must be measured with different concentrations of A and B in order to determine the values of k , a , and b . The three rates can be expressed as

$$R_1 = k[A]_1^a[B]_1^b \quad R_2 = k[A]_2^a[B]_2^b \quad R_3 = k[A]_3^a[B]_3^b$$

The rate constants have no subscripts because they are the same for each experiment if the temperature is the same. The rate constant is eliminated by taking the ratios of the rates.

$$\frac{R_1}{R_2} = \frac{k[A]_1^a[B]_1^b}{k[A]_2^a[B]_2^b} = \frac{[A]_1^a[B]_1^b}{[A]_2^a[B]_2^b} \quad \text{and} \quad \frac{R_2}{R_3} = \frac{k[A]_2^a[B]_2^b}{k[A]_3^a[B]_3^b} = \frac{[A]_2^a[B]_2^b}{[A]_3^a[B]_3^b}$$

The above equations could be solved by taking the logarithms of both sides and solving the two simultaneous equations. However, the algebra can be simplified by isolating the effect of one reactant at a time. In this method, the effect of one reactant is isolated by varying its concentration while maintaining constant concentrations for all other reactants. This type of experiment is referred to an *isolation experiment*. Thus, to isolate the effect of the concentration of A on the reaction rate, we change its concentration, $[A]_1 \neq [A]_2$, while holding the concentration of B constant, $[B]_1 = [B]_2$. Then, the effect of B is isolated by maintaining a constant concentration of A, $[A]_2 = [A]_3$, and varying that of B, $[B]_2 \neq [B]_3$. This experimental design considerably reduces the algebra because $1^a = 1^b = 1$, and the above ratios simplify to

$$\frac{R_1}{R_2} = \frac{[A]_1^a}{[A]_2^a} = \left(\frac{[A]_1}{[A]_2} \right)^a \quad \text{if } [B]_1 = [B]_2 \quad \text{Eq. 10.2a}$$

$$\frac{R_2}{R_3} = \frac{[B]_2^b}{[B]_3^b} = \left(\frac{[B]_2}{[B]_3} \right)^b \quad \text{if } [A]_2 = [A]_3 \quad \text{Eq. 10.2b}$$

In order to solve for the exponential orders, we take the logarithm of both sides to obtain

$$a = \frac{\log\left(\frac{R_1}{R_2}\right)}{\log\left(\frac{[A]_1}{[A]_2}\right)} \quad \text{and} \quad b = \frac{\log\left(\frac{R_2}{R_3}\right)}{\log\left(\frac{[B]_2}{[B]_3}\right)} \quad \text{Eq. 10.3}$$

Alternatively, we can use experimental design to make the concentration ratios small whole numbers so that the exponents can be determined by inspection.* Examples 10.3 and 10.4 and Practice Example 10.2 demonstrate this method.

* In fact, Equation 10.3 is given for completeness only. All of the examples treated in this chapter will be done by inspection.

Example 10.3

The kinetics of the decomposition of HI at 700 °C were followed by monitoring the appearance of iodine. Fresh HI was added to the reaction flask, and the times required for the concentration of the iodine to reach 1.00×10^{-4} M were determined at different initial concentrations of HI.

Initial [HI]	time
0.0200 M	140.3 s
0.0400 M	35.1 s

The decomposition of HI is what order in HI, and what is the specific rate constant for the decomposition at 700 °C?

$\Delta[I_2] = 1.00 \times 10^{-4}$ M in each experiment and the time required for the change (Δt) is given in the table. The reaction is $2HI(g) \rightarrow H_2(g) + I_2(g)$, so the reaction rate is equal to the rate of formation of I_2 . Thus, we can express the initial rate as

$$R = \frac{\Delta[I_2]}{\Delta t} = \frac{1.0 \times 10^{-4} \text{ M}}{t} = k[HI]^y$$

Substitution of the given information for each experiment yields

$$R_1 = \frac{1.00 \times 10^{-4} \text{ M}}{140.3 \text{ s}} = 7.13 \times 10^{-7} \text{ M} \cdot \text{s}^{-1} = k(0.0200)^y \text{ and}$$

$$R_2 = \frac{1.00 \times 10^{-4} \text{ M}}{35.1 \text{ s}} = 2.85 \times 10^{-6} \text{ M} \cdot \text{s}^{-1} = k(0.0400)^y$$

The order of HI is determined by taking the ratios of the two rates.

$$\frac{R_2}{R_1} = \frac{2.85 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}}{7.13 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}} = 4.00 = \left(\frac{[HI]_2}{[HI]_1} \right)^y = \left(\frac{0.0400 \text{ M}}{0.0200 \text{ M}} \right)^y = 2.00^y$$

The equation to be solved is $(2.00)^y = 4.00$, which is readily solved as $y = 2^*$. The reaction is second order in HI and the rate equation is

$$\frac{\Delta[I_2]}{\Delta t} = \text{rate} = k[HI]^2$$

The second-order rate constant can be determined by substitution of the calculated rates and known concentrations into the rate law.

$$k = \frac{\text{rate}}{[HI]^2} = \frac{2.85 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}}{(0.0400 \text{ M})^2} = 1.78 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

The rate of appearance of I_2 and rate of disappearance of HI at 700 °C are

$$\frac{\Delta[I_2]}{\Delta t} = 1.78 \times 10^{-3} [HI]^2 \text{ and } -\frac{\Delta[HI]}{\Delta t} = 2 \left(\frac{\Delta[I_2]}{\Delta t} \right) = 3.56 \times 10^{-3} [HI]^2$$

The rate constants are different because HI disappears twice as fast as I_2 is formed.

* Alternatively, the equation can be solved by taking the log of both sides and solving for y:

$$y \log(2.00) = \log(4.00)$$

$$y = \frac{\log 4.00}{\log 2.00} = \frac{0.602}{0.301} = 2$$

Example 10.4

The kinetics of the formation of HI at 700 °C were followed by measuring the time required for the concentration of the iodine to drop by 1.00×10^{-4} M.

[H ₂]	[I ₂]	time
0.0100	0.0100	16.0 s
0.0200	0.0100	8.00 s
0.0200	0.0200	4.00 s

The reaction is $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$, and the rate of reaction is equal to the rate of disappearance of iodine. Proceeding as in Exercise 10.3, we first determine the rates of disappearance of the iodine as

$$R = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1.0 \times 10^{-4} \text{ M}}{t} = k[\text{H}_2]^x [\text{I}_2]^z$$

$$R_1 = \frac{1.0 \times 10^{-4} \text{ M}}{16.0 \text{ s}} = 6.25 \times 10^{-6} \text{ M} \cdot \text{s}^{-1} = k(0.0100)^x (0.0100)^z$$

$$R_2 = \frac{1.0 \times 10^{-4} \text{ M}}{8.00 \text{ s}} = 1.25 \times 10^{-5} \text{ M} \cdot \text{s}^{-1} = k(0.0200)^x (0.0100)^z$$

$$R_3 = \frac{1.0 \times 10^{-4} \text{ M}}{4.00 \text{ s}} = 2.50 \times 10^{-5} \text{ M} \cdot \text{s}^{-1} = k(0.0200)^x (0.0200)^z$$

Get the H₂ order from the ratio of the rates in which the I₂ concentration is constant.

$$\frac{R_2}{R_1} = \frac{1.25 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}}{6.25 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}} = 2.00 = \left(\frac{0.0200 \text{ M}}{0.0100 \text{ M}} \right)^x \left(\frac{0.0100 \text{ M}}{0.0100 \text{ M}} \right)^z = 2.00^x$$

Solving $2.00^x = 2.00$ for x , we determine that the reaction is first order in hydrogen. To determine the effect of I₂ on the rate, we obtain the ratio of two rates in which the H₂ concentration is held constant.

$$\frac{R_3}{R_2} = \frac{2.50 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}}{1.25 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}} = 2.00 = \left(\frac{0.0200 \text{ M}}{0.0200 \text{ M}} \right)^x \left(\frac{0.0200 \text{ M}}{0.0100 \text{ M}} \right)^z = 2.00^z$$

Solving $2.00^z = 2.00$ for z , we determine that the reaction is also first order in iodine. The rate law for the disappearance of iodine is

$$-\frac{\Delta[\text{I}_2]}{\Delta t} = \text{rate} = k[\text{H}_2][\text{I}_2]$$

Determine the rate constant by substituting the rate and concentrations of any experiment into the rate law.

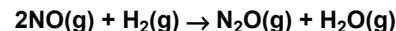
$$k = \frac{\text{rate}}{[\text{H}_2][\text{I}_2]} = \frac{6.25 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}}{(0.0100 \text{ M})(0.0100 \text{ M})} = 6.25 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$$

The rate laws for the disappearance of I₂ and the formation of HI at 700 °C are*

$$-\frac{\Delta[\text{I}_2]}{\Delta t} = 6.25 \times 10^{-2} [\text{H}_2][\text{I}_2] \quad \text{or} \quad \frac{\Delta[\text{HI}]}{\Delta t} = 2 \left(-\frac{\Delta[\text{I}_2]}{\Delta t} \right) = 0.125 [\text{H}_2][\text{I}_2]$$

PRACTICE EXAMPLE 10.2

The initial rates data at some temperature for the reaction



are given in the following table.

Exp	[NO]	[H ₂]	Rate (M/min)
I	0.10	0.80	0.26
II	0.30	0.80	2.34
III	0.30	0.40	1.17

What is the rate law for the reaction?

Order of NO:

Order of H₂:

The rate law is R =

What is the specific rate constant at this temperature?

* The rate constant for the formation of I₂ is $0.0625 \text{ M}^{-1} \cdot \text{s}^{-1}$, while that for the disappearance of HI is $0.125 \text{ M}^{-1} \cdot \text{s}^{-1}$ because 2HI must disappear for each I₂ that forms. The coefficient of I₂ in the equation is 1, so the rate constant for the reaction equals the rate constant for the formation of I₂.

CONCENTRATION VERSUS TIME BEHAVIOR

The order of a reactant can also be determined graphically by following its concentration over time, but the rate law must first be converted into a function of concentration and time. We consider only the cases of first- and second-order reactions.

First-order kinetics

Consider the generic first-order reaction $A \rightarrow \text{Products}$, which has a rate law $-\frac{\Delta[A]}{\Delta t} = k[A]$. The rate law can be rearranged to $-\frac{\Delta[A]}{[A]} = k\Delta t$, which can be solved by integration (See Equation 10.4A in the margin) to yield the variation of the concentration of a reactant with time in a first-order reaction. The concentration of a reactant in a first-order reaction as a function of time is given by Equation 10.4,

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

$$y = b + mx$$
Eq. 10.4

$[A]_0$ is the reactant concentration at time $t = 0$. Equation 10.4 has the form $y = b + mx$, which is the general equation of a straight line with a y-intercept of b and a slope of m . Thus, a plot of the natural logarithm of the reactant concentration versus time for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $\ln [A]_0$. The fact that a plot of $\ln [A]$ versus t is a straight line is evidence that the reaction is first order in the reactant A . Using the identity $\ln x - \ln y = \ln (x/y)$, we can express Equation 10.4 as

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt$$
Eq. 10.4b

which can also be expressed as an exponential

$$[A] = [A]_0 e^{-kt}$$
Eq. 10.5

Equation 10.5 shows that the concentration of the reactant drops exponentially with time. This behavior is called **exponential decay**.

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

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

Eq. 10.4a Integration of the first-order rate law produces the integrated rate law for first order reactions.

Example 10.5

The decomposition of dimethyl ether, $\text{H}_3\text{C-O-CH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2(\text{g}) + \text{CO}(\text{g})$, is first order with a rate constant of $4.0 \times 10^{-4} \text{ s}^{-1}$ at 500°C . If the initial concentration of dimethyl ether is 0.050 M , what is its concentration after 1.00 hour ?

The rate constant has units of s^{-1} , so the time must be converted to seconds. Then Equation 10.5 can be used with $kt = (4.0 \times 10^{-4} \text{ s}^{-1})(3600 \text{ s}) = 1.44$

$$[\text{H}_3\text{C-O-CH}_3] = [\text{H}_3\text{C-O-CH}_3]_0 e^{-kt} = (0.050) e^{-1.44} = 0.012 \text{ M}$$

Example 10.6

The concentration of azomethane ($\text{C}_2\text{N}_2\text{H}_6$) as a function of time during its decomposition at 300°C is shown in the table below. Verify that the decomposition is first order and determine the first-order rate constant at 300°C .

t (s)	[A]	ln [A]	t (s)	[A]	ln [A]
0	0.00600	-5.116	12000	0.00088	-7.036
2000	0.00436	-5.436	14000	0.00064	-7.356
4000	0.00316	-5.756	16000	0.00046	-7.676
6000	0.00230	-6.076	18000	0.00034	-7.996
8000	0.00167	-6.396	20000	0.00024	-8.316
10000	0.00121	-6.716			

The decomposition reaction is $\text{H}_3\text{C}-\text{N}=\text{N}-\text{CH}_3(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{N}_2(\text{g})$.

Equation 10.4 indicates that, if the reaction is first order, a plot of $\ln [\text{C}_2\text{N}_2\text{H}_6]$ versus time should be a straight line with an intercept of $\ln [\text{azomethane}]_0$ (the initial concentration) and a slope of $-k$. We begin by determining the natural logarithms of the concentrations, which are also shown in the table. Figure 10.3a is a plot of concentration versus time and shows the exponential decay expected for a first-order reaction.

However, the fact that the reaction is indeed first order is established in Figure 10.3b, which shows that the plot of the natural logarithm of the azomethane concentration versus time is linear. The analytical expression represented by Figure 10.3b is

$$\ln [\text{C}_2\text{N}_2\text{H}_6] = \ln [\text{C}_2\text{N}_2\text{H}_6]_0 - kt$$

The slope, $\frac{\Delta[\text{C}_2\text{N}_2\text{H}_6]}{\Delta t} = -k$, can be determined from two points on the line. For example, let us determine the slope between the $t = 0$ concentration and the $t = 8000$ seconds concentration. The slope is then $\{\ln [\text{C}_2\text{N}_2\text{H}_6] \text{ at } 8000 \text{ seconds} - \ln [\text{C}_2\text{N}_2\text{H}_6] \text{ at } t = 0\}$ divided by $\Delta t = 8000 - 0$ seconds.

$$\text{slope} = \frac{-6.396 - (-5.116)}{8000 - 0} = \frac{-1.280}{8000} = -1.60 \times 10^{-4} \text{ s}^{-1}$$

The slope of the line in Figure 10.3b is $-1.60 \times 10^{-4} \text{ s}^{-1}$, so the first-order rate constant is $k = 1.60 \times 10^{-4} \text{ s}^{-1}$. All of the data points in this example are on the best line, so the slope found from the difference between two points yields the best answer. However, this is not usually the case due to experimental error, and if one or both points deviate from the best line, then the slope determined in this manner can be off substantially. Consequently, the slope should be determined by the method of least squares, which uses all of the points.

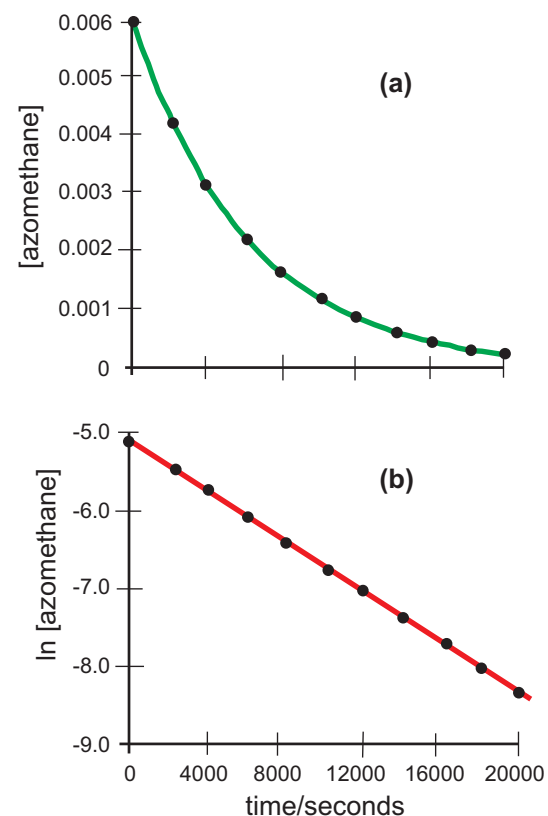


Figure 10.3 First order kinetics of the decomposition of azomethane at 300°C

A plot of concentration versus time is linear, so the reaction is first order.

The **half-life** of a reaction ($t_{1/2}$) is the time required for half of the existing reactant to disappear. Thus, $t = t_{1/2}$ and $[A] = 1/2 [A]_0$ at the half-life. Substitution of these half-life quantities and the identity $\ln(1/x) = -\ln x$ into Equation 10.4b yields

$$\ln \left(\frac{1/2 [A]_0}{[A]_0} \right) = \ln \left(\frac{1}{2} \right) = -\ln 2 = -kt_{1/2}$$

Solving for the half-life, we obtain

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Eq. 10.6

Equation 10.6 shows that the half-life of a first-order reaction is constant.

Example 10.7

What is the half-life for the decomposition of diazomethane at 300 °C?

The rate constant for the decomposition was determined to be $1.60 \times 10^{-4} \text{ s}^{-1}$ in Example 10.6. Using this rate constant in Equation 10.6, we obtain

$$t_{1/2} = \frac{0.693}{1.60 \times 10^{-4} \text{ s}^{-1}} = 4.33 \times 10^3 \text{ s}$$

This means that it would take 4330 seconds (72 minutes) for half of a sample to decompose – no matter how large or small the sample is! This is demonstrated in Figure 10.4, which is a plot of concentration versus time for the decomposition of azomethane discussed in Example 10.6. The concentration of the azomethane is halved every 4330 seconds. Thus, the initial concentration is 0.006 M, but the concentration drops to 0.003 M after one half-life, to 0.0015 M after two half-lives, and to 0.00075 M after three half-lives.

Second-order kinetics

If the reaction $A \rightarrow \text{Product}$ is second order, the rate law is $-\frac{\Delta[A]}{\Delta t} = k[A]^2$,

which can be rearranged to $-\frac{\Delta[A]}{[A]^2} = k\Delta t$ and solved by integration as shown in

Equation 10.7a in the margin. Equation 10.7 shows the reactant concentration as a function of time for a second-order reaction:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad \text{Eq. 10.7}$$

$[A]_0$ is the initial concentration, and k is the second-order rate constant for the reaction.

A plot of $1/[A]$ versus t is a straight line with a y-intercept of $1/[A]_0$ and a slope of k .

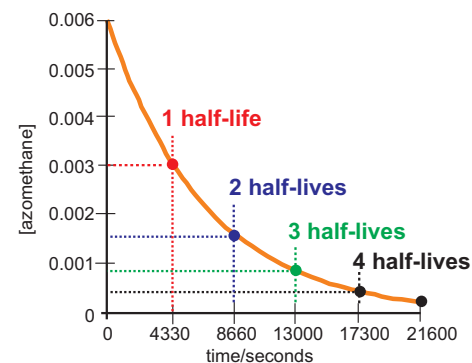


Figure 10.4 Concentration of azomethane versus time

The concentration is halved every 4330 s, so the half-life of the decomposition of azomethane at 300 °C is 4330 seconds.

PRACTICE EXAMPLE 10.3

If a first-order reaction has a 23.5 minute half-life, how long would it take for it to reach 90% completion?

$k =$

at 90% completion, $[A]/[A]_0 =$

$$\ln ([A]/[A]_0) = \underline{\hspace{2cm}}$$

Use Equation 10.4b to obtain the time.

$t =$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt \Rightarrow \frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Eq. 10.7a Integration of the second-order rate law yields the integrated rate law for second-order reactions.

Example 10.8

The concentration of NO_2 versus time during its decomposition at 350°C is shown in the table below. The natural logarithms and reciprocals of the concentrations are also included in the table. Determine if the decomposition is first or second order and the rate constant for the decomposition at 350°C .

t	$[\text{NO}_2]$	$\ln [\text{NO}_2]$	$[\text{NO}_2]^{-1}$	t	$[\text{NO}_2]$	$\ln [\text{NO}_2]$	$[\text{NO}_2]^{-1}$
0.0	0.0100	-4.605	100	400.0	0.0013	-6.612	744
100.0	0.0038	-5.565	261	500.0	0.0011	-6.808	905
200.0	0.0024	-6.045	422	600.0	0.0009	-6.972	1066
300.0	0.0017	-6.368	583				

The decomposition reaction is $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$

Figure 10.5a is a plot of the concentration of NO_2 versus time. At first glance, it looks very much like Figure 10.3a, and it would be tempting to conclude that this is a first-order reaction, but Equations 10.4 and 10.7 must be applied to determine the order of the reaction.

We test for first-order kinetics by plotting $\ln [\text{NO}_2]$ versus time, but the result, shown in Figure 10.5b, is not a straight line. The reaction is, therefore, not first order. To determine if the reaction is second order, we plot $1/[\text{NO}_2]$ versus time. This plot, shown in Figure 10.5c, is a straight line, and we conclude that the reaction follows second-order kinetics.

The second-order rate constant for the disappearance of NO_2 is equal to the slope of the line shown in Figure 10.5c. It can be determined by dividing the change in $1/[\text{NO}_2]$ by the time required to accomplish the change. For example, we could determine the slope by using the points at 500 and 100 seconds as follows:

$$k' = \text{slope} = \frac{905 \text{ M}^{-1} - 261 \text{ M}^{-1}}{500 \text{ s} - 100 \text{ s}} = \frac{644 \text{ M}^{-1}}{400 \text{ s}} = 1.61 \text{ M}^{-1} \cdot \text{s}^{-1}$$

The reaction is second order in NO_2 , so the rate of disappearance of NO_2 at 350°C is

$$-\frac{\Delta[\text{NO}_2]}{\Delta t} = 1.61[\text{NO}_2]^2$$

However, the coefficient of NO_2 in the balanced equation is two, so the second-order rate constant for the reaction at 350°C is

$$k = k'/2 = 1.61/2 = 0.805 \text{ M}^{-1} \cdot \text{s}^{-1}.$$

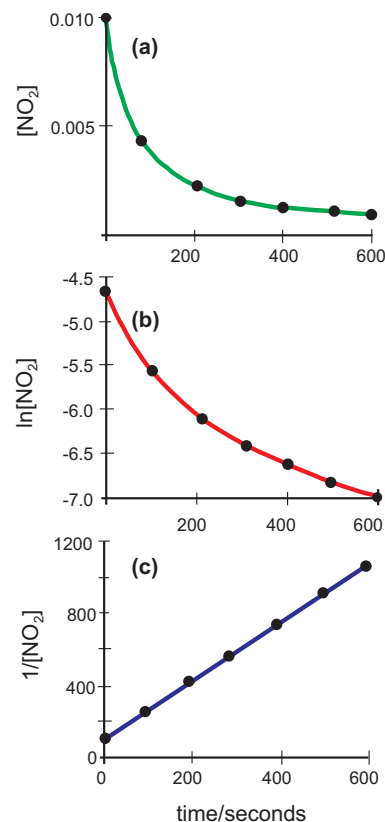
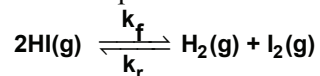


Figure 10.5 Determining the order of NO_2 decomposition

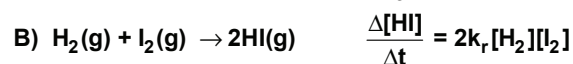
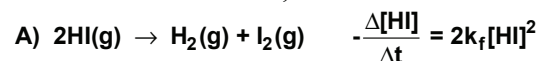
Of the plots, only that of the reciprocal of concentration versus time is linear, so the reaction is second order.

ANOTHER LOOK AT THE RELATIONSHIP BETWEEN EQUILIBRIUM AND KINETICS

HI decomposes into H_2 and I_2 , but it is also formed from the reaction of H_2 and I_2 . The fact that the reaction proceeds in either direction is represented as follows:



k_f is the rate constant for the forward reaction, and k_r is the rate constant for the reverse reaction. The forward reaction is second order in HI, while the reverse reaction is first order in each H_2 and I_2 . The rate constants at 700°C are $k_f = 1.8 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_r = 6.3 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}^{-1}$. To summarize,



The 2 in the rate law is due to the coefficient of HI in the balanced equation. As shown in Figure 10.6, a plot of $1/[\text{HI}]$ versus time for the decomposition (Reaction A) is linear at the beginning of the experiment, consistent with second order behavior, but it deviates from linearity after about 2000 s. The observed HI concentration at times longer than 2000 s is less than that predicted by simple second-order kinetics because it is being formed by Reaction B. As the reaction proceeds, Reaction A slows because the concentration of HI drops, but the rate of Reaction B increases because the concentrations of H_2 and I_2 increase. The net rate of disappearance of HI is equal to its rate of disappearance in Reaction A minus its rate of formation in Reaction B. At equilibrium, the concentration of HI no longer changes because it is formed at the same rate that it disappears.

$$k_f[\text{HI}]^2 = k_r[\text{H}_2][\text{I}_2] \quad \text{or rate of disappearance of HI} = \text{rate of formation of HI}$$

Gathering concentrations to one side and the rate constants to the other we obtain

$$\frac{k_f}{k_r} = \frac{1.8 \times 10^{-3} \text{ s}^{-1}}{6.3 \times 10^{-2} \text{ s}^{-1}} = 0.029 = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = K_c$$

K_c is the equilibrium constant for the reaction $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ at 700°C . We conclude that *the equilibrium constant is equal to the ratio of the forward and reverse rate constants*. The equilibrium concentrations in the decomposition of 0.020 M HI at 700°C are $[\text{HI}] = 0.015 \text{ M}$, and $[\text{H}_2] = [\text{I}_2] = 0.0025 \text{ M}$, so HI is consumed at a rate of $2(1.8 \times 10^{-3})[0.015]^2 = 8.0 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}$ and formed at a rate of $2(6.3 \times 10^{-2})[0.0025][0.0025] = 8.0 \times 10^{-7} \text{ M} \cdot \text{s}^{-1}$. Thus, its equilibrium concentration does not change because it is formed and consumed at the same rate.

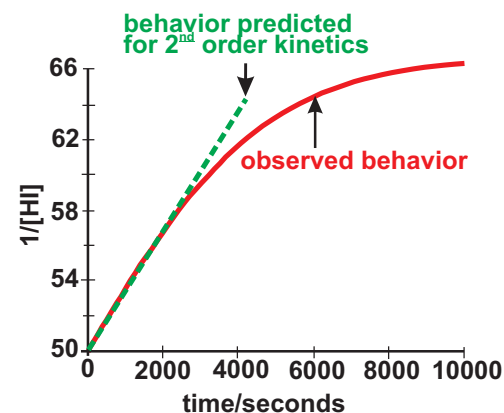
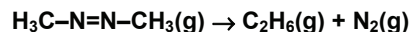


Figure 10.6. A plot of $1/[\text{HI}]$ versus time for the decomposition of HI at 700°C

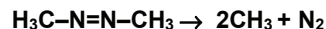
The reaction is second order in HI, but the plot deviates from linear behavior at later times due to competition from the reverse reaction.

10.4 REACTION MECHANISMS AND RATE LAWS

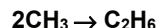
Most reactions occur by a series of elementary steps called the **reaction mechanism**. Consider the decomposition of azomethane discussed in Example 10.6.



The reaction has a two-step mechanism. First, the two N–C bonds break and the N≡N bond forms.



Next, the highly reactive CH₃ groups quickly combine to form ethane.



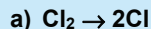
Each step of a mechanism involves a single molecular event called an **elementary reaction**. The two elementary reactions above combine to give the reaction mechanism for the decomposition of azomethane. *The sum of the elementary processes must yield the net reaction.* The two methyl groups, which are formed in the first step and consumed in the second, do not appear in the net reaction, so they are **intermediates**. Intermediates typically are short-lived, but they can frequently be observed during reaction and sometimes even isolated. Indeed, evidence for a proposed intermediate is excellent support for a mechanism.

The number of molecules reacting in an elementary reaction is called the **molecularity** of the elementary reaction. An elementary reaction is **unimolecular**, **bimolecular**, or **termolecular** if it involves one, two, or three molecules, respectively. Thus, the first step in the decomposition of azomethane is unimolecular while the second step is bimolecular. Termolecular processes are very rare and slow because the simultaneous collision of three reactant molecules is very rare. Processes with molecularities greater than three do not occur at all.

In order for two or three molecules to react, they must collide with one another. As a result, the rate of an elementary reaction is proportional to the collision frequency of the reactants. The **collision frequency**, which is the number of collisions between the reacting particles in a specified volume per unit time, can be shown to be directly proportional to the product of the molar concentrations of the colliding particles. Thus, *the rate law of an elementary reaction is equal to a proportionality constant (the rate constant) times the product of the molar concentrations of the reactants*. The particle concentration is squared if the collision is between two identical particles (Example 10.9c).

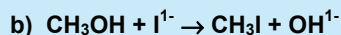
Example 10.9

Write the rate law governing each of the following elementary reactions.



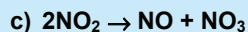
Unimolecular processes are first order because there is only one reactant and its coefficient is one.

$$\text{Rate} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = k[\text{Cl}_2]$$



Bimolecular processes are always second order because the sum of the coefficients is always two.

$$\text{Rate} = -\frac{\Delta[\text{CH}_3\text{OH}]}{\Delta t} = k[\text{CH}_3\text{OH}][\text{I}^{1-}]$$



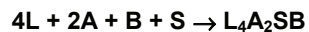
This is a bimolecular process, so it must be second order ($2\text{NO}_2 = \text{NO}_2 + \text{NO}_2$)

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2][\text{NO}_2] = k[\text{NO}_2]^2$$

We now address the problem of determining the reaction mechanism. As demonstrated in Example 10.9, the rate law of an elementary process can be determined from the stoichiometry of the process. Thus, a mechanism is proposed for a reaction; the rate law for each step is determined from the balanced equations; the rate laws of the elementary processes are combined to yield a rate law for the reaction. *A mechanism is acceptable only if the rate law derived from it agrees with the experimentally determined rate law.* However, it is often the case that more than one mechanism yields the experimental rate law, so mechanisms are usually proposed not proven. However, finding evidence for a proposed intermediate strongly supports a proposed mechanism and can sometimes prove that it is correct.

Combining the rate laws of the elementary processes into a reaction rate law can be a formidable task for complicated reactions, so we restrict our discussion to reactions in which one step of the multi-step mechanism is much slower than any of the others. In this case, the reaction rate is dictated by the rate of the slow step, which is called the **rate-determining step (RDS)**, and the rate law of the reaction is the rate law of the RDS.

As a simple example of a process with a rate-determining step, consider one in which three workers are constructing chairs in an assembly line. The process involves attaching four legs (L), two arms (A) and a back (B) to the seat (S) to make a chair (L_4A_2SB):



The first worker attaches the seat to the back to make the intermediate SB.



The SB units are made at a rate of 60 an hour and placed in a box for the next worker, who attaches four legs.



The L_4SB units, also intermediates, are made at a rate on 20 an hour and placed in a box for the next worker, who attaches the two arms and thus finishes the chair.

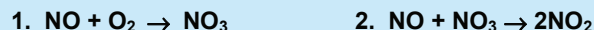


The final worker can make 40 chairs an hour if all of the components are available, but the L_4SB units arrive at a rate of only 20 an hour. Consequently, the final worker makes a chair and then waits for the second worker to put another unit in the box. The third step cannot proceed any faster than the second step for lack of supplies. The first worker starts making units at a rate of 60 an hour and puts them in the box, but they are removed from the box at a rate of only 20 an hour. Consequently, the box gets full and the first worker must wait for the second worker to remove a unit before a new SB unit can be made. The first step has reached equilibrium, and the rate at which SB units are produced is limited by the rate at which the second worker removes units from the box. The rates of the two rapid steps are limited by the slow (rate-determining) step, so only 20 chairs an hour can be produced in this assembly line.

The rate law of the reaction is rate law of the rate-determining step. However, the rate law involves the concentrations of the reactants and occasionally products but not intermediates. Consequently, the concentrations of any intermediates must be eliminated from the rate law of the rate-determining step to obtain the experimental rate law. This is done by assuming that the rapid steps that precede the rate-determining step all reach equilibrium. Thus, the concentrations of any intermediate can be obtained in terms of the concentrations of the reactants and the equilibrium constants of the preceding reactions. The method is demonstrated in Examples 10.10 and 10.11 and Practice Example 10.4.

Example 10.10

The following two-step mechanism has been proposed for the oxidation of NO.



a) What is the net reaction?

NO_3 is an intermediate (formed in Step 1 and consumed in Step 2), so the net reaction is
 $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

b) What is the rate law of the reaction if the first step is rate-determining?

The first step is a bimolecular reaction, which is first order in NO and first order in O_2 . Because both molecules are reactants in the reaction, the rate law of this step is the same as the rate law of the reaction.

$$\text{rate} = k_1[\text{NO}][\text{O}_2] = k[\text{NO}][\text{O}_2]$$

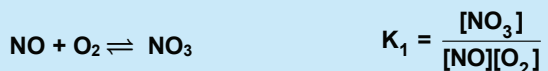
The rate constant for the reaction (k) is the rate constant for the first step (k_1).

c) What is the rate law of the reaction if the second step is rate-determining?

The second step is also bimolecular, being first order each in NO and NO_3 , so

$$\text{rate} = k_2[\text{NO}][\text{NO}_3]$$

However, this rate law contains the concentration of the intermediate NO_3 , which must be eliminated to obtain the rate law for the reaction. We do this by assuming that the first step reaches a rapid equilibrium.



Next, solve the equilibrium constant expression for the intermediate concentration.

$$[\text{NO}_3] = K_1[\text{NO}][\text{O}_2]$$

This expression for the concentration of NO_3 is then used in the rate law for the RDS to obtain the rate law for the oxidation.

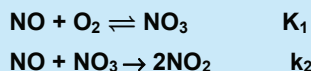
$$\text{rate} = k_2[\text{NO}][\text{NO}_3] = k_2[\text{NO}]\{K_1[\text{NO}][\text{O}_2]\} = k_2K_1[\text{NO}]^2[\text{O}_2]$$

$$\text{rate} = k[\text{NO}]^2[\text{O}_2], \text{ where } k = k_2K_1$$

Note that the rate constant for the reaction is the product of the rate constant of the rate-determining step and the equilibrium constant for the rapid step that preceded it.

The experimental rate law for the reaction is $-\frac{\Delta[\text{O}_2]}{\Delta t} = k[\text{NO}]^2[\text{O}_2]$, which is consistent

with the second step being rate determining. Thus, we would propose that the experimental rate constant is $k = k_2K_1$, and the mechanism of the reaction is



However, there may be other second order mechanisms, so the NO_3 intermediate would have to be identified in the reaction to verify the proposed mechanism.

Example 10.10 indicates that *the rate law of a reaction involves all of the reactant molecules except those that are involved in steps after the rate determining step*. For example, only one NO and an O₂ were involved in the first step, so the rate law is rate = k[NO][O₂] if the first step is the RDS. However, one molecule of NO is involved in the second step, but another molecule of NO and a molecule of O₂ are involved in the prior step; *i.e.*, two molecules of NO and one of O₂ are involved, so the rate law is rate = k[NO]²[O₂] if the second step is rate determining.

Example 10.11

The reaction of nitric oxide with hydrogen,
 $2\text{NO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)}$

is believed to proceed by the following three-step mechanism, which is consistent with the experimental rate law.

- | | |
|--|---|
| 1. $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ | rapid equilibrium with equilibrium constant K_1 |
| 2. $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ | slow step with rate constant k_2 |
| 3. $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ | fast step |

What is the rate law derived from this mechanism?

The second step is the slow and, therefore, rate-determining step. We thus start with the rate law for that step. It is a bimolecular process, which is first order in the intermediate N₂O₂ and the reactant H₂:

$$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]$$

In order to eliminate the concentration of the intermediate from the expression, we set up the equilibrium expression for the rapid equilibrium step that precedes the rate-determining step and solve for the concentration of N₂O₂.

$$K_1 = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \Rightarrow [\text{N}_2\text{O}_2] = K_1[\text{NO}]^2$$

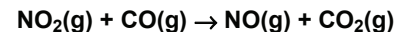
Next, substitute this concentration into the rate law for the rate-determining step.

$$\text{rate} = k_2\{K_1[\text{NO}]^2\}[\text{H}_2] = k_2K_1[\text{NO}]^2[\text{H}_2] = k[\text{NO}]^2[\text{H}_2]$$

The reaction is second order in NO and first order in H₂.

PRACTICE EXAMPLE 10.4

The reaction,



is believed to occur by the following two-step mechanism

- I. $2\text{NO}_2\text{(g)} \rightarrow \text{NO}_3\text{(g)} + \text{NO(g)}$
- II. $\text{NO}_3\text{(g)} + \text{CO(g)} \rightarrow \text{NO}_2\text{(g)} + \text{CO}_2\text{(g)}$

What is the molecularity of each step?

Step I:

Step II:

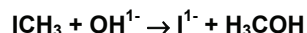
Identify the intermediate(s): _____

What is the rate law if Step I is rate determining?

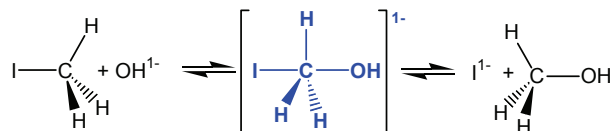
What is the rate law if Step II is rate determining?

10.5 THE EFFECT OF TEMPERATURE ON REACTION RATES

The rate of reaction depends upon both the reactant concentrations and the temperature. We have discussed the concentration dependence and now treat the temperature dependence. Consider the reaction between methyl iodide and hydroxide ion:



The reaction is an elementary process, so it is first order in each reactant. In order for the reaction to occur, a hydroxide ion must collide with a CH_3I molecule, and it must collide between the three hydrogen atoms. As the distance between the hydroxide ion and the carbon atom decreases, the carbon-iodine bond stretches, and the three hydrogen atoms are pushed back, which forces the $\text{H}-\text{C}-\text{H}$ angles to increase from 109° . These changes result in an energy increase, which reaches a maximum when the bond angle is 120° and the carbon is five coordinate as shown below.



The five-coordinate species in blue is called the **transition state** of the reaction because the reaction must proceed through this state to make the transition from reactants to products. The transition state can lead to or be formed from either side of the reaction (iodide ion can collide with CH_3OH to lead to the same transition state). The transition state cannot be isolated or directly observed. It is not an intermediate but rather a highly energetic species through which the reaction proceeds. The energy required to reach the transition state is called the **activation energy**. Figure 10.7 shows that the variation of energy along a complicated combination of $\text{C}-\text{I}$ and $\text{C}-\text{O}$ bond lengths and $\text{H}-\text{C}-\text{H}$ bond angles called the **reaction coordinate**. The activation energy of the forward reaction, $E_a(f)$, is much less than that of the reverse reaction, $E_a(r)$, because the energy of the reactants is greater than the energy of the products; *i.e.*, the reaction is exothermic.

There are two factors that dictate whether a collision achieves the transition state: the steric factor and the energy. The **steric factor** indicates the fraction of collisions in which the reactants have the correct orientation to react. As shown in Figure 10.8, there are a number of ways in which CH_3I and OH^{1-} can collide, but only a fraction have the correct orientation to reach the transition state. The second factor is energy because, even if the

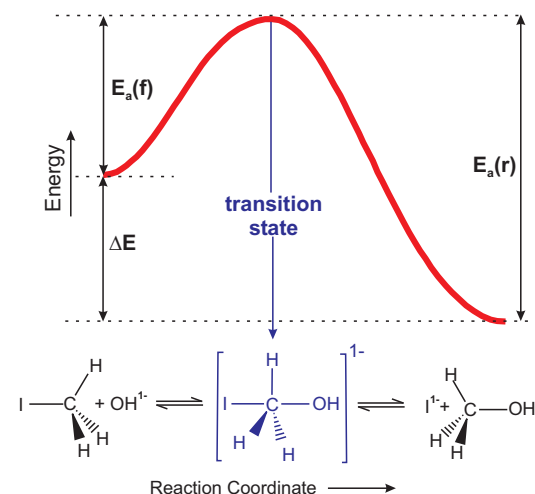


Figure 10.7 Energy diagram for $\text{CH}_3\text{I} + \text{OH}^{1-} \rightarrow \text{CH}_3\text{OH} + \text{I}^{1-}$

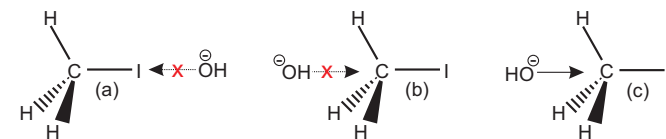


Figure 10.8 The steric factor

Collisions like (a) and (b) cannot lead to the transition state because the reactants are not aligned properly. Collision (c) can lead to the transition state but only if the colliding particles have sufficient energy to overcome the activation energy.

reactants have the correct orientation to react, they cannot do so unless there is sufficient energy in the collision to achieve the transition state. The average energy available in a collision depends on the thermal energy ($\sim RT$). Thus, as the temperature increases, the thermal energy increases, and the fraction of collisions with sufficient energy to achieve the transition state increases. Increasing the temperature, however, increases the rate of both the forward and reverse reactions. The fraction of collisions with energy equal to or exceeding the activation energy is given by $e^{-E_a/RT}$.

The rate constant represents the fraction of collisions that lead to the transition state, and it is the product of the steric and energy factors as shown in Equation 10.8.

$$k = Ae^{-E_a/RT} \quad \text{Eq. 10.8}$$

A is referred to as the **pre-exponential**, which includes the steric factor. Equation 10.8, known as the **Arrhenius equation**, shows the temperature dependence of the rate constant. If we take the natural logarithm of both sides, we can rewrite the Arrhenius equation as shown in Equation 10.9.

$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad \text{Eq. 10.9}$$

Equation 10.9 indicates that a plot of $\ln k$ versus $1/T$ should be a straight line with a y -intercept of $\ln A$ and a slope of $-E_a/R$. A plot of $\ln k$ versus $1/T$ is referred to as an **Arrhenius plot**.

Example 10.12

The following rate constants have been measured for the decomposition of azomethane discussed in Example 10.6. Show that the data are consistent with the Arrhenius equation. What is the activation energy for the reaction?

T (K)	k (s ⁻¹)	1/T (K ⁻¹)	ln k
532	1.8x10 ⁻⁶	0.00188	-13.23
541	1.5x10 ⁻⁵	0.00185	-11.11
560	6.0x10 ⁻⁵	0.00179	-9.72
576	1.6x10 ⁻⁴	0.00174	-8.74
593	9.5x10 ⁻⁴	0.00169	-6.96

The Arrhenius equation predicts that a plot of $\ln k$ versus $1/T$ should be linear. Thus, we first convert the experimentally determined temperature and rate constant data (the two columns on the left of the table above) to one consisting of the reciprocals of the temperatures and the natural logarithms of the rate constants (the two columns on the right of the table).

A plot of $\ln k$ versus $1/T$ is shown in Figure 10.9. The data can be fitted with a straight line, so we conclude that azomethane follows Arrhenius behavior, and that the slope of the best straight line is $-E_a/R$; *i.e.*, $E_a = -R(\text{slope})$. The experimental slope is $-2.9 \times 10^4 \text{ K}^{-1}$, so the activation energy of the reaction is determined to be

$$E_a = -R(\text{slope}) = -R \left(\frac{\Delta \ln k}{\Delta (T^{-1})} \right) = -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(-2.9 \times 10^4 \text{ K}) = 2.4 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$$

$$E_a = 240 \text{ kJ} \cdot \text{mol}^{-1}$$

In order to determine the activation energy of a reaction, the rate constant of the reaction must be determined for a minimum of two temperatures. The activation energy and the value of A do not change, so the following expressions for the rate constants can be obtained:

$$\ln k_1 = \ln A - \frac{E_a}{R} \times \frac{1}{T_1} \quad \text{and} \quad \ln k_2 = \ln A - \frac{E_a}{R} \times \frac{1}{T_2}$$

Taking the difference between the two expressions eliminates the $\ln A$ term

$$\ln k_2 - \ln k_1 = \frac{E_a}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Eq. 10.10a}$$

The difference between two logarithms is the logarithm of the quotient:

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{Eq. 10.10b}$$

Equation 10.10b can then be solved for the activation energy in terms of the rate constants at two different temperatures.

$$E_a = \frac{R \ln \left(\frac{k_2}{k_1} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \text{Eq. 10.11}$$

Equation 10.11 can be used to calculate the activation energy of a reaction from two rate constants. However, it is always best to use as much data as possible in the determination, so a least squares fit of the Arrhenius plot would be preferred.

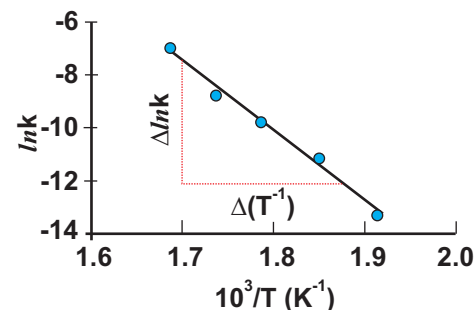


Figure 10.9 Arrhenius plot in the range of 520 to 600 K for the decomposition of azomethane

The slope of the line is $-E_a/R = -2.9 \times 10^4 \text{ K}$.

Example 10.13

- a) Use the rate constants at 532 and 593 K for the decomposition of azomethane to determine the activation energy of the decomposition.

Use the data in Example 10.12 and assign $T_1 = 532$ K, so $k_1 = 1.8 \times 10^{-6} \text{ s}^{-1}$, and assign $T_2 = 593$ K, so $k_2 = 9.5 \times 10^{-4} \text{ s}^{-1}$. Substitute the values into Equation 4.11 to arrive at

$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \cdot \ln \left(\frac{9.5 \times 10^{-4}}{1.8 \times 10^{-6}}\right)}{\left(\frac{1}{532} - \frac{1}{593}\right) \text{ K}^{-1}} = 2.7 \times 10^5 \text{ J} \cdot \text{mol}^{-1} = 270 \text{ kJ} \cdot \text{mol}^{-1}$$

The result is slightly different than that obtained in Example 10.12 ($240 \text{ kJ} \cdot \text{mol}^{-1}$) because the two points do not lie on the best straight line. This demonstrates the importance of considering as many experimental points as possible.

- b) What is the predicted rate constant for the reaction at 550 K?

We use Equation 10.10a, $k_1 = 1.8 \times 10^{-6} \text{ s}^{-1}$, $T_1 = 532$ K, and $T_2 = 550$ K to get k_2 .

$$\ln k_2 = \ln \left(\frac{9.5 \times 10^{-4}}{1.8 \times 10^{-6}}\right) (1.8 \times 10^{-6}) + \frac{2.7 \times 10^5}{8.314} \times \left(\frac{1}{532} - \frac{1}{550}\right) = -11.23$$

$$k_2 = e^{-11.23} = 1.3 \times 10^{-5} \text{ s}^{-1}$$

PRACTICE EXAMPLE 10.5

What is the activation energy of a reaction if its rate at 75°C is four times what it is at 25°C ?

10.6 CATALYSIS

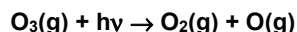
Catalysts increase the rate of reaction, but they are not changed by it. They function by altering the path (mechanism) of the reaction so as to reduce the activation energy. Catalysts increase the rates of both the forward and reverse reactions, but they do not affect the equilibrium constant; they increase the rate at which equilibrium is established, not the amount of product that is formed. By reducing the activation energy, catalysts also lower the temperature required for reaction. Catalysts can also be very specific, increasing the rate of desired reactions without affecting the rates of undesired reactions. **Enzymes** are very specialized catalysts used by biological organisms.

Catalysts are classified as either heterogeneous or homogeneous, depending on whether they are in a different phase or in the same phase as the reactants. In Section 14.5 of *CAMS*, we discussed the function of titanocene, a homogeneous catalyst for the hydrogenation of alkenes. We also examined the catalytic converter, a heterogeneous catalyst for the oxidation of molecules in automobile exhaust that have not been completely oxidized in the combustion of the gasoline. In this section, we use the catalytic

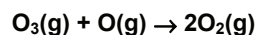
role of chlorofluorocarbons (CFC's) in the depletion of ozone in the stratosphere to explain the function of catalysts.

OZONE IN THE STRATOSPHERE

High energy ultraviolet (UV) light ($E = h\nu$) from the sun can damage living tissue because its energy is sufficient to break bonds in DNA, thus damaging genes. Fortunately, UV radiation is absorbed by ozone (O_3) in the stratosphere:



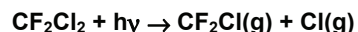
The oxygen atom produced can go on to react with another oxygen molecule to regenerate the ozone, which helps maintain the ozone level in the stratosphere. However, the oxygen atom can also react with an ozone molecule.



Rxn 10.1

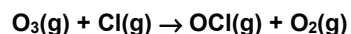
This reaction would deplete the ozone level, but it has a fairly high activation energy ($17 \text{ kJ}\cdot\text{mol}^{-1}$) and few collisions in the stratosphere result in reaction.

CFC's are used as air conditioner refrigerants and in the production of plastics. They are very stable and relatively unreactive. However, when they rise to the stratosphere, they can absorb high energy photons to produce chlorine atoms. Consider the (photochemical) reaction of CF_2Cl_2 , commonly referred to as Freon-12:



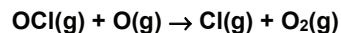
Rxn 10.2

The chlorine atoms can go on to catalyze the reaction shown in Reaction 10.1 by the mechanism discussed below, which has the energy diagram shown in Figure 10.10. The chlorine atom first attacks the ozone to form an OCl intermediate:*



Rxn 10.3

The activation energy for the reaction of chlorine atoms and ozone is only $2.1 \text{ kJ}\cdot\text{mol}^{-1}$ (E'_a in Figure 10.10), so it proceeds quite rapidly. The OCl is also very reactive and goes on to react with the atomic oxygen as shown in Reaction 10.4:



Rxn 10.4

Summing Reactions 10.3 and 10.4 yields Reaction 10.1 (Cl is a catalyst and OCl is an intermediate†). Note that the catalytic chlorine atom is unchanged by the reaction and is free to react with another ozone molecule. Thus, the presence of catalytic chlorine atoms lowers the activation energy for the reaction from $17 \text{ kJ}\cdot\text{mol}^{-1}$ down to $2 \text{ kJ}\cdot\text{mol}^{-1}$ and dramatically speeds the reaction. However, the catalyst does not affect the initial or final

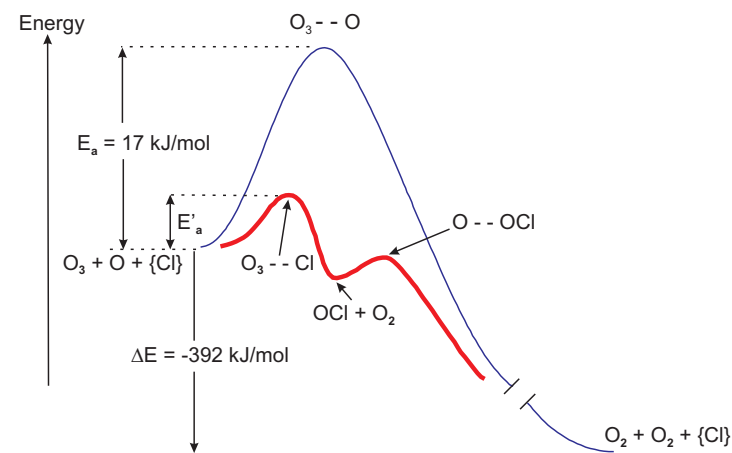


Figure 10.10 Energy diagram for $O_3(g) + O(g) \rightarrow 2O_2(g)$

Curves are in the absence (blue) and in the presence (red) of catalytic chlorine atoms. The activation energy E'_a is $2.1 \text{ kJ}\cdot\text{mol}^{-1}$. Note that OCl lies in a shallow well between the reactants and the products, which is typical of intermediates, while the transition states O_3-O , O_3-Cl , and $O-OCl$ all lie at peak maxima.

* There was considerable controversy about the catalytic action of chlorine atoms until high concentrations of OCl were detected in experiments carried on balloons over the South Pole. Observation of this intermediate strongly supported the proposed mechanism.

† Neither intermediates nor catalysts are in the net equation. An intermediate is produced and then consumed by the reaction, while a catalyst is a reactant from a different source that is also produced in the reaction. Thus, catalysts can appear in the rate law because they are reactants, but intermediates do not.

states, so it does not affect the thermodynamics and equilibrium constant of the reaction.

Figure 10.10 also demonstrates the difference between an intermediate and a transition state. The *energies of transition states (such as O_3-Cl , $O-OCl$, and O_3-O) lie at the peak maxima, while the energy of intermediates (such as OCl) lie in minima*. The slope is downhill in both directions for a transition state, so the transition state is simply passed through. The slope is uphill in both directions for an intermediate, so, if the well is deep enough, the intermediate can be isolated.

10.7 CHAPTER SUMMARY AND OBJECTIVES

Kinetics is the study of the rates and mechanisms of chemical reactions. The rate of formation of a product or disappearance of a reactant at a given time is defined as the rate of change in concentration of the substance per unit time. It is numerically equal to the slope of the tangent of the concentration versus time graph at the time in question. The rate of a reaction can be expressed in terms of its rate law. The rate law must be determined experimentally and is a function of a rate constant and the concentrations of the reactants each raised to some exponent. In this chapter, we considered only the case where the function consisted of a rate constant times the product of the concentrations of the reactants each raised to an experimentally determined exponent. The exponents are called the orders of the reactants, and the sum of the exponents is known as the order of the reaction.

Reaction orders can be determined by the method of initial rates or by analyzing the concentration versus time data. If a reaction is first order in a reactant, then a plot of the natural logarithm of the reactant concentration versus time is a straight line. The slope of the line is $-k$, the first-order rate constant. Of special importance is the time required for half of the reactant to disappear. This time is known as the half-life of the reaction, and it is equal to $0.693/k$. If a reaction is second order in a reactant, then a plot of the reciprocal of the reactant concentration versus time will be a straight line with a slope equal to the second-order rate constant.

Reactions proceed by a series of elementary reactions called the reaction mechanism. The molecularity of an elementary reaction is defined as the number of molecules involved in an elementary process. Elementary reactions can be unimolecular, bimolecular or termolecular depending on whether they involve one, two or three molecules, respectively. The rate of an elementary reaction is equal to the rate constant for that

process times the concentration of each reactant raised to an exponent equal to their coefficient in the elementary reaction. There is often one elementary reaction that is substantially slower than any others. The rate law of this rate-determining step then determines the rate law for the reaction. However, the rate-determining step often contains intermediates that are not in the experimental rate law. The concentrations of the intermediates are removed from the rate law by assuming that all steps prior to the rate-determining step have reached equilibrium. Thus, the experimentally determined rate constant of a reaction is often a mixture of rate constants and equilibrium constants of the elementary processes that comprise the reaction.

The rate of reaction depends not only on the concentrations of the reactants but also on a steric factor and the activation energy of the reaction. These two terms are incorporated into the rate constant in the Arrhenius equation: $k = Ae^{-E_a/RT}$. The activation energy can be determined by measuring the temperature dependence of the rate constant. A plot of $\ln k$ versus $1/T$ is called an Arrhenius plot and is a straight line with a slope of $-E_a/R$.

After studying the material presented in this chapter, you should be able to:

1. express the relative rates of consumption of reactants and formation of products from the coefficients in a balanced chemical reaction (Section 10.1);
2. determine the rate of a reaction given the rate law, the rate constant, and concentrations of reactants (Section 10.2);
3. determine the rate constant given the rate law, and a rate at a given set of concentrations (Section 10.2);
4. use the method of initial rates to determine the rate law of a reaction (Section 10.3);
5. use integrated first- and second-order rate laws to determine concentrations at any time or the time required to achieve a concentration (Section 10.3);
6. use half-life equations for a first-order reaction to determine $t_{1/2}$ from k or vice versa (Section 10.3);
7. determine the reaction orders from plots of concentration *versus* time data (Section 10.3);
8. identify the intermediates in a reaction mechanism and use an experimental rate law to identify the rate determining step (Section 10.4);
9. determine the molecularity of an elementary step (Section 10.4);
10. determine if a mechanism is consistent with the rate law (Section 10.4);
11. use the Arrhenius equation to solve for a variable (Section 10.5);
12. sketch a potential energy profile for a reaction and interpret it in either the forward or reverse direction (Section 10.5); and
13. explain how the addition of a catalyst affects the reaction rate (Section 10.6).

ANSWERS TO PRACTICE EXAMPLES

- 10.1 NH_3 : $0.64 \text{ M}\cdot\text{s}^{-1}$; O_2 : $0.48 \text{ M}\cdot\text{s}^{-1}$; H_2O : $0.96 \text{ M}\cdot\text{s}^{-1}$
 10.2 $R = (32.5 \text{ M}^{-2}\cdot\text{min}^{-1})[\text{NO}]^2[\text{H}_2]$
 10.3 78.1 minutes, 3.3 half-lives
 10.4 $R = k_1[\text{NO}]^2$; $R = k[\text{NO}_2]^2[\text{CO}][\text{NO}]^{-1}$
 10.5 $E_a = 24 \text{ kJ}\cdot\text{mol}^{-1}$

10.8 EXERCISES

REACTION RATES

1. Distinguish between kinetic and thermodynamic regions of a reaction.
2. How does an increase in pressure affect the rate of a gas-phase reaction? What effect on the rate would doubling the pressure of A in a reaction that is second order in A?
3. How does an increase in temperature affect the rate of reaction?
4. What is the reaction rate? How is the rate of disappearance of a reactant related to the rate of reaction?
5. Why does the rate of reaction decrease as the reaction proceeds?
6. Sketch the concentrations of X and Y versus time for the first order decomposition of X by the reaction $X \rightarrow 2Y$ with the following equilibrium constants. Label the thermodynamic and kinetic regions.

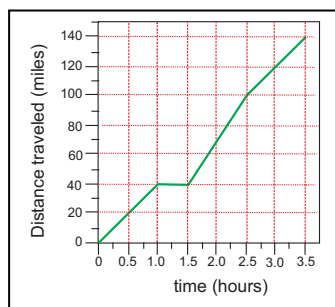
a) $K \gg 1$ b) $K < 1$

7. Distinguish between average and instantaneous rates of reaction.

8. Consider the following plot of distance traveled versus time:

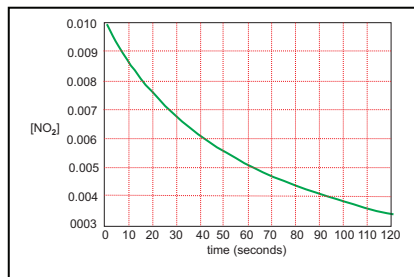
- a) What is the average speed of the trip?
- b) What is the instantaneous speed at the following times?

- i) 0.5 hr ii) 1.2 hr
- iii) 2.0 hr iv) 3.0 hr



9. Consider the following plot of $[\text{NO}_2]$ versus time.

- a) What is the average rate of disappearance of NO_2 over the time of the experiment?
- b) Use the graphical methods presented in Section 10.1 to determine the rate of disappearance of NO_2 at 20 seconds and 80 seconds.



10. What is the rate of consumption of oxygen in a combustion reaction carried out in a 10.0-L flask if 3.32 mmol of O_2 is consumed in 18.3 μs ?
11. What is the rate of formation ($\text{M}\cdot\text{s}^{-1}$) of NOBr gas in a reaction in which 13.4 μmol of NOBr is produced in a 38.9 mL-flask in 26.8 minutes?
12. Consider the following reaction: $3\text{O}_2(\text{g}) + 2\text{N}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_3(\text{g})$. By what factor must the rate of disappearance of N_2 be multiplied to obtain the following:
 - a) the rate of disappearance of O_2
 - b) the rate of formation of N_2O_3
 - c) the rate of the reaction
13. What are the rates of appearance of NO_2 and O_2 at a time when the rate of disappearance of N_2O_5 is $2.0 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}$?
 $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
14. The combustion of ammonia is the first step in the Ostwald process, which is used in the production of nitric acid.
 $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$

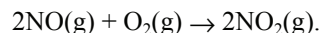
What is the rate of disappearance of ammonia and the rates of formation of nitric oxide and water at a time when the rate of consumption of oxygen is $2.5 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}$?

RATE LAWS

15. What is an exponential decay? What type of kinetics is characterized by an exponential decay?
16. A reaction has the experimentally determined rate law: $\text{rate} = k[\text{NO}_2][\text{F}_2]$. What is the reaction order? What is the order with respect to fluorine?
17. A reaction has the experimentally determined rate law: $\text{rate} = k[\text{A}][\text{B}]^2$. What is the reaction order? What is the order with respect to A and with respect to B?
18. The reaction of hydrogen with iodine monochloride to produce hydrogen chloride and iodine is first order in both hydrogen and iodine monochloride. Write the balanced chemical equation and the rate law.
19. The reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ is second order in NO_2 . What is the second-order rate constant if the rate of formation of O_2 is $5.0 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}$ when the concentration of NO_2 is 0.012 M?

DETERMINING RATE LAWS

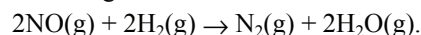
20. The following initial rates data were obtained for



Experiment	$[\text{NO}]_0$	$[\text{O}_2]_0$	$-(\Delta[\text{O}_2]/\Delta t)_0 \text{ M}\cdot\text{s}^{-1}$
I	0.0150	0.0100	0.0184
II	0.0300	0.0100	0.0738
III	0.0300	0.0300	0.2214

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

21. The following initial rate data were obtained for



Experiment	$[\text{NO}]_0$	$[\text{H}_2]_0$	$(\Delta[\text{N}_2]/\Delta t)_0 \text{ M}\cdot\text{s}^{-1}$
I	0.326	0.118	0.0859
II	0.109	0.118	0.00954
III	0.326	0.0295	0.0215

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

22. The reaction
- $5\text{Br}^{1-}(\text{aq}) + \text{BrO}_3^{1-}(\text{aq}) + 6\text{H}^{1+}(\text{aq}) \rightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
- has the following initial rates.

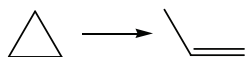
Exp	$[\text{Br}^{1-}]_0$	$[\text{BrO}_3^{1-}]_0$	$[\text{H}^{1+}]_0$	$(\Delta[\text{Br}^{1-}]/\Delta t)_0 \text{ M}\cdot\text{s}^{-1}$
I	0.10	0.10	0.10	6.8×10^{-4}
II	0.15	0.10	0.10	1.0×10^{-3}
III	0.10	0.20	0.10	1.4×10^{-3}
IV	0.10	0.10	0.25	4.3×10^{-3}

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

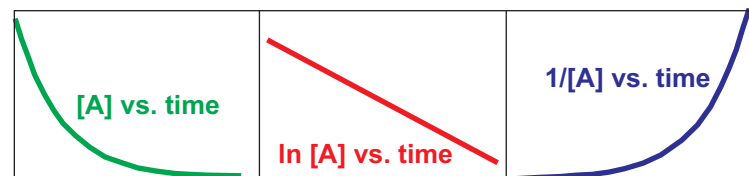
23. The kinetics of the conversion of cyclopropane to propene (see below) were studied at 500 °C by monitoring the concentration of cyclopropane versus time. The following data were obtained:

t	0	7.0	15.0	35.0	57.0	75.0	min
$[\Delta]$	0.256	0.193	0.140	0.0626	0.0259	0.0126	M

Verify the first-order kinetics and determine the rate constant and half-life of the reaction at 500 °C.



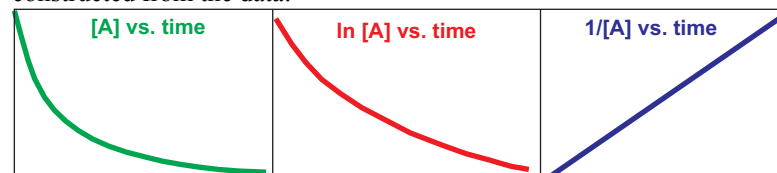
24. The kinetics of the reaction
- $3\text{A} \rightarrow \text{B}$
- was studied by monitoring the concentration of A as a function of time. The following graphs were constructed from the data:



- a) What is the rate law for the reaction?
 b) Given the following concentrations, determine the specific rate constant for the reaction at the temperature of the experiment.

t	0	1000	10000	s
[A]	0.100	0.0878	0.0273	M

25. The kinetics of the reaction
- $2\text{A} \rightarrow \text{C}$
- was studied by monitoring the concentration of A as a function of time. The following graphs were constructed from the data:



- a) What is the rate law for the reaction?
 b) Given the following concentrations, determine the specific rate constant for the reaction at the temperature of the experiment.

t	0	2.000	5.000	s
[A]	0.2600	0.0892	0.0450	M

26. Nitrosyl bromide decomposes by the reaction
- $2\text{NOBr}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$
- . Show that the following data are consistent with a second-order reaction and determine the second-order rate constant for the reaction.

t	0	5	15	25	30	35	s
$[\text{NOBr}]$	0.0652	0.0514	0.0361	0.0278	0.0249	0.0226	M

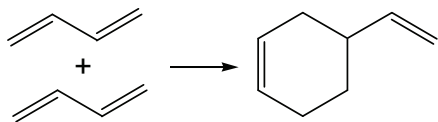
What is the rate law for the reaction and the value of the rate constant at the temperature of the experiment?

27. Explain how the rate of a reaction would change if the hydronium ion concentration were doubled and the reaction is

- a) First order in H^{1+} b) Second order in H^{1+}

28. Consider the first-order reaction $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$ at 500°C where its half-life is 21 minutes.
- How long does it take for the concentration of C_2H_6 to drop from 5.0 mM to 1.0 mM and from 1.0 mM to 0.2 mM?
 - If the original concentration of ethane is 5.0 mM, what is the concentration after 2.0 hours?
 - How long will it take for the reaction to be 95% complete?
29. Living organisms maintain a constant level of carbon-14, but upon death of the organism, the carbon-14 decays with first-order kinetics with a half-life of 5730 years. The decay is the basis of *carbon dating*. The carbon-14 level in a piece of charcoal at an archeological dig was found to be 62% of the constant level maintained by living organisms. Approximate the age of the charcoal.
30. The hydrolysis of sucrose to glucose and fructose is catalyzed by the enzyme sucrase. The hydrolysis is first order in sucrose with a half-life of 4.8×10^3 s at 20°C . What fraction of sucrose will be hydrolyzed after 3.0 hours? How long is required to hydrolyze 99% of the sucrose?
31. The gas-phase dimerization of butadiene (see below) was monitored at 326°C . Determine the order of the reaction and the rate constant at 326°C .

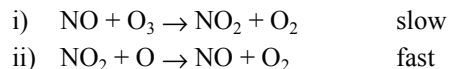
t	0	10.1	24.	49.5	90.1	135.7	min
$[\text{C}_4\text{H}_6]$	16.79	14.64	12.26	9.67	7.29	5.67	mM



REACTION MECHANISMS AND RATE LAWS

32. The rate law for the reaction $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ is $\text{rate} = k[\text{NO}_2]^2$. Is this reaction a single elementary reaction or does it occur by a more complicated mechanism? Explain.
33. Each of the following is an elementary reaction. Indicate the molecularity and write the rate law for each.
- $\text{I}_2 \rightarrow 2\text{I}$
 - $2\text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$
 - $\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I}$
 - $2\text{H}_2 \rightarrow 4\text{H}$
 - $\text{HO} + \text{H} \rightarrow \text{H}_2\text{O}$
 - $\text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl}$
34. Consider the following three-step mechanism:
- $2\text{A} \rightleftharpoons \text{B} + \text{C}$ fast
 - $\text{C} + \text{B} \rightarrow \text{D}$ slow
 - $\text{D} + \text{E} \rightarrow \text{F}$ fast
- What is the molecularity of each step?
 - Identify any intermediate(s).
 - What is the reaction?
 - What is the rate law?
35. Consider the following three-step mechanism:
- $\text{A} + \text{B} \rightleftharpoons \text{C}$ fast
 - $\text{D} + \text{C} \rightarrow \text{E}$ slow
 - $\text{E} + \text{F} \rightarrow \text{G} + \text{H}$ fast
- What is the molecularity of each step?
 - Identify any intermediate(s).
 - What is the reaction?
 - What is the rate law?
36. Consider the two-step mechanism below.
- $\text{I}_2 \rightarrow 2\text{I}$
 - $\text{H}_2 + 2\text{I} \rightarrow 2\text{HI}$
- What is the reaction?
 - Identify all intermediates.
 - What is the molecularity of each step?
 - Based on the mechanism, which step is more likely rate determining? Why?
 - What is the rate law if the first step is rate determining?
 - What is the rate law if the second step is rate determining and the previous step reaches equilibrium?
37. Consider the following two-step mechanism:
- $\text{NO}_2 + \text{Cl}_2 \rightarrow \text{NO}_2\text{Cl} + \text{Cl}$
 - $\text{Cl} + \text{NO}_2 \rightarrow \text{NO}_2\text{Cl}$
- Write the reaction.
 - What is the intermediate?
 - The first step is the rate-determining step. What is the rate law?

38. Nitrogen monoxide also catalyzes the depletion of ozone in the stratosphere by the two-step mechanism shown below:

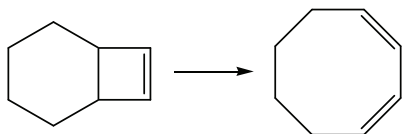


- a) What is the net reaction?
 b) What is the rate law for the reaction?
 c) If the activation energy for the first step is $11.9 \text{ kJ}\cdot\text{mol}^{-1}$, how does the rate of this reaction compare to that catalyzed by Cl? Refer to Figure 10.10.
39. Consider the two mechanisms shown below. The rate law for the reaction is $\text{rate} = k[\text{NO}_2]^2$. Which mechanism is *not* acceptable? Explain. What is the reaction and what is the rate-determining step?
- | | |
|--|---|
| Mechanism I | Mechanism II |
| $2\text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$ | $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ |
| $\text{NO}_3 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{OF}$ | $\text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F}$ |
| $\text{NO} + \text{OF} \rightarrow \text{NO}_2\text{F}$ | |
40. Consider the mechanisms shown below. The rate law for the reaction is $\text{rate} = k[\text{X}_2][\text{Y}]$. Which mechanism is acceptable? Explain. What is the reaction and what is the rate-determining step?
- | | | |
|--|--|--|
| Mechanism I | Mechanism II | Mechanism III |
| $\text{X}_2 + \text{Z} \rightarrow \text{XZ} + \text{X}$ | $\text{Y} + \text{Z} \rightarrow \text{YZ}$ | $\text{X}_2 + \text{Y} \rightarrow \text{XY} + \text{X}$ |
| $\text{X} + \text{Y} \rightarrow \text{XY}$ | $\text{YZ} + \text{X}_2 \rightarrow \text{XY} + \text{XZ}$ | $\text{X} + \text{Z} \rightarrow \text{XZ}$ |

EFFECT OF TEMPERATURE ON REACTION RATES

41. What is an Arrhenius plot? How is it used?
 42. What factors dictate the fraction of collisions that lead to the transition state? How are these factors incorporated into the rate law?
 43. The following rate constant data were obtained for the isomerization reaction shown below. What is the activation energy for the isomerization?

t (°C)	236	248	259	267	285
$10^4 \times k \text{ (s}^{-1}\text{)}$	0.376	1.08	2.44	4.61	16.6



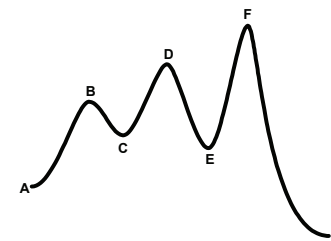
44. The first-order rate constant for the conversion of cyclopropane to propene at 800°C is $2.7 \times 10^{-3} \text{ s}^{-1}$. If the reaction has an activation energy of $274 \text{ kJ}\cdot\text{mol}^{-1}$, what is the rate constant at 900°C ?
 45. The rate constant for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is $4.3 \times 10^{-7} \text{ M}^{-1}\cdot\text{s}^{-1}$ at 500 K and 6.3×10^{-2} at 700 K . What is the activation energy for the reaction and what is the rate constant at 600 K ?

CATALYSIS

46. What is a catalyst? How does it function?
 47. Distinguish between a homogeneous catalyst and a heterogeneous catalyst.
 48. What effect does a catalyst have on the rate, the mechanism, the activation energy, and the equilibrium constant of a chemical process?
 49. What distinguishes a catalyst from an intermediate?

MISCELLANEOUS

50. Given the following reaction diagram indicate whether each labeled position is a reactant, a product, a transition state, or an intermediate. Which intermediate has the best chance of being isolated?



51. Consider the following three-step mechanism:
- $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ K_1 , rapid equilibrium
 - $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO}$ RDS
 - $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$ fast
- a) What is the reaction?
 b) What are the intermediates?
 c) What is the rate law?
52. Calculate the activation energy for $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ if the specific rate constant for the decomposition is $4.30 \times 10^{-5} \text{ s}^{-1}$ at $300. \text{ K}$ and $6.97 \times 10^2 \text{ s}^{-1}$ at $500. \text{ K}$. A plot of energy versus reaction coordinate for this reaction consists of several maxima and minima. To what process does this activation energy apply? See Exercise 51 for the mechanism.

CHAPTER 11

Nuclear Chemistry

11.0 Introduction

11.1 The Nucleus

11.2 Nuclear Reactions and Radioactivity

11.3 Kinetics of Radioactivity

11.4 Nuclear Radiation and Living Tissue

11.5 Nuclear Fission

11.6 Nuclear Fusion

11.7 Origin of the Heavy Elements

11.8 Chapter Summary and Objectives

11.9 Exercises

11.0 INTRODUCTION

Most of chemistry focuses on the changes in the electronic structure of the atoms and molecules because it is those changes that result in bond breaking and bond formation (*i.e.*, in chemical reactivity). In this chapter, we examine reactions that involve changes in the nucleus. This branch of chemistry is called **nuclear chemistry** or **radiochemistry**.

Most of us have a love-hate relationship with nuclear chemistry. Its promise of vast amounts of energy to replace fossil fuels and possible cures for diseases is exciting, but its threat of nuclear war and nuclear waste contamination is threatening. Is its promise worth the risk? The goal of this chapter is to give you a background that may help you answer that question.

THE OBJECTIVES OF THIS CHAPTER ARE TO DISCUSS

- balanced nuclear reactions;
- stable versus unstable nuclei;
- half-lives of radioactive substances;
- effects of nuclear radiation on the human body;
- conversion of mass and energy into one another;
- fission and fusion;
- nuclear power plants; and
- nuclear reactions in stars.

11.1 THE NUCLEUS

There are three major subatomic particles: electrons, protons and neutrons. Their masses and charges are summarized in Table 11.1. Notice that electrons and protons carry a net charge, but neutrons are neutral. Also, the mass of the neutron and the proton are each very close to 1 amu ($M_m \sim 1 \text{ g}\cdot\text{mol}^{-1}$) while the mass of an electron is much smaller. Because neutrons and protons reside within the nucleus, they are referred to as **nucleons**. The number of protons in the nucleus is given by the **atomic number, Z**, while the number of **nucleons** (protons plus neutrons) in the nucleus is given by the **mass number, A**. The symbol N_n will be used to denote the number of neutrons in the nucleus. Thus,

$$A = Z + N_n$$

Eq. 11.1

Equation 11.1 simply indicates that the total number of nucleons (A) is the sum of the number of protons (Z) and the number of neutrons (N_n). Because the mass of a neutron and a proton are each nearly equal to 1 amu, the mass number is the integer that is closest to the mass of the nucleus.

The atomic number is the number that characterizes the atom. Two atoms with different atomic numbers are atoms of different elements. Atoms of the same atomic number but with different mass numbers are called **isotopes**. Thus, isotopes differ in the number of neutrons in the nucleus. Isotopes are distinguished by indicating the mass number as a superscript in front of the symbol of the element. For example, ^{13}C (carbon-13), is an isotope of carbon that has seven neutrons ($N_n = A - Z = 13 - 6 = 7$). The atomic mass of ^{13}C is 13.003 amu. The atomic mass scale is based on the assignment of the mass of a carbon-12 atom (^{12}C), which is defined as *exactly* 12.00... amu. The reason that the atomic mass of carbon is 12.011 and not 12.000 is that the **atomic mass** of an element is the mass-weighted average of the masses of all of its naturally occurring isotopes. Naturally occurring carbon is a mixture containing 98.9 % ^{12}C and 1.1% ^{13}C , so a mole of carbon contains 0.989 mol ^{12}C and 0.011 mol ^{13}C and has a mass of

$$(0.989 \text{ mol } ^{12}\text{C})(12.000 \text{ g}\cdot\text{mol}^{-1}) + (0.011 \text{ mol } ^{13}\text{C})(13.003 \text{ g}\cdot\text{mol}^{-1}) = 12.011 \text{ g}$$

Example 11.1 shows why the molar mass of magnesium is $24.31 \text{ g}\cdot\text{mol}^{-1}$.

Table 11.1 The major subatomic particles

Particle	Mass (amu) ^a	Charge ^b
electron	5.49×10^{-4}	-1
proton	1.00728	+1
neutron	1.00867	0

a) An amu is an atomic mass unit. The mass of a nucleus in amu is numerically equal to the mass of a mole of nuclei in grams.

b) The charge is given in terms of the fundamental unit of charge, $1.60 \times 10^{-16} \text{ C}$.

Example 11.1

Naturally occurring magnesium exists as a mixture of three isotopes. Determine the atomic mass of magnesium given the masses and abundances of the three isotopes.

Isotope	Mass	Abundance
^{24}Mg	23.9850	78.70 %
^{25}Mg	24.9858	10.13 %
^{26}Mg	25.9826	11.17 %

One mole of magnesium contains 0.7870 mol of ^{24}Mg , 0.1013 mol of ^{25}Mg and 0.1117 mol of ^{26}Mg . One mole therefore contains

$$(0.7870 \text{ mol } ^{24}\text{Mg})(23.9850 \text{ g}\cdot\text{mol}^{-1}) = 18.88 \text{ g } ^{24}\text{Mg}$$

$$(0.1013 \text{ mol } ^{25}\text{Mg})(24.9858 \text{ g}\cdot\text{mol}^{-1}) = 2.53 \text{ g } ^{25}\text{Mg}$$

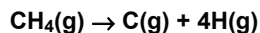
$$(0.1117 \text{ mol } ^{26}\text{Mg})(25.9826 \text{ g}\cdot\text{mol}^{-1}) = 2.90 \text{ g } ^{26}\text{Mg}$$

$$\text{total mass of one mole of Mg} = 24.31 \text{ g Mg}$$

The molar mass of magnesium is $24.31 \text{ g}\cdot\text{mol}^{-1}$.

NUCLEAR STABILITY

How stable one nucleus is compared to another is an important consideration in nuclear reactions, and we now address the manner in which relative nuclear stabilities are measured. We do so by analogy with molecular stability. An atomization enthalpy (Section 3.8) is the energy required to breakdown a molecule into its atoms; that is, to break all of the bonds in a molecule. Consequently, the atomization enthalpy depends upon both the number and the strength of the bonds. For example, the enthalpy of atomization (ΔH_{atom}) of methane is the enthalpy change for the following process:



$$\Delta H_{\text{atom}} = 1.66 \times 10^3 \text{ kJ}$$

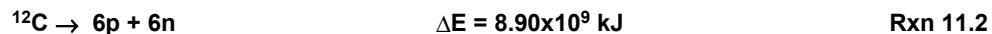
Rxn 11.1

The process involves breaking four C-H bonds. However, a molecule needs only one weak bond to become unstable, so molecular stability is related to the strength of individual bonds not the total energy required to break all of the bonds. In the case of CH_4 , the average C-H bond energy ($D_{\text{C-H}}$) is the atomization energy divided by the number of C-H bonds.

$$D_{\text{C-H}} = \frac{\Delta H_{\text{atom}}}{\text{number of C-H bonds}} = \frac{1.66 \times 10^3 \text{ kJ}}{4 \text{ mol CH bonds}} = 415 \text{ kJ}\cdot\text{mol}^{-1}$$

The bonds in CH_4 have high bond energies, which makes CH_4 a stable molecule.

Nuclear stability is measured in a similar manner. First, the **binding energy** of the nucleus (the energy required to separate the nucleus into its nucleons) is determined. The binding energy of a ^{12}C nucleus is the energy change for the following process:



Just as it is the energy per bond not the atomization energy of a molecule that dictates its stability, it is the energy per nucleon not the binding energy that dictates the stability of a nucleus. The binding energy per nucleon of a ^{12}C nucleus is

$$\frac{\text{nuclear binding energy}}{\text{number of nucleons}} = \frac{8.90 \times 10^9 \text{ kJ} \cdot \text{mol}^{-1}}{12 \text{ nucleons}} = 7.42 \times 10^8 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{nucleon}^{-1}$$

Figure 11.1 shows that the binding energy per nucleon* (nuclear stability) reaches a maximum for nuclei with mass numbers in the range of 50 - 60. Thus, nuclei with mass numbers close to that of iron ($A = 56$) are thermodynamically the most stable nuclei.

To understand the origin of the binding energy, we examine the nuclear mass in detail. The mass of a ^{12}C nucleus is the mass of the atom (exactly 12 amu) less the mass of the six electrons.

$$\text{mass of } ^{12}\text{C} \text{ nucleus} = 12.00000 - 6(0.000549) = 11.9967 \text{ amu}$$

The nucleons of a ^{12}C nucleus, six protons (p) and six neutrons (n), have a mass of

$$\text{mass of nucleons} = (6\text{p})(1.00728 \text{ amu} \cdot \text{p}^{-1}) + (6\text{n})(1.00867 \text{ amu} \cdot \text{n}^{-1}) = 12.0957 \text{ amu}$$

Consequently, the mass of the nucleus is less than the mass of its nucleons; that is, mass is not conserved in Reaction 11.2. The mass difference is called the **mass defect**, Δm .

$$\Delta m = \text{final mass} - \text{initial mass} = \text{mass of product} - \text{mass of reactant} \quad \text{Eq. 11.2}$$

The mass defect for Reaction 11.2, which is the mass defect of a ^{12}C nucleus, is

$$\Delta m = \text{mass of nucleons} - \text{mass of nucleus} = 12.0957 - 11.9967 = 0.0990 \text{ amu}$$

The mass defect for a ^{12}C nucleus is $0.0990 \text{ g} \cdot \text{mol}^{-1}$ or $9.90 \times 10^{-5} \text{ kg} \cdot \text{mol}^{-1}$.

The origin of mass defect can be understood in terms of Einstein's famous equation that relates mass and energy.

$$E = mc^2 \quad \text{Eq. 11.3}$$

Or, in terms of changes in energy due to changes in mass:

$$\Delta E = \Delta mc^2 \quad \text{Eq. 11.4}$$

* There is no general agreement on the sign convention for binding energy. Indeed, most general chemistry books define the binding energy as the energy change for the reverse process and report it as a negative value. We choose the convention above to be consistent with atomization and bond energies, which are always positive and define the same type of processes.

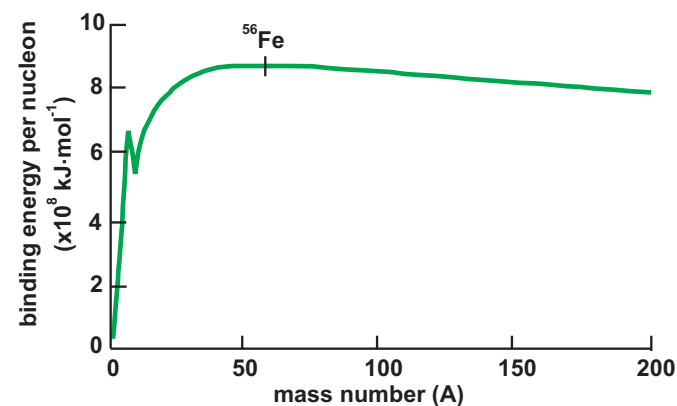


Figure 11.1 Binding Energy per nucleon versus mass number

A nucleus of ^{56}Fe has the highest energy per nucleon, so it is the most stable nucleus.

Equations 11.3 and 11.4 show the equivalence of mass and energy, and the term **mass-energy** is sometimes used to express the equivalence. Indeed the law of conservation of mass and the law of conservation of energy are combined into the law of conservation of mass-energy: the total mass-energy of the universe is constant.

The binding energy of a nucleus is determined from its mass defect and the application of Equation 11.4. A joule is a $\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$, so, in order to obtain ΔE in joules, Δm *must be expressed in kg*. The speed of light is $c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$.

Example 11.2

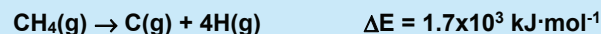
What is the binding energy of a ^{12}C nucleus?

The mass defect for ^{12}C was determined in the preceding discussion to be $\Delta m = 0.0990$ amu. An amu is numerically equal to the molar mass expressed in grams, so we can also write that $\Delta m = 0.0990 \text{ g}\cdot\text{mol}^{-1} = 9.90 \times 10^{-5} \text{ kg}\cdot\text{mol}^{-1}$. Applying Equation 11.4, we obtain the binding energy.

$$\Delta E = \Delta mc^2 = (9.90 \times 10^{-5} \text{ kg}\cdot\text{mol}^{-1})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})^2 = 8.90 \times 10^{12} \text{ J}\cdot\text{mol}^{-1}$$

Example 11.3

What is the mass defect for the atomization of CH_4 ?



The energy change of the reaction must be converted to a mass defect, so we apply Equation 11.4.

$$\Delta m = \frac{\Delta E}{c^2} = \frac{1.7 \times 10^6 \text{ J}\cdot\text{mol}^{-1}}{(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})^2} = 1.9 \times 10^{-11} \text{ kg}\cdot\text{mol}^{-1} = 1.9 \times 10^{-8} \text{ g}\cdot\text{mol}^{-1}$$

The mass defect for this reaction is negligible because it is far less than can be measured on a laboratory balance. Indeed, the mass defects for all chemical reactions are negligible, which is the reason that the law of conservation of mass states that mass is conserved in *chemical reactions*. It is really an approximation, but it is a very good one for chemical reactions.

Example 11.4

Show that a ^{56}Fe nucleus is thermodynamically favored over a ^{209}Bi nucleus. The atomic masses are: $^{56}\text{Fe} = 55.9349$ and $^{209}\text{Bi} = 208.9804$

The more stable nucleus is the one with the greater binding energy per nucleon, so we must first determine the number of protons and neutrons present in each nucleus from the periodic table.

$Z_{\text{Fe}} = 26$ and $Z_{\text{Bi}} = 83$ protons

The number of neutrons in each nucleus is then obtained by subtraction.

$N_{\text{Fe}} = A_{\text{Fe}} - Z_{\text{Fe}} = 56 - 26 = 30$ neutrons

$N_{\text{Bi}} = A_{\text{Bi}} - Z_{\text{Bi}} = 209 - 83 = 126$ neutrons

Next, determine the mass defect and then use Equation 11.4 to obtain the binding energy. Finally, divide the binding energy by the number of nucleons (A) to get the binding energy per nucleon.

^{56}Fe

$$m_{\text{nucleus}} = m_{\text{atom}} - m_{\text{electrons}} = 55.9349 - 26(0.000549) = 55.9206 \text{ g}\cdot\text{mol}^{-1}$$

$$m_{\text{nucleons}} = m_{\text{protons}} + m_{\text{neutrons}} = 26(1.00728) + 30(1.00867) = 56.4494 \text{ g}\cdot\text{mol}^{-1}$$

$$\Delta m = m_{\text{nucleons}} - m_{\text{nucleus}} = 56.4494 - 55.9206 = 0.5288 \text{ g}\cdot\text{mol}^{-1} = 5.285 \times 10^{-4} \text{ kg}\cdot\text{mol}^{-1}$$

$$\Delta E = mc^2 = (5.285 \times 10^{-4} \text{ kg}\cdot\text{mol}^{-1})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})^2 = 4.750 \times 10^{13} \text{ J}\cdot\text{mol}^{-1}$$

$$\frac{\Delta E}{A} = \frac{4.750 \times 10^{13} \text{ J}\cdot\text{mol}^{-1}}{56 \text{ nucleons}} = 8.482 \times 10^{11} \text{ J}\cdot\text{mol}^{-1} \cdot \text{nucleon}^{-1}$$

^{209}Bi

$$m_{\text{nucleus}} = m_{\text{atom}} - m_{\text{electrons}} = 208.9804 - 83(0.000549) = 208.9348 \text{ g}\cdot\text{mol}^{-1}$$

$$m_{\text{nucleons}} = m_{\text{protons}} + m_{\text{neutrons}} = 83(1.00728) + 126(1.00867) = 210.6967 \text{ g}\cdot\text{mol}^{-1}$$

$$\Delta m = 210.6967 - 208.9348 = 1.7619 \text{ g}\cdot\text{mol}^{-1} = 1.7619 \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$$

$$\Delta E = mc^2 = (1.7619 \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})^2 = 1.5836 \times 10^{14} \text{ J}\cdot\text{mol}^{-1}$$

$$\frac{\Delta E}{A} = \frac{1.5836 \times 10^{14} \text{ J}\cdot\text{mol}^{-1}}{209 \text{ nucleons}} = 7.5770 \times 10^{11} \text{ J}\cdot\text{mol}^{-1} \cdot \text{nucleon}^{-1}$$

Although the total binding energy of ^{209}Bi is greater than that of ^{56}Fe , the binding energy per nucleon is greater for the ^{56}Fe nucleus. Consequently, the ^{56}Fe nucleus is thermodynamically favored.

PRACTICE EXAMPLE 11.1

Determine the binding energy per nucleon for a ^{64}Zn nucleus (atomic mass = 63.9291).

mass of protons:

mass of neutrons:

mass of nucleus:

mass defect:

binding energy:

binding energy per nucleon:

11.2 NUCLEAR REACTIONS AND RADIOACTIVITY

In Example 11.4, we showed that ^{56}Fe is thermodynamically favored over ^{209}Bi , but both nuclei are stable. Indeed, most nuclei found in nature are stable. Nuclei that are not stable are said to be **radioactive**. Radioactive nuclei spontaneously emit particles and electromagnetic radiation to change into other more stable nuclei. Radioactive nuclei are also called **radioisotopes**. All of the first 83 elements except technetium ($Z = 43$) have at least one stable nucleus. However, the ^{209}Bi nucleus is the heaviest stable nucleus. Furthermore, many of the elements that have stable nuclei also have radioisotopes. In this section, we examine the different types of radioactive decay and present some observations that help us predict the mode of decay that a particular radioisotope is likely to undergo. We begin with a discussion about how nuclear reactions are written.

WRITING NUCLEAR REACTIONS

The atomic number (Z) is the number that characterizes an element. If a nucleus contains 17 protons, then it is the nucleus of a chlorine atom. The symbol Cl means $Z = 17$ and *vice versa*. Thus, there is little reason to include both the atomic number and the symbol of an element. We include the mass number when referring to a specific isotope (*e.g.*, chlorine-35 is ^{35}Cl), but we do not usually include the atomic number. However, as in chemical reactions, nuclear reactions involve balancing both mass and charge. In a chemical reaction, the charge is given explicitly on each ion, but in a nuclear reaction, the charge is the charge on the nucleus, and that is given by the atomic number. Thus, the atomic number is included with the symbol in nuclear reactions to aid in charge balance. The element with the symbol X, a mass number A, and an atomic number Z is represented as ^A_ZX . For example, the two isotopes of chlorine are $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$.

Table 11.2 lists the names and symbols of several small particles that are encountered in nuclear reactions. A neutron is represented as ^1_0n because it has a mass number of 1 but carries no charge. A proton is ^1_1p , which indicates a mass number of 1 and a +1 charge. An electron has a mass number of zero and a charge of -1, so its symbol is $^0_{-1}\text{e}$. An electron is also called a β (beta) particle and is often represented as $^0_{-1}\beta$ or simply β^- . A **positron** has the same mass as the electron, but it is positively charged. It is represented as $^0_{+1}\beta$ or $^0_{+1}\text{e}$ or simply β^+ . An **alpha particle** ($\alpha = ^4_2\alpha = ^4_2\text{He}$) is a helium-4 nucleus.

Table 11.2 Common particles in nuclear reactions

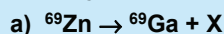
Particle	Second name	Symbol
proton		^1_1p
neutron		^1_0n
electron	beta particle	$^0_{-1}\text{e} = ^0_{-1}\beta = \beta^-$
positron		$^0_{+1}\text{e} = ^0_{+1}\beta = \beta^+$
helium nucleus	alpha particle	$^4_2\text{He} = ^4_2\alpha = \alpha$

Like chemical equations, nuclear equations are balanced so as to conserve both mass and charge. However, in nuclear equations, mass is given by the mass numbers and charge by the atomic numbers. Thus, a balanced nuclear equation must have both

- **charge balance:** the sum of the atomic numbers (Z) of the products must equal the sum of the atomic numbers of the reactants; i.e., $\sum Z(\text{products}) = \sum Z(\text{reactants})$, and
- **mass balance:** the sum of the atomic masses of the products must equal the sum of the atomic masses of the reactants; i.e., $\sum A(\text{products}) = \sum A(\text{reactants})$.

Example 11.5

Identify the unknown particle, X, in each of the following reactions.

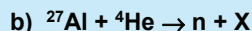


First, rewrite the reactions to include the atomic numbers: ${}_{30}^{69}\text{Zn} \rightarrow {}_{31}^{69}\text{Ga} + {}_Z^AX$

Then apply charge balance to obtain Z: $30 = 31 + Z \Rightarrow Z = 30 - 31 = -1$

and mass balance to obtain A: $69 = 69 + A \Rightarrow A = 0$.

The particle with a mass number of zero and -1 charge is the electron, ${}_{-1}^0\text{e}$ or β^- .



Rewriting with atomic numbers, we obtain ${}_{13}^{27}\text{Al} + {}_2^4\text{He} \rightarrow {}_0^1\text{n} + {}_Z^AX$

Applying charge balance, we obtain Z. $13 + 2 = 0 + Z \Rightarrow Z = 15$.

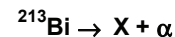
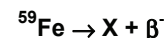
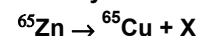
An atomic number of 15 indicates that the particle is a phosphorus nucleus.

Apply mass balance to obtain A. $27 + 4 = 1 + A \Rightarrow A = 27 + 4 - 1 = 30$

The particle is ${}^{30}\text{P}$.

PRACTICE EXAMPLE 11.2

Identify X in each of the following:



TRENDS IN NUCLEAR STABILITY

Nuclear forces are not understood well enough to allow us to predict whether a nucleus is stable or not. However, we present two empirical observations about nuclear stability that indicate the importance of the neutron to proton ratio and the size of the nucleus.

Neutron/proton ratios: Neutrons play an important role in holding the nucleus together, and every stable nucleus (except ${}^1\text{H}$ and ${}^3\text{He}$) contains at least one neutron per proton. Figure 11.2 shows the number of protons and neutrons in the stable nuclei. The relative number of protons and neutrons in the stable nuclei lie in a narrow band, referred to as the **band** or **belt of stability**. Only one neutron per proton is sufficient for the lighter elements. However, the number of neutrons exceeds the number of protons in the stable

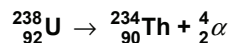
nuclei of the larger elements. Thus, the neutron/proton ratio remains near one through the third period ($Z = 18$) then it begins to rise reaching a maximum of 1.52 for $^{209}_{83}\text{Bi}$ ($\frac{N}{Z} = \frac{209-83}{83}$), the heaviest stable nucleus.

Total number of protons: There are no stable nuclei with atomic numbers greater than 83. All elements with $Z > 83$ are radioactive.

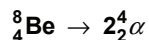
TYPES OF DECAY

We now consider how an unstable nucleus decays to a stable one. The decay pathway may involve many steps, but each step involves either the emission of one of three particles (α , β^- , or β^+) or the capture of an electron. The decay of an unstable nucleus to a more stable nucleus is an exothermic process, and the energy released in the decay is often carried away by the emitted particle; but, if the energy release is large, much of the energy is released in the form of gamma rays. γ -ray photons, which are represented as $^0_0\gamma$ or simply γ , do not enter into charge or mass balance considerations; they simply represent energy released in the process. In nuclear decay reactions, the decaying nucleus is referred to as the **parent** and the produced nucleus as the **daughter**. Refer to Figure 11.2 for the regions expected for each type of decay.

Alpha decay is the loss of an alpha particle. The loss reduces the mass number by four and the atomic number by two. *Alpha decay is the most common mode of decay for the heavy nuclei* because the alpha particle is the most massive particle of the common decay particles. ^{238}U undergoes α -decay to ^{234}Th :



α -decay is not limited to heavier nuclei, but it is found in only a few of the lighter elements. ^8Be is the lightest element to undergo alpha decay.



Beta decay is the ejection of an electron *by the nucleus*. It results in an increase of one in the atomic number. The electron that is emitted is produced by the disintegration of a neutron, $^1_0\text{n} \rightarrow ^1_1\text{p} + ^0_{-1}\text{e}$. Because β -decay results from the conversion of a neutron into a proton, it decreases the neutron/proton ratio. As such, *β -decay is the common mode of decay for those nuclei lying above the belt of stability*. For example, the neutron/proton ratio of ^{14}C is $8/6 = 1.3$, which is well above the value of 1.0 found for stable nuclei of the

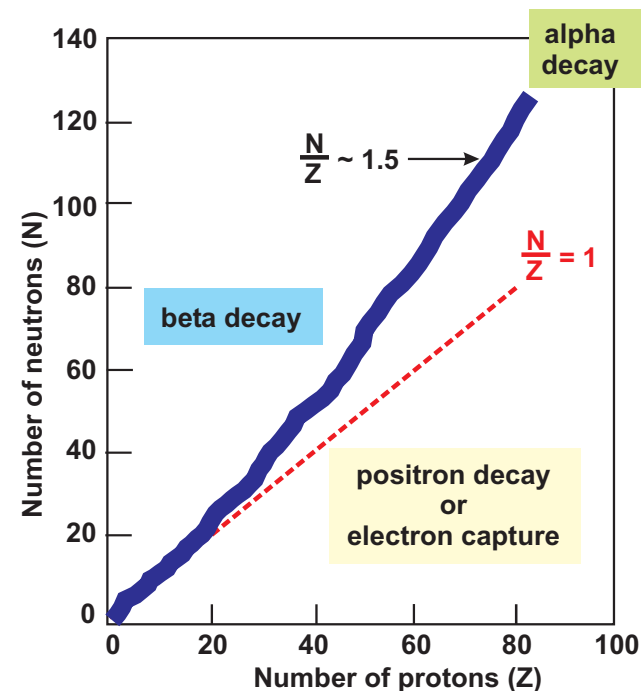
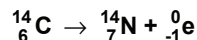


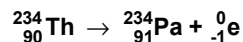
Figure 11.2 N/Z ratios for the stable nuclei

The $N/Z = 1$ line is shown for comparison. The expected modes of decay is given in each region.

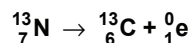
first three periods. Consequently ^{14}C undergoes β -decay to a stable ^{14}N nucleus with $N_n/Z = 7/7 = 1.0$.



α -decay, the most common decay among the heavy elements, is the loss of two protons and two neutrons, which increases N_n/Z slightly. Thus, successive α -decays produce isotopes with unfavorable N_n/Z ratios. Consequently, some heavy nuclei formed by α -decay undergo β -decay in order to maintain $N_n/Z \sim 1.5$. ^{234}Th , formed from the α -decay of ^{238}U , is a heavy nucleus and might be expected to undergo α -decay, but it also has a very high neutron/proton ratio of $(234-90)/90 = 1.60$. *Reducing a high neutron/proton ratio is usually favored over reducing the mass in heavy nuclei.* Consequently, ^{234}Th undergoes β -decay to ^{234}Pa , which has an N_n/Z ratio 1.57.

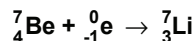


Positron decay is the emission of a positron. It has the opposite effect of β -decay. That is, positron decay converts a proton into a neutron ($^1_1\text{p} \rightarrow ^1_0\text{n} + ^0_{+1}\text{e}$), which reduces the atomic number by one. As a result, *positron emission is a common mode of decay for nuclei below the belt of stability.* Positron emission of ^{13}N produces ^{13}C , which results in an increase of N_n/Z from 0.86 to 1.2.



A positron is the **antimatter** analog of the electron because it is identical to the electron in every respect except charge. Occasionally, the emitted positron collides with an orbital electron. The collision results in the annihilation of the two antiparticles (*i.e.*, the particles disappear as their mass is converted to energy: $\beta^- + \beta^+ \rightarrow \gamma$).

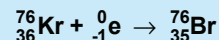
The last mode of decay we consider is **electron capture (EC)**, the capture by the nucleus of an electron from an inner-shell orbital. EC, like positron emission, increases the neutron/proton ratio by converting a proton into a neutron, $^1_1\text{p} + ^0_{-1}\text{e} \rightarrow ^1_0\text{n}$. It is a common decay used by nuclei below the belt of stability. For example, ^7Be ($N_n/Z = 0.75$) undergoes electron capture to become ^7Li ($N_n/Z = 1.3$).



Example 11.6

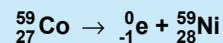
- a) The most abundant isotope of krypton is ^{84}Kr . Predict the mode of decay of the radioactive nucleus ^{76}Kr and write the nuclear reaction for the decay.

The atomic number of krypton is 36. $N_n/Z = 1.33$ for the stable isotope and 1.11 for the unstable isotope. Thus, N_n/Z is low for ^{76}Kr , so a proton must be converted into a neutron. This can be accomplished by either electron capture or positron emission. We cannot predict more than that with only the guidelines given above. However, ^{76}Kr undergoes electron capture, and the reaction is



- b) Cobalt occurs naturally as ^{59}Co . Predict the mode of decay of the radioisotope ^{62}Co .

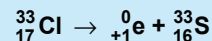
The atomic number of cobalt is 27. The naturally occurring isotope contains 32 neutrons ($59 - 27$), so $N_n/Z = 32/27 = 1.19$. ^{62}Co contains 35 protons, so $N_n/Z = 1.30$ for the unstable isotope. Thus, the N_n/Z ratio is high for ^{62}Co , and β^- decay is predicted. The decay process is



The product, ^{62}Ni , has a neutron/proton ratio of $31/28 = 1.11$ and is stable.

- c) Identify the particle emitted by a chlorine-33 nucleus.

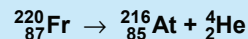
The neutron/proton ratio for this second-period nucleus is $16/17 = 0.94$, which is less than the stable value of 1.0, so we predict either electron capture or positron emission. The particle is emitted, so it must be a positron.



The product of the positron emission is ^{33}S , a stable isotope.

- d) Predict the mode of decay of ^{220}Fr and write the nuclear reaction.

The atomic number exceeds 83, so α -decay is a possibility. However, we first check the neutron/proton ratio. $N_n/Z = (220 - 87)/87 = 1.53$, which is fairly close to the stable ratio of ~ 1.55 for large nuclei. Consequently, α -decay is the predicted mode of decay.



PRACTICE EXAMPLE 11.3

^{56}Fe is the most abundant isotope of iron. Predict the mode of decay of ^{59}Fe and write the decay equation.

$$Z = \quad N_n(^{56}\text{Fe}) = \quad N_n(^{59}\text{Fe}) = \quad$$

$$N_n/Z \text{ for } ^{56}\text{Fe} =$$

$$N_n/Z \text{ for } ^{59}\text{Fe} =$$

mode of decay expected is _____ decay

Decay Equation: _____

What particle is emitted by ^{58}Cu ? What stable nucleus results?

molar mass of copper = _____

Based on the molar mass of copper, does a ^{58}Cu nucleus contain too many or too few neutrons?

The predicted mode of decay is _____ decay.

Decay Equation: _____

What particle is emitted by ^{221}Ra ?

$$Z = \quad N_n = \quad N_n/Z = \quad$$

The likely mode of decay is _____ decay.

Decay Equation: _____

11.3 KINETICS OF RADIOACTIVITY

Radioactive decay is unimolecular, so it follows first-order kinetics as discussed in Section 10.4. One form of the integrated rate law for first-order kinetics was given in Equation 10.4b as the following:

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

[A] is the concentration of the radioisotope at time t , and $[A]_0$ is the radioisotope concentration at the beginning of the experiment. The concentrations can be expressed as the number of moles (n) divided by the volume (V).

$$\ln \left(\frac{n/V}{n_0/V} \right) = -kt$$

The volumes in the above equation are identical and cancel. Furthermore, the ratio of moles of nuclei equals the ratio of their masses because the molar masses also cancel in the ratio. Making these two substitutions yields Equation 11.5,

$$\ln \left(\frac{n}{n_0} \right) = \ln \left(\frac{m}{m_0} \right) = -kt \quad \text{Eq. 11.5}$$

where n is the number of moles of radioactive nuclei and m is its mass at time t . Equation 11.5 is the rate law for radioactive decay. It can be expressed without logarithms as shown in Equation 11.6.

$$n = n_0 e^{-kt} \quad \text{Eq. 11.6}$$

The rate constants for radioactive decays are most frequently given in terms of the half-life as given in Equation 10.6 and reproduced below.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Example 11.7

- a) **Magnesium-23 undergoes positron decay. What is the product of the decay, and what is its half-life if 17.9% of the ^{23}Mg remained in a sample after 30.0 seconds?**

We represent the decay as $^{23}_{12}\text{Mg} \rightarrow {}^A_Z\text{X} + {}^0_1\text{e}^+$. Balancing charge, we determine that for Na, $Z = 11$. Mass balance indicates that $A = 23$. Thus, the decay can be written as $^{23}_{12}\text{Mg} \rightarrow ^{23}_{11}\text{Na} + {}^0_1\text{e}^+$.

We now use Equation 11.5 to obtain the rate constant. We are told that $N/N_0 = 0.179$ when $t = 30.0$, so we may write the following:

$$\ln 0.179 = -k(30.0 \text{ s}) \Rightarrow k = -\frac{\ln 0.179}{30.0 \text{ s}} = 0.0573 \text{ s}^{-1}$$

We can now use this rate constant and Equation 10.6 to determine the half-life.

$$t_{1/2} = \frac{0.693}{0.0573 \text{ s}^{-1}} = 12.1 \text{ s}$$

Every 12.1 seconds half of a ^{23}Mg sample decays no matter how large the sample is.

b) How long would it take for 99.9% of the ^{23}Mg to disintegrate?

We now know the rate constant and are asked for the time at which n/n_0 reaches a particular value. We again apply Equation 11.5. A common mistake in a problem like this is to substitute the given fraction for n/n_0 . However, n/n_0 is the fraction remaining, not the fraction disintegrating. We use the fact that the fraction remaining is equal to one minus the fraction disintegrating.

$$\frac{n}{n_0} = 1.000 - 0.999 = 0.001$$

We use the preceding value in Equation 11.5 along with the rate constant determined in Part A to obtain the following.

$$\ln 0.001 = -(0.0573 \text{ s}^{-1})t \Rightarrow t = -\frac{\ln 0.001}{0.0573 \text{ s}^{-1}} = 120 \text{ s}$$

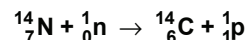
Thus, it would take only 2 minutes for 99.9% of this isotope to disappear.

RADIOACTIVE DATING

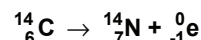
Radioactive dating is the process of determining the age of an object from its radioactive components. It is based on Equation 11.5, which indicates that the time required for some known initial amount of radioisotope to decay to another known amount can be determined if the rate constant (half-life) for the decay is known. Determining the amount of radioisotope present in the object today is straightforward, and we outline the approximations used in two techniques to obtain the initial amounts. One technique is used for historical time scales and the other for geological time scales.

Historical ages are frequently determined with carbon-14 dating, which is based on the fact that there is a constant exchange of carbon containing compounds between living organisms and the atmosphere. Atmospheric CO_2 is used in photosynthesis to produce

organic compounds that are ingested by animals, and the carbon that was in the CO_2 becomes incorporated into the compounds in the organism. The organism returns some of the carbon back to the atmosphere in the form of CO_2 to continue the cycle. A small fraction of the carbon is in the form of radioactive ^{14}C , which is formed in the upper atmosphere by the following reaction:



^{14}C then undergoes β -decay with a half-life of 5730 years ($k = \frac{\ln 2}{5730 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$).



The two competing processes have resulted in an equilibrium ^{14}C : ^{12}C ratio of $1:10^{12}$ in the atmosphere. This ratio is also maintained in all living organisms and results in a ^{14}C radioactivity of 15.3 disintegrations per minute per gram of carbon ($\text{d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$). However, when the organism dies, it no longer replaces the decaying ^{14}C , and the disintegration rate drops. As shown in Example 11.8, the age of material can be estimated by measuring the rate of ^{14}C disintegration and assuming that the rate has remained constant.

Example 11.8

A piece of charred bone found in the ruins of an American Indian village has a ^{14}C disintegration rate of $9.2 \text{ d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. What is the approximate age of the bone?

We assume that, when the organism died, the disintegration rate was $15.3 \text{ d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$, so n/n_0 is determined as follows:

$$\frac{n}{n_0} = \frac{9.2}{15.3} = 0.60$$

Use this ratio and the known rate constant for ^{14}C decay ($k = 1.21 \times 10^{-4} \text{ yr}^{-1}$) in Equation 11.5 to determine how many years have passed since the animal died.

$$\ln 0.60 = -(1.21 \times 10^{-4} \text{ yr}^{-1})t \Rightarrow t = -\frac{\ln 0.60}{1.21 \times 10^{-4} \text{ yr}^{-1}} = 4.2 \times 10^3 \text{ yr}$$

The bone belonged to an animal that died over four thousand years ago.

Carbon dating can be used to estimate the age of materials that are up to 50,000 years old. The rate of decay for older objects is too slow to be measured. Thus, when a geological age is required, a radioisotope with a much longer half-life must be used. One method used to determine the age of rocks is based on the decay of ^{238}U to ^{206}Pb , a process with a half-life of 4.5×10^9 (4.5 billion) years. In this method, it is assumed that all

PRACTICE EXAMPLE 11.4

^{132}I undergoes beta decay to ^{132}Xe with a half-life of 2.3 hours. How old is a sample that is 85% ^{132}Xe if it was pure ^{132}I initially?

$k =$

of the ^{206}Pb found in the rock originated from ^{238}U , so

$$\frac{n}{n_o} = \frac{\text{moles of } ^{206}\text{Pb in the sample}}{(\text{moles of } ^{206}\text{Pb} + \text{moles of } ^{238}\text{U}) \text{ in the sample}}$$

This presumes that none of the lead was in the rock when it was formed, which is an acceptable assumption if there is not much of the more abundant ^{208}Pb present.

11.4 NUCLEAR RADIATION AND LIVING TISSUE

When a substance absorbs visible or ultraviolet light, one of its electrons is excited into an excited state, but the energy is soon given off as heat or light when the electron returns to the ground state. The electron remains in the atom during the process, so the radiation is said to be **non-ionizing radiation**. Radio and TV waves, microwaves, and infrared radiation are also non-ionizing. However, the energy of x-rays and γ -rays is so great that their absorption results in the loss of the electron and the production of an ion. Thus, x-rays and γ -rays are said to be **ionizing radiation**. α -particles and β -particles are also ionizing. In this section, we discuss some of the harmful effects of ionizing radiation.

In order for ionizing radiation to be harmful, it must encounter tissue. Thus, ionizing radiation produced in an experiment conducted in a laboratory next door would have to pass through at least one wall and your clothing before it could harm you. The ability of radiation to pass through material is called its **penetrating power**. The penetrating power decreases as the mass and charge of the particle increases. Alpha particles are both highly charged and massive, which results in very poor penetrating power. α -particles are stopped by a piece of paper or by the layer of dead skin cells covering the body. They can be very damaging to internal organs, but they must be ingested or inhaled to do so.

Approximately 40% of the background radiation to which humans are exposed is produced by radon that is formed by the decay of ^{238}U to ^{206}Pb . The other members of the decay pathway are also radioactive, but they are solids and remain in the rock. However, radon is a gas and can pass from the rocks into our homes. It is a source of α -particles ($^{222}_{86}\text{Rn} \rightarrow ^{218}_{84}\text{Po} + ^4_2\text{He}$, $t_{1/2} = 3.8$ days) that has been attributed to up to 10% of lung cancer deaths. As a gas, radon is readily inhaled and, after inhalation, the resulting α -particles can bombard the lung tissue. In addition, ^{218}Po is also an alpha emitter ($t_{1/2} = 3$ minutes), but it is a solid and is not exhaled. ^{218}Po in the lungs bombards the lung tissue constantly, which damages the tissue and the growth-regulation mechanism of the cells; causing the uncontrolled cell reproduction called cancer.

Beta particles are not as highly charged and not nearly as massive as α -particles. Consequently, they have greater penetrating power. However, even β -particles are stopped by a sheet of metal or wood. β -particles can cause damage to the skin and the surface of organs, but they also do their worst damage if ingested or inhaled. Gamma rays are photons and have excellent penetrating power because they have neither charge nor mass. Dense materials like lead or concrete are required to stop γ -rays. Recall that γ -rays are used to carry excess energy away from a nuclear reaction. Consequently, many radioisotopes emit γ -rays. ^{60}Co is a γ -emitter that is used in cancer treatment by bombarding the tumor with γ -rays to destroy the cancerous cells.

11.5 NUCLEAR FISSION

Nuclear fission is the process of splitting a large nucleus into smaller nuclei. These processes are extremely exothermic and are the basis for nuclear power plants and weaponry. We consider the most common example, the fission of a ^{235}U nucleus after neutron capture.



As with all nuclear reactions, the energy change for this reaction can be determined from the mass defect as discussed in Section 11.1 and demonstrated in Example 11.9.

Example 11.9

Determine how much energy is released when 1.00 g of ^{235}U undergoes the above fission reaction.

The atomic masses are: $^{235}\text{U} = 235.0439$; $^{92}\text{Kr} = 91.9263$; and $^{141}\text{Ba} = 140.9144$

The mass defect for a reaction is $\Delta m = \text{mass of products} - \text{mass of reactants}$.

$$\text{mass of products: } 3(1.0087) + 91.9263 + 140.9144 = 235.8668 \text{ g}\cdot\text{mol}^{-1}$$

$$\text{mass of reactants: } 235.0439 + 1.0087 = 236.0526 \text{ g}\cdot\text{mol}^{-1}$$

$$\Delta m = 235.8668 - 236.0526 = -0.1858 \text{ g}\cdot\text{mol}^{-1} = -1.858 \times 10^{-4} \text{ kg}\cdot\text{mol}^{-1}$$

The mass defect is converted to energy by using Equation 11.4: $\Delta E = \Delta mc^2$

Δm must be expressed in kg and c is the speed of light in $\text{m}\cdot\text{s}^{-1}$.

$$\Delta E = (-1.858 \times 10^{-4} \text{ kg}\cdot\text{mol}^{-1})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})^2 = -1.670 \times 10^{13} \text{ J}\cdot\text{mol}^{-1}$$

Finally, use the molar ΔE above to determine ΔE for 1.00 g of ^{235}U

$$1.00 \text{ g U} \times \frac{1 \text{ mol U}}{235.0439 \text{ g U}} \times \frac{-1.670 \times 10^{13} \text{ J}}{\text{mol U}} = -7.11 \times 10^{10} \text{ J}$$

Thus, the fission of 1 g of uranium-235 *releases* 7.11×10^7 kJ of energy. Compare that with burning 1 gal of octane (a component of gasoline), which liberates 10^5 kJ of heat. In other words, the fission of one gram of uranium-235 produces the same amount of energy as the combustion of about 600 gallons of gasoline.

The fission reaction of ^{235}U considered above is represented in Figure 11.3. A single neutron (a) starts the reaction, which produces three more neutrons (b). Reaction of each of these three neutrons produces the nine neutrons shown in (c). If each of these nine neutrons goes on to react with nine ^{235}U nuclei, 27 neutrons would be produced in the next step. In general, 3^n neutrons are produced in the n^{th} step. Thus, in the 10^{th} step, 3^{10} or 59,049 neutrons are produced. Reactions like the fission of ^{235}U in which one of the products of the reaction initiates further reaction are called **chain reactions**.

The ^{235}U fission reaction involves a bimolecular collision between a neutron and a ^{235}U nucleus. Consequently, the rate of this elementary reaction is proportional to the product of the two concentrations:

$$\text{rate} = k[\text{n}][^{235}\text{U}]$$

Eq. 11.7

where $[\text{n}]$ is the concentration of neutrons. As the reaction proceeds, the concentration of neutrons increases faster than the concentration of ^{235}U decreases, which causes the rate of the reaction to increase. Furthermore, each step of the reaction produces three times the energy of the previous step. If it is not controlled, the chain reaction results in an explosion as a vast amount of energy is released in a very short period of time.

Equation 11.7 indicates that the rate of fission can be reduced by reducing either the neutron concentration or the uranium-235 concentration. ^{235}U does not undergo a chain reaction in nature because both concentrations are low. The natural abundance of ^{235}U in uranium ore is only 0.7%, which means that $[^{235}\text{U}]$ is low. Indeed, the uranium must be enriched to levels of around 4% if it is to serve as a nuclear fuel. Even enriched uranium does not get out of control if the sample size is kept small. This is because many of the neutrons produced in the fission process are near the surface and escape the sample without colliding with other ^{235}U nuclei. However, as the sample size increases, the fraction of neutrons initiating fission increases. The minimum mass of uranium required

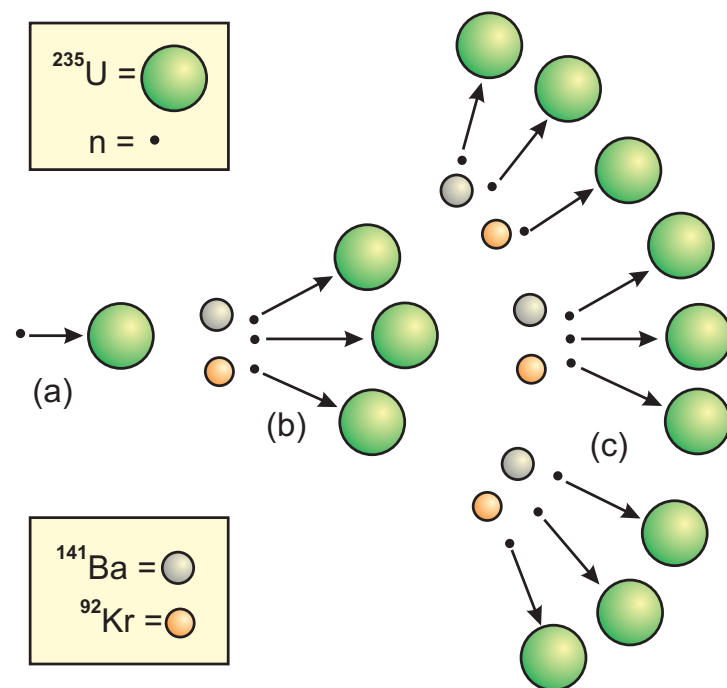


Figure 11.3 Fission of ^{235}U results in a chain reaction

- A single neutron collides with a single ^{235}U nucleus to produce $^{141}\text{Ba} + ^{92}\text{Kr} + 3\text{n}$.
- The three neutrons produced in (a) collide with three other ^{235}U nuclei to produce $3^{141}\text{Ba} + 3^{92}\text{Kr} + 9\text{n}$.
- The nine neutrons produced in (b) collide with nine other ^{235}U nuclei. The result would be $9^{141}\text{Ba} + 9^{92}\text{Kr} + 27\text{n}$.

to maintain a chain reaction is called the **critical mass**. At the critical mass, one neutron from each fission encounters a uranium nucleus. Masses that are less than the critical mass are said to be **subcritical**. Subcritical masses cannot sustain a chain reaction because less than one neutron per fission initiates a subsequent fission. Masses in excess of the critical mass are called **supercritical**. In a supercritical mass, most of the neutrons initiate further reaction. The critical mass of ^{235}U , which depends upon its purity, the shape of the sample, and the energy of the neutrons, ranges from about 15 kg to over 50 kg.

The atomic bomb is an example of uncontrolled fission. The design of the first bomb, shown schematically in Figure 11.4, is quite simple. It is transported with the fissionable uranium divided into two sections, each with a subcritical mass and located at the opposite ends of a large gun barrel. A chemical explosive, TNT, is used to send one subcritical mass into the other. The combined mass of the two samples exceeds the critical mass, and an uncontrolled chain reaction is initiated. The first bomb dropped on Japan at the end of World War II produced an explosion equivalent to 19,000 tons of TNT.

A **nuclear reactor**, which is shown schematically in Figure 11.5, is a controlled chain reaction. Enriched ^{235}U in the form UO_2 is contained in fuel rods, which are tubes made of a zirconium alloy. The reaction is controlled by maintaining a constant rate of reaction (Equation 11.7). At the beginning of the reaction, the concentration of ^{235}U is relatively high, but it drops throughout the reaction. In order to maintain a constant rate of reaction, the concentration of neutrons used in the reaction must increase at the same rate that the concentration of ^{235}U decreases. The number of neutrons is controlled with rods made from cadmium or boron, both of which absorb neutrons. By adjusting the height of these **control rods**, the rate at which neutrons strike ^{235}U nuclei can be maintained at a constant level. When there is new fuel present, the rods are lowered to capture a greater number of neutrons, but as the fuel is consumed, the rods are raised to increase the number of neutrons available to initiate fission. The control rods can also be lowered completely to shut off the reactor.

Heat generated by the nuclear reaction is carried out of the reactor core by high-pressure water (300 °C, 2250 psi) in the primary water loop. Over 300,000 gal·min⁻¹ can flow through this loop in a large reactor. The heat is used to boil water in a steam generator. The escaping steam in a secondary water loop drives a turbine connected to a generator. The steam leaving the turbine is condensed and cooled in the condenser with cooling water from a lake or river. The cooled water is then returned to the steam generator. The cooling water leaves the condenser about 20 °C warmer than it enters, an

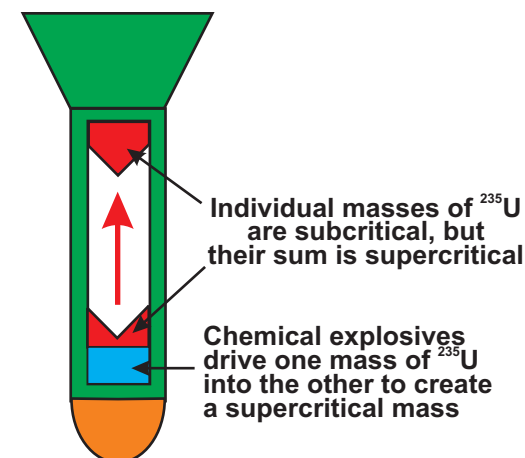


Figure 11.4 Schematic of an atomic bomb

Chemical explosive (TNT) is used to drive one subcritical mass into another. If the sum of the two subcritical masses exceeds the critical mass, an uncontrolled chain reaction is initiated.

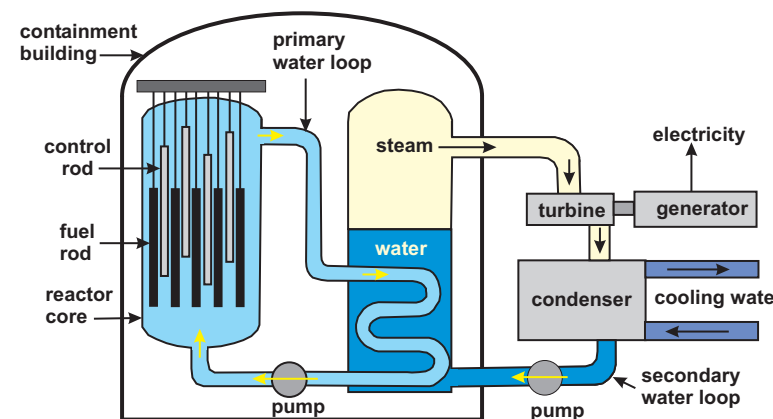


Figure 11.5 Schematic of a nuclear power plant

increase that would heat the lake or river beyond safe levels. Consequently, cooling towers or canals are constructed to allow the heat in the water to dissipate prior to returning the water to the river or lake. It should be noted that no mixing occurs between the primary loop, secondary loop, or cooling water. Both the primary and secondary loops are self-contained.

The fuel in a nuclear plant cannot explode like an atomic bomb, but if the reaction gets out of control, the reactor can experience a 'melt down'. The worst nuclear disaster occurred at Chernobyl in the Ukraine in 1986. Operators disabled the safety system to carry out some tests. During the tests, the reactor cooled and nearly shut down, so, to avoid a costly shut down, they removed most of the control rods. In the absence of the control rods and with the safety system disabled, the reactor heated beyond safe limits. The excess heat boiled the superheated water and melted the fuel rods, which then mixed with the superheated water. High-pressure steam generated by boiling the superheated water blew off the top of the reactor, and spread the radioactive fuel into the atmosphere. A malfunction of the cooling system was also responsible for the Three Mile Island accident in 1979, but no explosion accompanied that partial melt down and only a very small amount of radiation was released.

Nuclear reactors are built with many levels of safeguards that have proved effective in preventing accidents except in the case of gross operator error. However, there is one other problem presented by the use of nuclear power. The major concern surrounding nuclear power today is nuclear waste disposal. Not all of the radioactive fuel in the fuel rod can be consumed, and many of the products of the fission reactions are radioactive with long half-lives. Three problems arise: where do you store this radioactive waste, how do you get it there, and how do you keep it secure? Nobody wants to live near a nuclear waste site, and there is major opposition to the transport of radioactive material along our highways and railways. Consequently, the spent fuel rods are usually kept at sites close to the reactor. There are bills before congress to build a national repository for radioactive waste. A nuclear waste repository has been approved for Yucca Mountain, Nevada. The plan for nuclear waste storage calls for the transportation of the waste by railroad. However, as with any plan calling for cross-country transportation of nuclear waste, there is still a great amount of opposition due to safety and security concerns.

11.6 NUCLEAR FUSION

In **nuclear fusion**, two lighter atoms combine, or *fuse*, to form a heavier atom. It is the process that powers the sun and other stars. As in fission, some of the mass of the fusing nuclei is converted into energy. The most studied fusion reaction is the fusion of *deuterium* (^2H) with *tritium* (^3H) to form helium and a neutron:



Even with a natural abundance of only 0.015 %, deuterium is a readily available isotope because it is present in water. Tritium atoms can be prepared by bombarding lithium atoms with the neutrons released in the above reaction:



The fusion of deuterium and tritium offers almost limitless energy.

The reason we do not have fusion power plants is that the activation energy for a fusion reaction is enormous. The potential energy of two nuclei as a function of the distance between them rises very sharply at distances less than the bond length. The rise in energy is due to the repulsion between the two positively charged nuclei. In order for fusion to occur, this high repulsion energy must be overcome. Consequently, extremely high temperatures are required to bring about fusion. For this reason, fusion reactions are also called **thermonuclear**. Instead of a critical mass that must be exceeded, fusion reactions have temperatures that must be exceeded. The fusion of deuterium and tritium has the lowest threshold temperature for any fusion reaction, a mere 40,000,000 K! The uncontrolled fusion of deuterium and tritium is called a hydrogen bomb. The threshold temperatures required for the fusion in a hydrogen bomb are achieved by first detonating a fission bomb!

In order to achieve controlled fusion, the nuclei not only have to have sufficient energy to fuse, they must also be held together long enough for fusion to occur. As we shall see in Section 11.7, stars use enormous gravitational fields to both heat the nuclei and to confine them. Scientists are trying two techniques to produce fusion in the laboratory. In **magnetic confinement**, the nuclei are confined by a strong magnetic field and heated by powerful microwaves. In **inertial confinement**, a pellet of frozen hydrogen is compressed and heated by an intense energy beam so quickly that fusion occurs before the atoms can fly apart. Fusion has been achieved in the laboratory, but the nuclei fly apart before a self-sustained reaction can be initiated. Consequently, more energy is pumped

into the system than is extracted from it. However, it is expected that fusion reactions that produce more energy than they consume will be achieved relatively soon, but the predictions are that commercial fusion will not be available for decades.

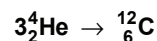
11.7 ORIGIN OF THE HEAVY ELEMENTS

Nature has mastered fusion in nuclear reactors called stars, and the by-products of these thermonuclear reactions are the elements that populate the periodic table. The universe is comprised mostly of hydrogen, and the story of how the heavier elements came into being is illuminating.

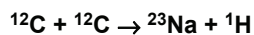
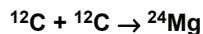
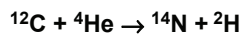
Hydrogen atoms in space are attracted to one another by gravitational forces. As the number of atoms that are attracted to one another increases, the gravitational forces between the atoms also increases, causing the system to begin to collapse. As the body of hydrogen atoms collapses, the pressure at the center begins to build, and the increase in pressure results in an increase in temperature. If there is sufficient mass, the system continues to collapse until the temperature reaches about 4×10^7 K, at which point the density is about $100 \text{ g}\cdot\text{cm}^{-3}$. At this temperature, the protons begin to fuse, and a star is born. Further collapse of the star is offset by the enormous energy released by the fusion process, and the star stabilizes as long as the fuel lasts. The overall reaction is



After about 10% of the hydrogen has been consumed, the core again begins to collapse. When the temperature reaches about 2×10^8 K and the density is around $10,000 \text{ g}\cdot\text{cm}^{-3}$, ${}^4_2\text{He}$ begins to burn:



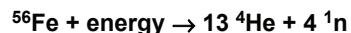
The energy released by burning helium expands the hydrogen into a sphere over a hundred times larger than the original star. At this point, the star is called a *red giant*. When the concentration of ${}^{12}_6\text{C}$ gets sufficiently high, it begins to burn and produce other elements.



Further collapse and heating produces elements up to ${}^{56}_{26}\text{Fe}$. Reactions of this type are

highly exothermic, but reactions to form elements heavier than ^{56}Fe are endothermic (refer to Figure 11.1) and are produced by neutron capture, which is a very slow process. Thus, once a star contains mostly ^{56}Fe there is no further nuclear fuel and the star collapses to a *white dwarf* with a radius similar to earth's and a density of 10^4 to $10^8 \text{ g}\cdot\text{cm}^{-3}$. This is the fate that awaits our sun.

However, if the star is large enough, the collapse continues to even greater densities and temperatures of $4 \times 10^9 \text{ K}$, where many neutron-releasing reactions are initiated:



This final collapse occurs in minutes or less with the release of immense amounts of energy and neutrons. The elements in the outer shell of the star absorb many neutrons almost simultaneously and very large masses ($A = 238$) are achieved. The shell is then blown off at near the speed of light in a *supernova*, leaving a core of many solar masses, a diameter $\sim 10 \text{ km}$, and a density of $10^{14} \text{ g}\cdot\text{cm}^{-3}$. At such pressures, electrons are captured by the protons to form neutrons. Eventually, the core consists of nothing but neutrons and is called a *neutron star*. It is interesting to realize that all of the atoms that are heavier than iron were formed in supernovas, which makes a gold necklace all the more interesting.

11.8 CHAPTER SUMMARY AND OBJECTIVES

Atoms with unstable nuclei emit particles to become different atoms that have more stable nuclei in a process known as nuclear decay. We considered three types of decay:

- α -decay (loss of a ^4He nucleus);
- β -decay (loss of an electron produced by the conversion of a neutron to a proton); and
- β^+ -decay (loss of a positron produced when a proton is converted into a neutron).

Nuclei can also capture inner shell electrons in a process known as electron capture. The captured electron converts a proton into a neutron.

The mode of decay of an unstable nucleus depends upon the ratio of neutrons to protons. If N_n/Z is greater than the stable ratio, a neutron is converted into a proton by β^- decay. If N_n/Z is less than the stable ratio, a proton is converted into a neutron by positron emission or electron capture. The most common mode of decay for nuclei with $Z > 83$ is α -decay.

Nuclei are held together by their binding energy, $\Delta E = \Delta mc^2$, where Δm , the mass defect, is equal to the mass of the nucleons minus the nuclear mass. The binding energy per nucleon is a measure of the thermodynamic stability of the nucleus.

All nuclear decay is unimolecular and follows first order kinetics. The first-order rate constants are usually given in terms of half-lives. The age of certain materials can be determined by measuring the relative amounts of certain isotopes that they contain in a process called radioactive dating. The ratio of ^{14}C present in the sample to the amount present in a living organism is used to estimate the age of the sample.

Nuclear fission is the breaking apart of a nucleus into smaller nuclei. The energy changes that accompany nuclear fission can be enormous. Fission of one gram of uranium-235 releases as much energy as the combustion of 600 gallons of gasoline. A chain reaction is a reaction that produces more reactant than it consumes. Fission of ^{235}U produces more neutrons than it consumes, so their concentration increases and the rates of reaction and energy production also increase with time. In the controlled fission of a nuclear reactor, the rate of reaction is regulated with control rods to absorb excess neutrons. Atomic bombs are examples of uncontrolled fission.

In fusion (or thermonuclear reactions), two smaller nuclei are combined to form a larger one. These processes also produce vast amounts of energy. However, they also have extremely high activation energies, and the lowest temperature at which fusion can occur is forty million degrees. Fusion offers an almost limitless supply of energy, but the enormous technological barriers, such as temperatures in excess of forty million degrees and a way to confine the nuclei at these temperatures long enough for them to fuse, must be overcome.

After studying the material presented in this chapter, you should be able to:

1. determine the number of protons and neutrons in a nucleus given its symbol or atomic number and its mass number (Section 11.1);
2. determine the atomic weight of an element from the masses and natural abundance of its isotopes (Section 11.1);
3. calculate the mass defect of a nucleus from the number of protons and neutrons it contains and the mass of the nucleus (Section 11.1);
4. convert between mass and energy (Section 11.1);
5. determine the binding energy per nucleon of a nucleus and predict which of several nuclei is most stable (Section 11.1);
6. define the terms radioactive and radioisotopes (Section 11.2);
7. identify a missing particle in a nuclear reaction (Section 11.2);
8. identify the decay particles by name and symbol (Section 11.2);
9. predict the probable mode of decay of an unstable nucleus (Section 11.2);

10. determine the time required for a given fraction of a radioactive material to disappear given the half-life or rate constant for the decay (Section 11.3);
11. determine the age of an organic material given its ^{14}C rate of decay, the rate of ^{14}C decay in living organisms and the half-life of ^{14}C (Section 11.3);
12. distinguish between ionizing and non-ionizing radiation (Section 11.4);
13. compare the penetrating power of α -particles, β -particles and γ -rays (Section 11.4);
14. describe nuclear fission and chain reactions (Section 11.5);
15. define critical mass and explain its origin (Section 11.5);
16. explain how fission is controlled in a nuclear reactor (Section 11.5);
17. describe what is meant by 'melt down' (Section 11.5);
18. describe nuclear fusion and the problems associated with controlling it (Section 11.6); and
19. explain where and how elements are formed (Section 11.7).

ANSWERS TO PRACTICE EXAMPLES

- 11.1 $8.434 \times 10^{-11} \text{ J} \cdot \text{mol}^{-1} \cdot \text{nucleon}^{-1}$
- 11.2 β^+ ; ^{59}Co ; ^{209}Tl
- 11.3 $^{59}\text{Fe} \rightarrow \beta^- + ^{59}\text{Co}$
 $^{58}\text{Cu} \rightarrow \beta^+ + ^{58}\text{Ni}$
 $^{221}\text{Ra} \rightarrow \alpha + ^{217}\text{Rn}$
- 11.4 6.3 hours

11.9 EXERCISES

THE NUCLEUS

- Indicate the number of neutrons in each of the following nuclei.
a) ^{10}Be b) ^{100}Mo c) ^{75}As d) ^{197}Au
- Indicate the number of neutrons in each of the following nuclei.
a) ^{192}Hg b) ^{115}Sn c) ^{34}S d) ^{85}Rb
- Write the symbol, including atomic number and mass, for each of the following isotopes.
a) $Z = 26, A = 56$ b) $A = 74, N_n = 40$ c) $Z = 54, N_n = 78$
- Write the symbol, including atomic number and mass, for each of the following isotopes.
a) $Z = 46, N_n = 64$ b) $A = 110, Z = 48$ c) $A = 212, N_n = 129$
- There are three naturally occurring isotopes of silicon. Use the data below to determine the atomic mass of silicon.

	Mass (amu)	Abundance
^{28}Si	27.97693	92.21%
^{29}Si	28.97649	4.70%
^{30}Si	29.97376	3.09%
- There are two naturally occurring isotopes of lithium: ^6Li and ^7Li , with atomic masses of 6.01512 and 7.01600, respectively. If the atomic mass of lithium is 6.939, what is the natural abundance of ^6Li ?
- The natural abundance of deuterium is 0.015%. How many deuterium nuclei are present in 100. mL of water?

NUCLEAR STABILITY

- What is meant by the term 'band of stability'?
- Determine the mass defects (in $\text{kg}\cdot\text{mol}^{-1}$) for the following nuclei.
a) ^{79}Br (Mass = 78.9183 amu)
b) ^{99}Ru (Mass = 98.9061 amu)
- Determine the mass defects (in $\text{kg}\cdot\text{mol}^{-1}$) for the following nuclei.
a) ^{142}Ce (Mass = 141.9090 amu)
b) ^{40}Ca (Mass = 39.96259 amu)

- What are the binding energies and binding energies per nucleon for each of the nuclei in Exercise 9?
- What are the binding energies and binding energies per nucleon for each of the nuclei in Exercise 10?
- Which nucleus in Exercise 11 is thermodynamically more stable?
- Which nucleus in Exercise 12 is thermodynamically more stable?

NUCLEAR REACTIONS AND RADIOACTIVITY

- Predict the mode of decay for each of the following:
a) ^{233}U b) ^{197}Pb c) ^{231}Ac d) ^{225}Th
- Predict the mode of decay for each of the following:
a) ^{110}Rh b) ^{98}Pd c) ^6He d) ^{25}Al
- Identify X in each of the following nuclear reactions:
a) $^{144}\text{Nd} \rightarrow ^{140}\text{Ce} + \text{X}$
b) $^{238}\text{U} + \text{n} \rightarrow 3\text{n} + ^{81}\text{Ge} + \text{X}$
c) $^{16}\text{O} + \alpha \rightarrow \text{X}$
- Identify X in each of the following nuclear reactions.
a) $^{69}\text{Ga} + \text{n} \rightarrow \text{X}$
b) $^{235}\text{U} + \text{n} \rightarrow 2\text{n} + ^{100}\text{Mo} + \text{X}$
c) $^{35}\text{Cl} + \text{p} \rightarrow \alpha + \text{X}$
- Write complete nuclear reactions for the following:
a) Potassium-40 undergoes beta decay.
b) Chlorine-34 emits a positron.
c) Arsenic-73 undergoes electron capture.
d) Bismuth-214 decays to thallium-210.
- Write complete nuclear reactions for the following.
a) Thorium-229 undergoes alpha decay.
b) Gold-198 emits a beta particle.
c) Antimony-118 emits a positron.
d) Cadmium-115 decays to indium-115.
- Radon-222 undergoes the following decay sequence to a stable nucleus: $\alpha, \alpha, \beta, \beta, \alpha, \beta, \alpha$. What is the identity of the resulting nucleus?
- Uranium-238 undergoes the following decay sequence: $\alpha, \beta, \beta, \alpha, \alpha, \alpha, \alpha, \alpha, \beta, \beta, \alpha, \beta$. What is the identity of the last nucleus?

KINETICS OF RADIOACTIVITY

23. ^{239}Pu is a very toxic material used in nuclear weapons that has a half-life of 2.44×10^4 years. How long will a sample of Pu have to be stored before only 1% of the original sample remains?
24. ^{131}I is a β -emitter that is used to treat thyroid disorders. If its half-life is 8.070 days, how many days are required to rid the body of 95% of any ingested ^{131}I ?
25. A 12.30-mg sample of ^{47}Ca is found to contain 3.24 mg of ^{47}Sc after 2.00 days, what is the half-life of ^{47}Ca in days? What type of decay does ^{47}Ca undergo?
26. A 4.56-mg sample of ^{228}Th , an α emitter, contains 2.58 mg of ^{228}Th after 575 days. What is the half-life of ^{228}Th in years?
27. The Shroud of Turin is a long linen cloth that bears an image of a bearded, longhaired man, with numerous lacerations over his body. Tradition, dating back to the fourteenth century, has it that the fabric is the burial shroud of Jesus Christ. In 1988, its age was determined by carbon dating. If a fiber of the shroud had a ^{14}C disintegration rate of $14.0 \text{ d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$, how old was the cloth. What conclusion can be drawn about the authenticity of the claim that it is the burial cloth of Jesus Christ? (The rate of decay of living organisms is $15.3 \text{ d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$, and the half-life of ^{14}C is 5730 years.)
28. The wood on an Egyptian coffin had a ^{14}C disintegration rate of $11.7 \text{ d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$, how old is the coffin? (The rate of decay of living organisms is $15.3 \text{ d}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$, and the half-life of ^{14}C is 5730 years.)
29. How old is a rock sample from a meteor if it contains 73.2 mg of ^{238}U and 20.2 mg of ^{206}Pb ? Assume that all of the ^{206}Pb was formed from ^{238}U . The half-life of the $^{238}\text{U} \rightarrow ^{206}\text{Pb}$ process is 4.5×10^9 years.
30. Geological times can also be estimated by Argon dating. ^{40}K undergoes electron capture to ^{40}Ar with a half-life of 1.28×10^9 years. Estimate the age of a moon rock sample if its $^{40}\text{Ar}/^{40}\text{K}$ mass ratio is 10.4.

NUCLEAR RADIATION

31. List beta particles, gamma rays and alpha particles in order of increasing penetrating power.
32. Why are houses checked for radon? How does radon get into a home?

NUCLEAR FISSION AND NUCLEAR FUSION

Use the following atomic masses and those in Table 11.1 for Exercises 33 and 34.

^4He	4.0026	^{13}C	13.0034	^{31}P	30.9737
^{16}O	15.9949	^{24}Mg	23.9850	^{226}Ra	226.0254
^{68}Zn	67.9248	^{72}Ge	71.9221	^{238}U	238.0508
^{230}Th	230.0331	^{234}Th	234.0436		
^{239}Pu	239.0522	^{242}Cm	242.0588		

33. Determine the mass defect in kilograms of each of the following reactions.
 - a) $2^{12}\text{C} \rightarrow ^{24}\text{Mg}$
 - b) $^{238}\text{U} \rightarrow ^{234}\text{Th} + \alpha$
 - c) $\beta^+ + \beta^- \rightarrow \gamma$
 - d) $^{239}\text{Pu} + ^4\text{He} \rightarrow ^{242}\text{Cm} + \text{n}$
34. Determine the mass defect in kilograms of each of the following reactions.
 - a) $^{230}\text{Th} \rightarrow ^{226}\text{Ra} + \alpha$
 - b) $2^{16}\text{O} \rightarrow ^{31}\text{P} + ^1\text{H}$
 - c) $^{13}\text{C} + ^4\text{He} \rightarrow ^{16}\text{O} + \text{n}$
 - d) $^{68}\text{Zn} + ^4\text{He} \rightarrow ^{72}\text{Ge}$
35. What is the energy change of each reaction listed in Exercise 33?
36. What is the energy change of each reaction listed in Exercise 34?
37. Classify each reaction in Exercise 33 as fission, fusion, decay or annihilation. If it is a decay, indicate what kind.
38. Classify each reaction in Exercise 34 as fission, fusion, decay or annihilation. If it is a decay, indicate what kind.
39. What is a chain reaction? How is the chain reaction in a nuclear power plant controlled?
40. Why is controlled fusion so difficult to achieve? Describe the two methods that are being used to produce controlled fusion.

Appendix A

Reporting Quantitative Measurements and Results

A.1 PRECISION

The **accuracy** of a measured or calculated quantity is the degree to which it agrees with the true value, while the **precision** of a measurement is the degree to which the measurement is reproducible. A reported measurement must contain units and should indicate both the numerical value of the measurement and the precision with which it was made. The **units** indicate the scale that was used to make the measurement. A measurement is useless without units. Reporting that the magnitude of a measurement is 3.618 reveals nothing to the reader because it does not indicate the scale used. The precision of the measurement is given by the number of digits to which the numerical value is reported. It is normally dictated by the measuring device. The last digit of a reported measurement should be assumed to be an estimate, and, unless stated otherwise, it is generally assumed good to ± 1 . Thus, if a mass is reported to be 3 g, the reader will assume that the mass is somewhere between 2 and 4 g. A reported mass of 3.0 g tells the reader that the measurement was made more precisely, and that the mass is between 2.9 and 3.1 g.

As an example of the use of precision in reporting numbers, consider the measurement of the blue bar in Figure A.1 with a ruler marked in centimeters. The ruler in Figure A.1a is a low precision ruler and the first digit is an estimate. The length appears to be slightly over $\frac{3}{4}$ of the ruler length, which makes the length about 6 cm ($\frac{3}{4} \times 8 = 6$). The reported length would be expressed as 6 cm, and a reader would imply that the 6 is an estimate. In Figure A.1b, a more precise ruler is used. The length is not quite halfway between 6 and 7 cm, and would be reported as 6.4 cm, which tells the reader that the length is between 6.3 and 6.5 cm. Again, the implication is that the last digit is an estimate. In Figure A.1c, the most precise ruler is used. The bar is between 6.4 and 6.5 cm, but it is clearly closer to 6.4 cm. The reported

length would be 6.42 cm. Someone else might make the measurement and report a length of 6.43 cm, which is consistent with the fact that the last digit is an estimate.

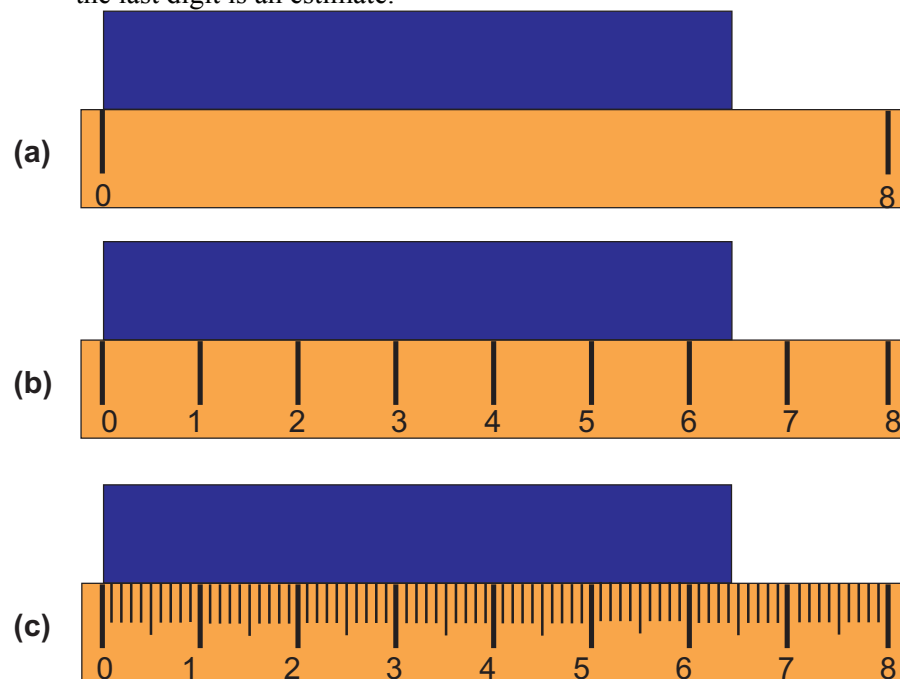


Figure A.1 Rulers with different precisions

A.2 SIGNIFICANT FIGURES

Significant figures are the digits that are obtained in a measurement. Thus, the precision of a measurement is indicated by the number of significant figures it contains. A measurement of 6.43 cm, which contains three significant figures, is more precise than a measurement of 6.4 cm, which contains only two significant figures. Reporting the number of significant figures correctly is an important part of any measurement because the number of significant figures indicates the

precision of the measurement. The most common mistake made in reporting a measurement is not reporting trailing zeros to the right of the decimal. However, in a science laboratory, there is a big difference between a measurement reported to be 3 g and one reported as 3.0000 A. It is important that your number show both the magnitude and precision correctly. Consider the case where you are trying to prove or disprove a prediction that the mass of the product of a reaction should be 2.8 A. A measurement of 3.0000 g indicates that the prediction is wrong, but a measurement of 3 g supports the prediction.

There are some simple rules that allow us to determine which digits in a number are significant.

1. All nonzero numbers in a reported measurement are significant.
2. Zeroes to the left of the decimal but to the right of all nonzero digits cannot be assumed significant. In this text, we use the practice of placing a decimal at the end of a number to indicate that the zeroes are significant. Thus, the number of significant figures in the number '300' is unclear while the number '300.' has three significant figures. The best way to indicate the number of significant figures is use scientific notation. The numbers 3×10^2 , 3.0×10^2 and 3.00×10^2 show a measurement of 300 to one, two and three significant figures, respectively.
3. Leading zeroes for numbers less than one are *not* significant, but other zeros in the number are significant. The number 0.00012 contains only two significant figures. This becomes apparent when the number is expressed in scientific notation, 1.2×10^{-4} .
4. All zeroes to the right of the decimal of numbers greater than one are significant. The number 1.00012 contains six significant figures.

If you are uncertain about the number of significant figures in a number, rewrite the number in scientific notation. All digits of a number expressed in scientific notation are significant.

EXAMPLE A.1

Indicate the number of significant figures in each of the following numbers.

a) 3.000

The number is greater than one so all zeroes to the right of the decimal are significant (Rule 4). This number contains four significant figures.

b) 320

The zero cannot be assumed to be significant, so the number would be assumed to have only two significant figures. To indicate that the zero is significant, write the number in scientific notation, 3.20×10^2 . In this text, we would write the number as '320.' to indicate that the zero was significant.

c) 0.0005606

Rule 3 indicates that leading zeroes in numbers less than one are not significant but the other zero is. This number has four significant figures. This becomes clear when the number is expressed in scientific notation, 5.606×10^{-4} .

A.3 REPORTING ANSWERS TO CALCULATIONS

It is frequently the case that the number to be reported is not the measurement itself, but a number obtained after a calculation involving several measurements. As with individual measurements, it is important to report the result of a calculation to the correct number of significant figures so that the reader understands the precision to which the result is known. A common mistake in reporting results of a calculation is to include all of the digits shown on the calculator. For example, consider a 5.2-mL sample that has a mass of 3.7 A. The

density of the material would be determined to be $\frac{3.7 \text{ g}}{5.2 \text{ mL}} = 0.711538$

$\text{g} \cdot \text{mL}^{-1}$, but if you report the density with that many significant figures, you would imply far more precision in your measurements than is warranted by the experiment. Thus, the answer must be **rounded** to the correct number of significant figures. The following two rules should help you report the result of a calculation correctly.

- **Multiplications and Divisions:** The number of significant figures in the result of a calculation involving multiplication or division is equal to the number of significant figures in the least precise number used in the calculation. Thus, the density discussed in the preceding paragraph should be rounded to $0.71 \text{ g}\cdot\text{mL}^{-1}$ because both the mass and the volume were measured to two significant figures.
- **Additions and Subtractions:** The number of decimal places in the result of an addition or subtraction is equal to the number of decimal places in the number used in the addition or subtraction that has the fewest decimal places. A good way to remember this rule is to realize that the result of the addition of a significant number and an insignificant number is insignificant. If you had \$3.25 and someone gave you change worth about \$2, you would have a total of about \$5, not \$5.25. However, if you were given \$2.00 in change, you would have \$5.25.

EXAMPLE A.2

Write the answer to the following operations to the correct number of significant figures.

a) 2.7×6.345

The calculator indicates that the answer is 17.1315. However, the correct number of significant figures must equal to the number of significant figures in the least precise number used in the calculation. Thus, the answer should be rounded to 17 because 2.7 has only two significant figures, which means that the answer can have only two significant figures.

b) $1.0 - 0.0003$

The calculator indicates that the answer is 0.9997, but the number with the fewest decimal places is good to only a tenth so the answer cannot be reported to better than a tenth. Consequently, the answer should be reported as 1.0. This is true because the number 1.0 implies an error of ± 0.1 , which is greater than the number being subtracted.

c) $12.3 - 11.2634$

The calculator answer is 1.0366. However, the number with the fewest decimal places is reported to only a tenth. Therefore, the answer should be reported as 1.0. Note, that the answer is good to only two significant figures, less than either of the original numbers. It is not unusual to lose significant figures in a subtraction, so you should avoid determining results that are small differences between large numbers.

d) $8.76 + 7.13$

The calculator answer is 15.89, and all of the figures are significant because both numbers in the calculation are good to two decimal places. Note that we have gained a significant figure in this addition.

e) $8.5128/3.20$

The result is 2.660250.0, but the least significant number contains three significant figures, so the result must be rounded to 2.66.

f) $\frac{12.3425 - 12.3417}{23.2268}$

The calculator result is 3.444297×10^{-5} . At first glance, it might appear that the answer should be reported to six significant figures because all of the numbers have six significant figures. However, the first step in the calculation is the subtraction, and the result of that is 0.0008, which has only one significant figure. Consequently, the result of the division is good only to one significant figure and should be reported as 3×10^{-5} . Significant figures are lost again because of a subtraction.

A.4 ROUNDING ERRORS

It is often the case that intermediate values in a calculation involving several steps must also be reported, and they should be reported to the correct number of significant figures. However, the use of the rounded values in subsequent calculations can lead to **rounding errors**. Two calculations, done in the same way except for rounding differences can lead to two different answers. Example A.3 is an example of rounding differences.

EXAMPLE A.3

- a) A mixture contains 4.0 g of N_2 ($M_m = 28.0 \text{ g}\cdot\text{mol}^{-1}$) and 4.0 g of O_2 ($M_m = 32.0 \text{ g}\cdot\text{mol}^{-1}$). How many moles of each gas are present in the mixture?

We divide the mass by the molar mass to obtain the number of moles of each gas. The results of the calculation as shown on a calculator are:

$$\text{moles of N}_2 = 4.0/28.0 = 0.14286 \text{ and moles of O}_2 = 4.0/32.0 = 0.125$$

However each answer is good to only two significant figures, so the number of moles of each gas would be rounded to 0.14 mol N_2 and 0.13 mol O_2

- b) What is the (moles of O_2) to (moles of N_2) ratio in the mixture?

Using the answers to part A as our starting point, we obtain the following:

$$0.13 \text{ mol O}_2 / 0.14 \text{ mol N}_2 = 0.93 \text{ mol O}_2 / \text{mol N}_2$$

However, if the calculation for the ratio is done in one step, the following is obtained:

$$(4.0/32.0)/(4.0/28.0) = 0.88 \text{ mol O}_2 / \text{mol N}_2$$

The calculation using the rounded values is about 6% higher than the true value due to rounding errors!

As demonstrated in Example A.3, rounding errors can be substantial, and they can get worse in calculations involving several steps. Consequently, calculations with rounded numbers should be avoided whenever possible. If rounded numbers must be used, they should be used with more digits than can be expected for the final answer. In this text, we show many intermediate answers, which have been rounded to the correct number of significant figures, but the final answer that is given is always calculated without the use of the rounded numbers. You should always keep that in mind when you compare your answers with those given in the text.

Appendix B

Selected Values of Thermodynamic Properties at 298.15K

Substance	ΔH_f° kJ·mol ⁻¹	ΔG_f° kJ·mol ⁻¹	S° J·mol ⁻¹ ·K ⁻¹	Substance	ΔH_f° kJ·mol ⁻¹	ΔG_f° kJ·mol ⁻¹	S° J·mol ⁻¹ ·K ⁻¹
Aluminum:				CCl ₄ (l)	-135.4	-68.6	216.4
Al(s)	0	0	28.3	HCN(g)	135	125	201.7
AlCl ₃ (s)	-704.2	-628.8	110.7	CH ₄ (g)	-74.9	-50.6	186.15
Al ₂ O ₃ (s)	-1676	-1582	50.92	CS ₂ (g)	117.4	67.15	237.7
Barium:				CS ₂ (l)	89.70	65.27	151.3
Ba(s)	0	0	28.3	C ₂ H ₂ (g)	226.7	209.2	200.8
Ba ²⁺ (aq)	-538.36	-560.7	13	C ₂ H ₄ (g)	52.28	68.12	219.5
BaCO ₃ (s)	-1219	-1139	112	C ₂ H ₆ (g)	-84.67	-32.89	229.5
Boron:				CH ₃ OH(g)	-201.2	-161.9	237.6
B(s)	0	0	5.86	CH ₃ OH(l)	-237.6	-166.23	126.8
BF ₃ (g)	-1137.0	-1120.3	254.12	C ₂ H ₅ OH(g)	-235.1	-168.6	282.6
Bromine:				C ₂ H ₅ OH(l)	-277.7	-174.76	160.7
Br ₂ (l)	0	0	152.23	CH ₃ COOH(l)	-484.5	-390	160
Br ₂ (g)	30.91	3.13	245.38	CH ₃ CHO(g)	-166	-133.7	266
Br(g)	111.9	82.40	174.90	C ₄ H ₁₀ (g)	-124.73	-15.71	310.0
Br ⁻ (aq)	-120.9	-102.8	80.71	C ₄ H ₁₀ (l)	-147.6	-15.0	231.0
HBr(g)	-36	-53.5	198.59	C ₆ H ₆ (g)	82.927	129.66	269.2
Calcium:				C ₆ H ₆ (l)	49.028	124.50	172.8
CaO(s)	-635.1	-603.5	38.2	C ₈ H ₁₈ (l)	-226		
Ca(OH) ₂ (s)	-986.09			Chlorine:			
CaCO ₃ (s)	-1,206.9	-1,128.8	92.9	Cl ₂ (g)	0	0	223.0
Carbon:				Cl(g)	121.7	105.7	165.2
C(s,graphite)	0	0	5.740	Cl ⁻ (aq)	-167.2	-131.2	56.5
C(s,diamond)	1.987	2.900	2.38	HCl(g)	-92.30	-95.31	186.80
C(g)	716.68	671.289	157.987	HCl(aq)	-167.2	-131.2	56.5
CO(g)	-110.52	-137.15	197.56				
CO ₂ (g)	-393.51	-394.36	213.6				
CO ₂ (aq)	-412.9	-386.2	121				
CCl ₄ (g)	-103	-53.7	309.7				

Substance	ΔH_f° kJ.mol ⁻¹	ΔG_f° kJ.mol ⁻¹	S° J.mol ⁻¹ .K ⁻¹	Substance	ΔH_f° kJ.mol ⁻¹	ΔG_f° kJ.mol ⁻¹	S° J.mol ⁻¹ .K ⁻¹
Chromium:				Lead:			
Cr ₂ O ₃ (s)	-1,138	-1,059	81.2	Pb(s)	0	0	68.85
(NH ₄) ₂ Cr ₂ O ₇ (s)	-1,807			Pb ²⁺ (aq)	1.6	-24.3	21
Copper:				PbBr ₂ (s)	-277.4	-260.7	161
Cu(s)	0	0	33.15	PbCl ₂ (s)	-359	-314	136
CuO(s)	-157	-128	42.63	PbO(s)	-219.0	-189.2	66.5
CuSO ₄ (s)	-771.36	-661.9	110	Magnesium:			
Cu ₂ S(s)	-79.5	-86.2	120.5	Mg(s)	0	0	32.69
Fluorine:				MgO(s)	-601.7	-569.4	26.94
F ₂ (g)	0	0	202.7	MgCl ₂ (s)	-641.6	-592.1	89.6
F(g)	78.99	61.92	158.64	Nitrogen:			
F ¹⁻ (aq)	-332.6	-278.8	-13.8	N ₂ (g)	0	0	191.5
HF(g)	-271	-273	173.67	N(g)	472.704	455.5	153.19
Hydrogen:				NH ₃ (g)	-46.11	-16.5	192.3
H ₂ (g)	0	0	130.57	NH ₃ (aq)	-80.29	-26.57	111.3
H(g)	217.97	203.26	114.60	NH ₄ Cl(s)	-314.4	-203.0	94.6
H ¹⁺ (aq)	0	0	0	NH ₄ NO ₃ (s)	-365.5	-184.0	151.1
H ₂ O(l)	-285.83	-237.2	69.91	NO(g)	90.29	86.60	210.65
H ₂ O(g)	-241.82	-228.59	188.7	NOCl(g)	52.6	66.07	261.6
H ₂ O ₂ (l)	-187.8	-120.4	109.6	NO ₂ (g)	33.84	51.84	240.45
H ₂ O ₂ (g)	-136.10	-105.48	232.9	N ₂ O ₄ (g)	9.66	98.28	304.3
Iodine:				HNO ₃ (g)	-134.3	-73.94	266.4
I ₂ (s)	0	0	116.14	Oxygen:			
I ₂ (g)	62.438	19.36	260.6	O ₂ (g)	0	0	205.03
I(g)	106.84	70.283	180.68	O(g)	249.17	231.75	160.95
HI(g)	26.5	1.71	206.48	O ₃ (g)	143	163	238.82
Iron:							
Fe(s)	0	0	27.3				
FeO(s)	-271.9	-255.2	60.75				
Fe ₂ O ₃ (s)	-824.2	-742.2	87.40				
Fe ₃ O ₄ (s)	-1117.1	-1014.2	146.4				

Substance	ΔH_f° kJ.mol ⁻¹	ΔG_f° kJ.mol ⁻¹	S° J.mol ⁻¹ .K ⁻¹	Substance	ΔH_f° kJ.mol ⁻¹	ΔG_f° kJ.mol ⁻¹	S° J.mol ⁻¹ .K ⁻¹
Phosphorus:				Sodium:			
P ₄ (s)	0	0	41.08	Na(s)	0	0	51.45
P(g)	316.4	280.0	163.2	Na(g)	107.7	77.3	153.7
PCl ₃ (g)	-288.07	-269.6	311.7	Na ¹⁺ (aq)	-240.1	-261.9	59.0
PCl ₃ (l)	-319.6	-272.4	217	NaCl(s)	-411.1	-384.0	72.12
PH ₃ (g)	5.4	13.4	210.2	NaCl(g)	-181.4	-201.3	229.8
P ₄ O ₁₀ (s)	-1640.1			Sulfur:			
POCl ₃ (g)	-542.2	-502.5	325	S(s, rhombic)	0	0	31.8
POCl ₃ (l)	-597.0	-520.9	222	SO ₂ (g)	-296.83	-300.19	248.1
H ₃ PO ₄ (aq)	-1288.3	-1142.6	158.2	SO ₃ (g)	-395.72	-371.1	256.6
Potassium:				S ₂ (g)	129	79.30	228.2
K(s)	0	0	64.67	H ₂ S(g)	-20.6	-33.6	205.7
KCl(s)	-436.7	-409.2	82.59	H ₂ SO ₄ (l)	-813.989	-690.101	156.90
KClO ₃ (s)	-397.7	-296.3	143.1	H ₂ SO ₄ (aq)	-909.3	-744.6	20.08
Silicon:				Tin:			
Si(s)	0	0	18.7	Sn(s)	0	0	51.2
Si(g)	368.2	323.9	167.8	SnO(s)	-286	-257	56.5
SiO ₂ (s)	-910.94	-856.67	41.84	SnO ₂ (s)	-580.7	-519.7	52.3
SiH ₄ (g)	34	56.9	204.5	SnCl ₄ (l)	-545.2	-474.0	259
Silver:				SnCl ₄ (g)	-471.5	-432.2	366
Ag(s)	0	0	42.55	Titanium:			
Ag ¹⁺ (aq)	105.90	77.11	73.93	Ti(s)	0	0	30.6
AgCl(s)	-127.0	-109.70	96.11	Ti(g)	468	422	180.3
Ag ₂ O(s)	-31.05	-11.20	121.3	TiO ₂ (s)	-944.7	-889.5	50.3
Ag ₂ S(s)	-32.6	-40.7	144.0	TiCl ₄ (l)	-804.2	-737.2	252.3
				TiCl ₄ (g)	-763.2	-726.8	354
				Zinc:			
				Zn(s)	0	0	41.6
				ZnO(s)	-348.0	-318.2	43.6
				ZnCl ₂ (s)	-415.1	-369.4	111.5

Appendix C

K_a's and pK_a's of Selected Acids at 25 °C by Acid Name

Name	Formula	K _a	pK _a
Acetic	HC ₂ H ₃ O ₂	1.8x10 ⁻⁵	4.74
Ascorbic	C ₆ H ₈ O ₆	8.0x10 ⁻⁵	4.10
	C ₆ H ₇ O ₆ ¹⁻	1.6x10 ⁻¹²	11.80
Ammonium	NH ₄ ¹⁺	5.6x10 ⁻¹⁰	9.25
Benzoic	C ₆ H ₅ COOH	6.5x10 ⁻⁵	4.19
Boric	H ₃ BO ₃	5.8x10 ⁻¹⁰	9.27
Carbonic	H ₂ CO ₃	4.3x10 ⁻⁷	6.37
	HCO ₃ ¹⁻	4.7x10 ⁻¹¹	10.33
Citric	H ₃ C ₆ H ₅ O ₇	7.1x10 ⁻⁴	3.15
	H ₂ C ₆ H ₅ O ₇ ¹⁻	1.7x10 ⁻⁵	4.77
	HC ₆ H ₅ O ₇ ²⁻	4.1x10 ⁻⁷	6.39
Formic	HCHO ₂	1.8x10 ⁻⁴	3.74
Hydrazoic	HN ₃	1.9x10 ⁻⁵	4.72
Hydrocyanic	HCN	4.0x10 ⁻¹⁰	9.40
Hydrohalic	HX (X=I,Br,Cl)	>> 1	< 0
Hydrofluoric	HF	7.2x10 ⁻⁴	3.14
Hydronium	H ₃ O ¹⁺	1.0	0.00
Hydrosulfuric	H ₂ S	1.0x10 ⁻⁷	7.00
	HS ¹⁻	1.3x10 ⁻¹³	12.89
Hypobromous	HBrO	2.0x10 ⁻⁹	8.70
Hypochlorous	HCIO	3.5x10 ⁻⁸	7.46
Hypoiodous	HIO	2.3x10 ⁻¹¹	10.64
Iodic	HIO ₃	0.17	0.77
Lactic	HC ₃ H ₅ O ₃	1.4x10 ⁻⁴	3.85
Nitrous	HNO ₂	4.0x10 ⁻⁴	3.40
Nitric	HNO ₃	>> 1	< 0
Oxalic	H ₂ C ₂ O ₄	5.9x10 ⁻²	1.23
	HC ₂ O ₄ ¹⁻	6.4x10 ⁻⁵	4.19

Name	Formula	K _a	pK _a
Perchloric	HClO ₄	>> 1	< 0
Phosphoric	H ₃ PO ₄	7.5x10 ⁻³	2.12
	H ₂ PO ₄ ¹⁻	6.2x10 ⁻⁸	7.21
	HPO ₄ ²⁻	4.8x10 ⁻¹³	12.32
Sulfuric	H ₂ SO ₄	>> 1	< 0
	HSO ₄ ¹⁻	1.2x10 ⁻²	1.92
Sulfurous	H ₂ SO ₃	1.5x10 ⁻²	1.82
	HSO ₃ ¹⁻	1.0x10 ⁻⁷	7.00
Water	H ₂ O	1.0x10 ⁻¹⁴	14.00

pK_a's at 25 °C by pK_a

HIO ₃	0.77	H ₂ CO ₃	6.37
H ₂ C ₂ O ₄	1.23	HC ₆ H ₅ O ₇ ²⁻	6.39
H ₂ SO ₃	1.82	HSO ₃ ¹⁻	7.00
HSO ₄ ¹⁻	1.92	H ₂ S	7.00
H ₃ PO ₄	2.12	H ₂ PO ₄ ¹⁻	7.21
HF	3.14	HCIO	7.46
H ₃ C ₆ H ₅ O ₇	3.15	HBrO	8.70
HNO ₂	3.40	NH ₄ ¹⁺	9.25
HCHO ₂	3.74	H ₃ BO ₃	9.27
HC ₃ H ₅ O ₃	3.85	HCN	9.40
C ₆ H ₈ O ₆	4.10	HCO ₃ ¹⁻	10.33
C ₆ H ₅ COOH	4.19	HOI	10.64
HC ₂ O ₄ ¹⁻	4.19	C ₆ H ₇ O ₆ ¹⁻	11.80
HN ₃	4.72	HPO ₄ ²⁻	12.32
HC ₂ H ₃ O ₂	4.74	HS ¹⁻	12.89
H ₂ C ₆ H ₅ O ₇ ¹⁻	4.77		

Appendix D

Selected Solubility Product Constants at 25 °C

Substance	K _{sp} at 25 °C	Substance	K _{sp} at 25 °C	Substance	K _{sp} at 25 °C
Aluminum		Copper		Manganese	
Al(OH) ₃	1.9 x 10 ⁻³³	Cu(OH) ₂	2.2 x 10 ⁻²⁰	Mn(OH) ₂	1.9 x 10 ⁻¹³
Barium		Cu ₂ S	1.6 x 10 ⁻⁴⁸	MnCO ₃	8.8 x 10 ⁻¹¹
Ba(OH) ₂	5.0 x 10 ⁻³	CuCO ₃	1.4 x 10 ⁻¹⁰	MnS	5.6 x 10 ⁻¹⁶
BaCO ₃	8.1 x 10 ⁻⁹	CuS	6.3 x 10 ⁻³⁶	Nickel	
BaSO ₄	1.1 x 10 ⁻¹⁰	Iron		Ni(OH) ₂	1.6 x 10 ⁻¹⁴
Ba ₃ (PO ₄) ₂	3.4 x 10 ⁻²³	Fe(OH) ₂	8.0 x 10 ⁻¹⁶	Silver	
Cadmium		FeS	6.3 x 10 ⁻¹⁸	AgCl	1.8 x 10 ⁻¹⁰
Cd(OH) ₂	2.5 x 10 ⁻¹⁴	Fe(OH) ₃	2.5 x 10 ⁻³⁹	AgBr	5.0 x 10 ⁻¹³
CdCO ₃	5.2 x 10 ⁻¹²	FePO ₄	9.9 x 10 ⁻²⁹	AgI	8.3 x 10 ⁻¹⁷
CdS	8.0 x 10 ⁻²⁷	Lead		AgCN	1.2 x 10 ⁻¹⁶
Calcium		Pb(OH) ₂	2.8 x 10 ⁻¹⁶	Ag ₂ S	6.3 x 10 ⁻⁵⁰
Ca(OH) ₂	5.5 x 10 ⁻⁶	PbF ₂	3.7 x 10 ⁻⁸	Ag ₂ CrO ₄	1.1 x 10 ⁻¹²
CaCO ₃	4.8 x 10 ⁻⁹	PbCl ₂	1.7 x 10 ⁻⁵	Ag ₃ PO ₄	2.6 x 10 ⁻¹⁸
Ca ₃ (PO ₄) ₂	1. x 10 ⁻²⁶	PbBr ₂	6.3 x 10 ⁻⁶	Tin	
CaF ₂	3.9 x 10 ⁻¹¹	PbI ₂	6.5 x 10 ⁻⁹	Sn(OH) ₂	1.4 x 10 ⁻²⁸
Chromium		PbCrO ₄	1.8 x 10 ⁻¹⁴	SnS	1.3 x 10 ⁻²³
Cr(OH) ₃	6.3 x 10 ⁻³¹	PbSO ₄	1.7 x 10 ⁻⁸	Zinc	
Cobalt		PbS	8.4 x 10 ⁻²⁸	ZnCO ₃	1.0 x 10 ⁻¹⁰
Co(OH) ₂	1.6 x 10 ⁻¹⁵	Magnesium		Zn(OH) ₂	4.5 x 10 ⁻¹⁷
CoS	4.0 x 10 ⁻²¹	Mg(OH) ₂	1.8 x 10 ⁻¹¹	ZnS	1.1 x 10 ⁻²¹

Appendix E

Selected Standard Reduction Potentials in Aqueous Solutions at 298 K

Ox + ne ¹⁻	⇌	Red	E° (V)	Ox + ne ¹⁻	⇌	Red	E° (V)
Li ¹⁺ + e ¹⁻	⇌	Li(s)	-3.04	Ag ₂ O(s) + H ₂ O + 2e ¹⁻	⇌	2Ag(s) + 2OH ¹⁻	+0.34
K ¹⁺ + e ¹⁻	⇌	K(s)	-2.92	ClO ₃ ¹⁻ + H ₂ O + 2e ¹⁻	⇌	ClO ₂ ¹⁻ + 2OH ¹⁻	+0.35
Ba ²⁺ + 2e ¹⁻	⇌	Ba(s)	-2.92	ClO ₄ ¹⁻ + H ₂ O + 2e ¹⁻	⇌	ClO ₃ ¹⁻ + 2OH ¹⁻	+0.36
Ca ²⁺ + e ¹⁻	⇌	Ca(s)	-2.84	O ₂ (g) + 2H ₂ O + 4e ¹⁻	⇌	4OH ¹⁻	+0.40
Na ¹⁺ + e ¹⁻	⇌	Na(s)	-2.71	I ₂ (s) + 2e ¹⁻	⇌	2I ¹⁻	+0.54
Mg ²⁺ + 2e ¹⁻	⇌	Mg(s)	-2.36	ClO ₂ ¹⁻ + H ₂ O + 2e ¹⁻	⇌	ClO ¹⁻ + 2OH ¹⁻	+0.59
Al ³⁺ + 3e ¹⁻	⇌	Al(s)	-1.66	2AgO(s) + H ₂ O + 2e ¹⁻	⇌	Ag ₂ O(s) + 2OH ¹⁻	+0.60
U ³⁺ + 3e ¹⁻	⇌	U(s)	-1.66	O ₂ (g) + 2H ¹⁺ + 2e ¹⁻	⇌	H ₂ O ₂	+0.70
Ti ²⁺ + 2e ¹⁻	⇌	Ti(s)	-1.63	Fe ³⁺ + e ¹⁻	⇌	Fe ²⁺	+0.77
Mn ²⁺ + 2e ¹⁻	⇌	Mn(s)	-1.18	BrO ¹⁻ + H ₂ O + 2e ¹⁻	⇌	Br ¹⁻ + 2OH ¹⁻	+0.77
2H ₂ O + 2e ¹⁻	⇌	H ₂ (g) + 2OH ¹⁻	-0.83	Ag ¹⁺ + e ¹⁻	⇌	Ag(s)	+0.80
Zn ²⁺ + 2e ¹⁻	⇌	Zn(s)	-0.76	O ₂ (g) + 4H ¹⁺ + 4e ¹⁻	⇌	2H ₂ O	+0.82*
Cr ³⁺ + 3e ¹⁻	⇌	Cr(s)	-0.74	H ₂ O ₂ + 2e ¹⁻	⇌	2OH ¹⁻	+0.88
HCHO + 2H ₂ O + 2e ¹⁻	⇌	CH ₃ OH + 2OH ¹⁻	-0.59	ClO ¹⁻ + H ₂ O + 2e ¹⁻	⇌	Cl ¹⁻ + 2OH ¹⁻	+0.89
Fe ²⁺ + 2e ¹⁻	⇌	Fe(s)	-0.44	NO ₃ ¹⁻ + 4H ¹⁺ + 3e ¹⁻	⇌	NO(g) + 2H ₂ O	+0.96
2H ₂ O + 2e ¹⁻	⇌	H ₂ (g) + 2OH ¹⁻	-0.41*	Hg ²⁺ + 2e ¹⁻	⇌	Hg(l)	+0.85
Cd ²⁺ + 2e ¹⁻	⇌	Cd(s)	-0.40	VO ₂ ¹⁺ + 2H ¹⁺ + e ¹⁻	⇌	VO ²⁺ + H ₂ O	+1.00
PbSO ₄ (s) + 2e ¹⁻	⇌	Pb(s) + SO ₄ ²⁻	-0.36	Br ₂ (l) + 2e ¹⁻	⇌	2Br ¹⁻	+1.09
In ³⁺ + 3e ¹⁻	⇌	In(s)	-0.34	ClO ₄ ¹⁻ + 2H ¹⁺ + 2e ¹⁻	⇌	ClO ₃ ¹⁻ + H ₂ O	+1.19
Co ²⁺ + 2e ¹⁻	⇌	Co(s)	-0.28	O ₂ (g) + 4H ¹⁺ + 4e ¹⁻	⇌	2H ₂ O	+1.23
Ni ²⁺ + 2e ¹⁻	⇌	Ni(s)	-0.23	Cr ₂ O ₇ ²⁻ + 14H ¹⁺ + 6e ¹⁻	⇌	2Cr ³⁺ + 7H ₂ O	+1.33
Sn ²⁺ + 2e ¹⁻	⇌	Sn(s)	-0.14	Cl ₂ (g) + 2e ¹⁻	⇌	2Cl ¹⁻	+1.36
Pb ²⁺ + 2e ¹⁻	⇌	Pb(s)	-0.13	Au ³⁺ + 3e ¹⁻	⇌	Au(s)	+1.50
2H ¹⁺ + 2e ¹⁻	⇌	H ₂ (g)	0.00	MnO ₄ ¹⁻ + 8H ¹⁺ + 5e ¹⁻	⇌	Mn ²⁺ + 4H ₂ O	+1.51
Sn ⁴⁺ + 2e ¹⁻	⇌	Sn ²⁺	+0.15	PbO ₂ (s) + 4H ¹⁺ + SO ₄ ²⁻ + 2e ¹⁻	⇌	PbSO ₄ (s) + 2H ₂ O	+1.69
Cu ²⁺ + e ¹⁻	⇌	Cu ¹⁺	+0.16	H ₂ O ₂ + 2H ¹⁺ + 2e ¹⁻	⇌	2H ₂ O	+1.76
AgCl(s) + e ¹⁻	⇌	Ag(s) + Cl ¹⁻	+0.22	S ₂ O ₈ ²⁻ + 2e ¹⁻	⇌	2SO ₄ ²⁻	+2.01
PbO ₂ (s) + 2H ¹⁺ + 2e ¹⁻	⇌	PbO(s) + H ₂ O	+0.28	O ₃ (g) + 2H ¹⁺ + 2e ¹⁻	⇌	O ₂ (g) + H ₂ O	+2.07
Cu ²⁺ + 2e ¹⁻	⇌	Cu(s)	+0.34	F ₂ (g) + 2e ¹⁻	⇌	2F ¹⁻	+2.87

* These half-cell potentials for O₂/H₂O and H₂O/H₂ couples are for neutral (pH = 7) water and are not standard reduction potentials where [OH¹⁻] or [H¹⁺] = 1.0 M.

Appendix F

Balancing Redox Reactions

F.1 THE HALF-REACTION METHOD

We used this method in Section 10.5, *CAMS*, where redox reactions were written as the sum of tabulated half-reactions. In this process, each half-reaction must be multiplied by an integer that makes the number of electrons gained in the reduction half-reaction equal to the number of electrons lost in the oxidation process. In this section, we discuss how those half-reactions are constructed.

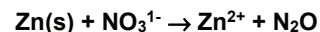
Charge and mass balance of redox reactions by the half-reaction method are accomplished by following the steps outlined below:

- Step 1 **Divide the reaction into an oxidation half-reaction and a reduction half-reaction.** The half-reactions should show only the species involved in the oxidation and reduction processes. For simplicity, the states of the reactants and products are omitted during the balancing procedure.
- Step 2 **Balance the atoms in the half reactions other than O and H with coefficients where necessary.**
- Step 3 **Balance the oxygen atoms by adding water to the side that is oxygen deficient.**
- Step 4 **Balance the hydrogen atoms with H^{1+} ions.**
- Step 5 **Balance the charge by adding electrons to the side with the more positive or less negative total charge.** The charge on each side is the sum of the charges of all of the *ions* on that side. The half-reactions are now balanced if the reactions occur in acidic solution.
- Step 5a **(Basic solutions only) Add OH^{1-} to both sides to eliminate the H^{1+} ions on one side.** The number of hydroxide ions added is equal to the number of H^{1+} ions in the equation. In Step 4, hydrogen atoms were balanced with H^{1+} ions. Although the use of H^{1+} ions is acceptable in an acidic solution, it is unacceptable in a basic solution where there is an excess of OH^{1-} . Thus, the H^{1+} ions are changed into OH^{1-} ions and H_2O molecules in this step because $OH^{1-} + H^{1+} \rightarrow H_2O$.

- Step 6 **Determine the lowest common multiple (LCM) of the electrons gained and lost.** This is the number of electrons transferred in the redox process. Multiply each half-reaction by the integer required to make the number of electrons gained or lost equal to the number that is transferred.
- Step 7 **Add the two half-reactions.** The electrons must cancel, but also *be careful that the final reaction does not contain the same substance on both sides of the equation.* If a substance does appear on both sides, subtract the smaller number of moles from each side, thus eliminating it from one side. The states of the reactants and products are now placed back into the reaction.
- Step 8 **Check the atom and charge balance.**

Example F.1

Balance the following reaction in acidic solution:



- Step 1 Zinc metal is oxidized and nitrate ion is reduced.
- Step 2 The zinc atoms in the Step 1a reaction are already balanced, but the nitrate ions must be multiplied by two to balance the nitrogen atoms.
- a) $Zn \rightarrow Zn^{2+}$ b) $2NO_3^{1-} \rightarrow N_2O$
- Step 3 The zinc half-reaction contains no other atoms and is unaffected by this step. Reaction b in Step 2 has six oxygen atoms on the left but only one on the right. We, therefore, add five water molecules to balance the oxygen atoms.
- a) $Zn \rightarrow Zn^{2+}$ b) $2NO_3^{1-} \rightarrow N_2O + 5H_2O$
- Step 4 There are 10 hydrogen atoms on the right side of the Step 3b reaction and none on the left side. Therefore, ten H^{1+} ions must be added to the left side to balance the hydrogen atoms.
- a) $Zn \rightarrow Zn^{2+}$ b) $10 H^{1+} + 2NO_3^{1-} \rightarrow N_2O + 5H_2O$

Step 5 We now balance charge by adding electrons to the more positive side of each half-reaction in Step 4. The left side of the Step 4a reaction has no charge, but the right side carries a +2 charge. Two electrons must, therefore, be added to the right side of the Zn half-reaction. The right side of the Step 4b reaction carries no charge while the left side carries a charge of +8 (+10 - 2 = 8), so eight electrons must be added to the more positive side.



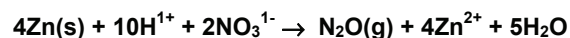
The two half reactions are now balanced.

Step 5a Not necessary in acidic solution.

Step 6 Zinc undergoes a two-electron oxidation while nitrate undergoes an eight-electron reduction. LCM - eight, and eight electrons are therefore transferred in this reaction. The zinc half-reaction is multiplied by four to get the eight electrons.



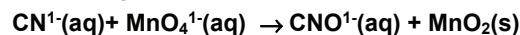
Step 7 The two half-reactions can now be added, and the states of the reactants and products are also added at this point.



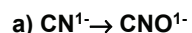
Step 8 The number of each atom and the overall charge (+8) balance.

Example F.2

Balance the following reaction in basic solution:

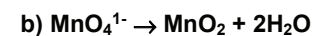


Step 1 Write abbreviated half-reactions.

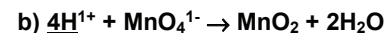
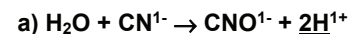


Step 2 The atoms other than oxygen and hydrogen are already balanced.

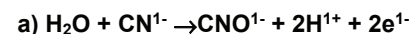
Step 3. Balance oxygen atoms with water.



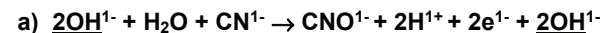
Step 4 Balance hydrogen atoms with H^{1+} .



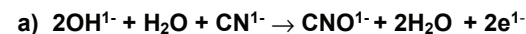
Step 5 Balance charge with electrons. The charge on the left side of the Step 4a reaction is -1, but it is +1 (-1 + 2 = 1) on the right side, so two electrons must be added to the right side. The charge on the left side of reaction b in Step 4 is +3 (+4 - 1 = 3) while it is zero on the right. Consequently, three electrons must be added to the left side.



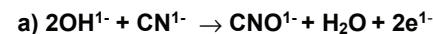
Step 5a This reaction takes place in a basic solution where OH^{1-} ions are plentiful and H^{1+} ions are scarce. Consequently, we must replace the H^{1+} ions in the two half-reactions shown in Step 5. We do this by adding OH^{1-} ions to both sides of each equation. The number of OH^{1-} ions added must equal the number of H^{1+} ions present in the reaction. Consequently, we must add 2OH^{1-} ions to both sides of reaction a in Step 6.



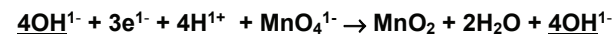
Substituting $2\text{H}_2\text{O}$ for $(2\text{H}^{1+} + 2\text{OH}^{1-})$ on the right side of the equation yields the following.



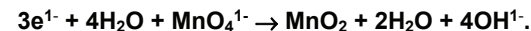
The above equation shows water on both sides. Consequently, we must subtract one H_2O molecule from each side to eliminate water from the left side and obtain the balanced half-reaction in basic solution.



Reaction b in Step 5 requires the addition of 4OH^{1-} to each side.



Substituting $4\text{H}_2\text{O}$ for $(4\text{H}^{1+} + 4\text{OH}^{1-})$ on the left side of the equation yields,

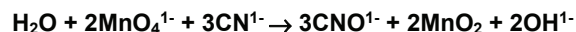
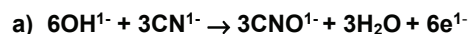


Once again, the reaction contains water on both sides, so we subtract two water molecules from each side to obtain the final balanced half-reaction in basic solution.



Step 6 The LCM of two and three is six. Consequently, the overall reaction is a six-electron transfer. Reaction a must be multiplied by three and reaction b by two. The result is shown in Step 7 where they are added.

Step 7 The two half-reactions obtained in Step 6 are added. The six electrons cancel. In addition, the six hydroxide ions on the left side of reaction a cancel six of the eight hydroxide ions appearing on the right side of reaction b, and the three waters appearing on the right side of reaction a cancel three of the four water molecules on the left side of reaction b.



Step 8 The atoms and total charge (-5 on each side) balance.

F.2 THE OXIDATION STATE CHANGE METHOD

The half-reaction method is fine for ionic reactions, but it is not easily applied to molecular reactions where there is no charge to balance. The oxidation state change method is much more applicable in these instances. To balance a reaction by the oxidation state change method,

Step 1 Identify the substances whose oxidation states are changing. These will usually involve a polyatomic ion or an element.

Step 2 Draw a line connecting the oxidized and reduced forms of the species being oxidized and a line connecting the oxidized and reduced forms of the species being reduced.

Step 3 Balance the only those atoms being oxidized and reduced by inserting appropriate coefficients into the equation.

Step 4 Assign oxidation states to the oxidized and reduced atoms. Place the oxidation states of the atoms on the connecting line. If more than one atom is oxidized or reduced, place the sum of the oxidation states on the line.

Step 5 Determine the number of electrons gained or lost in each process and place the numbers on the lines drawn in Step 2.

Step 6 Determine the lowest common multiple (LCM) of the electrons gained and lost. This is the number of electrons transferred during the reaction.

Step 7. Multiply the coefficients of the species involved in the oxidation and reduction processes by the integer required to make the electrons gained and the electrons lost equal to the number of electrons transferred as determined in Step 6.

Step 8. Balance any other non-oxygen atoms by inspection. If the reaction contains ions, balance the charge with H^{1+} in acidic solution or OH^{1-} in basic solution.

Step 9. Balance the hydrogen atoms by adjusting the coefficient of water.

Step 10. The reaction should now be balanced. The reaction can be checked by making sure that the oxygen atoms balance.

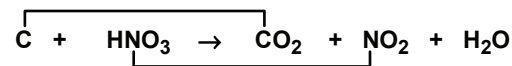
Example F.3

Balance the following by the oxidation state change method.



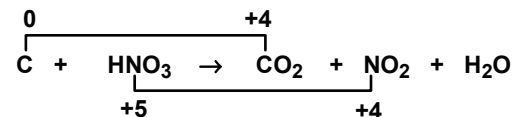
Step 1 Elemental C is oxidized to CO_2 , and nitric acid (contains a polyatomic ion) is reduced to NO_2 .

Step 2 Connect the oxidized and reduced forms involved in the redox process.



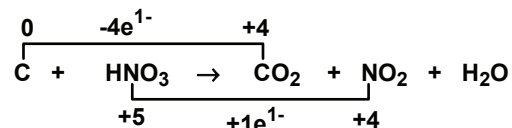
Step 3 The carbon atoms and the nitrogen atoms are already balanced.

Step 4 Assign oxidation states and place on connecting line.



Step 5 Determine the number of electrons gained or lost in each process. Carbon's oxidation state increases from zero to four, so

it loses four electrons. The nitrogen atom is +5 in HNO_3 and +4 in NO_2 , so it has gained one electron.



Step 6 The LCM of one and four is four.

Step 7 The coefficients of the nitrogen-containing species must be multiplied by four to make the number of electrons gained by nitric acid equal to the number lost by carbon.



Step 8 There is no charge to balance nor are there any atoms other than hydrogen or oxygen to balance.

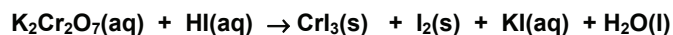
Step 9 There are four hydrogens on the left, so the coefficient of water must be 2.



Step 10 The oxygen atoms balance (12 on each side), so the equation is balanced.

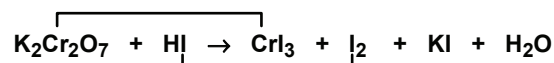
Example F.4

Balance the following reaction by the oxidation state change method.

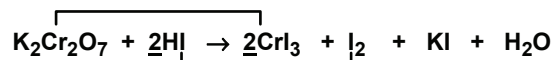


Step 1 The redox processes involve the reaction of a polyatomic ion ($\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{CrI}_3$) and the formation of an element ($\text{HI} \rightarrow \text{I}_2$).

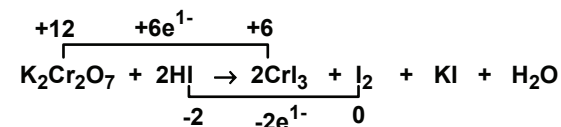
Step 2 Connect the oxidized and reduced forms involved in the redox process.



Step 3 Balance the Cr and I atoms. Two HI and two CrI_3 are required to balance the two I atoms in I_2 and the two Cr atoms in $\text{K}_2\text{Cr}_2\text{O}_7$.



Steps 4/5 Assign oxidation numbers, place them on the connecting line, and determine the number of electrons gained or lost in each process. The oxidation states of the Cr atoms are +6 in $\text{K}_2\text{Cr}_2\text{O}_7$ and +3 in CrI_3 , but there are two Cr atoms on each side, so we place a +12 and +6 on the connecting line. The two iodides on the left are each -1, so a -2 is placed above them while the iodine atoms on the right are each zero.



Step 6 LCM = 6, so this reaction involves a six-electron transfer.

Step 7 The coefficients of the HI/I_2 half-reaction must be multiplied by three to make the number of electrons gained equal to six.



Step 8 There is no charge, but the potassium and iodine atoms are not balanced. We place a two in front of KI to balance the two potassium atoms in $\text{K}_2\text{Cr}_2\text{O}_7$.



Now there are 14 iodine atoms on the right side, so the coefficient of HI must be 14. Note only six of the iodines are oxidized; the others are required for mass balance.



Step 9 Balance the hydrogen atoms with the coefficient of water.



Step 10 The oxygen atoms balance (7 on each side), and so the equation is balanced.

F.3 EXERCISES

1. Complete and balance the following reactions in acidic solution:
 - a) $\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+}$
 - b) $\text{MnO}_2 + \text{Cl}^{1-} \rightarrow \text{Mn}^{2+} + \text{Cl}_2$
 - c) $\text{CH}_3\text{OH} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} + \text{HCOOH}$
2. Complete and balance the following reactions in acidic solution:
 - a) $\text{I}^{1-} + \text{H}_2\text{O}_2 \rightarrow \text{I}_2$
 - b) $\text{C}_2\text{H}_4 + \text{MnO}_4^{1-} \rightarrow \text{Mn}^{2+} + \text{CO}_2$
 - c) $\text{Ni(s)} + \text{VO}^{2+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + \text{V}^{3+}(\text{aq})$
3. Complete and balance the following reactions in basic solution:
 - a) $\text{Mn}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2$
 - b) $\text{MnO}_4^{1-}(\text{aq}) + \text{NO}_2^{1-}(\text{aq}) \rightarrow \text{MnO}_2(\text{s}) + \text{NO}_3^{1-}(\text{aq})$
 - c) $\text{NO}_3^{1-}(\text{aq}) + \text{Pb(s)} \rightarrow \text{NH}_3(\text{aq}) + \text{Pb(OH)}_4^{2-}(\text{aq})$
4. Complete and balance the following reactions in basic solution:
 - a) $\text{Cl}_2 + \text{S}_2\text{O}_3^{2-} \rightarrow \text{Cl}^{1-} + \text{S}_4\text{O}_6^{2-}$
 - b) $\text{H}_2\text{O}_2 + \text{ClO}_2 \rightarrow \text{ClO}_2^{1-} + \text{O}_2$
 - c) $\text{I}_2 \rightarrow \text{I}^{1-} + \text{IO}_3^{1-}$
5. Balance the following reactions:
 - a) $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + \text{NO} + \text{H}_2\text{O}$
 - b) $\text{NO} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{N}_2$
 - c) $\text{H}_2\text{S} + \text{H}_2\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$
6. Balance the following reactions:
 - a) $\text{C} + \text{HNO}_3 \rightarrow \text{NO}_2 + \text{CO}_2 + \text{H}_2\text{O}$
 - b) $\text{H}_2\text{SO}_4 + \text{HI} \rightarrow \text{H}_2\text{S} + \text{I}_2 + \text{H}_2\text{O}$
 - c) $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$

Glossary

A

Absolute (or Kelvin) temperature scale is used for the temperature in all calculations involving T. The unit is the kelvin (K). The average kinetic energy of the molecules in a system is directly proportional to its temperature in kelvins.

Absolute zero is 0 K, which is $-273.16\text{ }^{\circ}\text{C}$. It is the temperature at which molecules have no kinetic energy.

Absorbance is a measure of the amount of light absorbed by a substance. The absorbance of a solution depends upon both the concentration and the molar absorptivity of the absorbing substance at the wavelength of the light, and the distance through the solution that the light travels. See Beer's Law.

Absorption of a photon increases the energy of an atom or a molecule by the energy of the photon ($h\nu$). A photon can be absorbed only if its energy matches the energy difference between two energy levels in the atom or molecule.

An **absorption spectrum** presents the absorbance of a substance as a function of the wavelength or frequency of light.

The **acceptor orbital** is the orbital on an oxidizing agent that accepts the transferred electrons in a redox reaction.

The **acid dissociation or ionization constant** is the equilibrium constant for the reaction of an acid with water: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{1+} + \text{A}^{1-}$.

An **acidic salt** is a salt in which the acidity of the cation is greater than the basicity of the anion.

An **acidic solution** is one with $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$. As a result, $\text{pH} < 7.0$ at $25\text{ }^{\circ}\text{C}$ for acidic solutions.

The **activation energy** is the energy of the transition state relative to that of the reactants or products. It is the minimum energy that the reactants must have in order for a reaction to occur.

An **active electrode** is one that is a participant in a reaction. For example, a copper electrode in a $\text{Cu}^{2+} + 2\text{e}^{1-} \rightarrow \text{Cu}$ half-cell is active because copper metal participates in the reaction.

The **activity** is the ratio of the concentration of a substance to its concentration in the standard state. It is unitless. The activities of pure solids and liquids are unity. The activity of a gas equals the partial pressure of the gas in atmospheres divided by 1 atm, while the activity of a solute equals its molar concentration divided by 1 M.

Addition polymers are formed by addition reactions.

An **addition reaction** is a reaction in which two reactants combine to form a single product.

Adhesive forces are forces between different molecules (compare with cohesive force).

An **alcohol** is a compound with the general formula R-OH , where R is a generic group of atoms and OH is the hydroxyl group.

An **alkali metal** is an element that belongs to Group 1A.

An **alkaline earth metal** is an element that belongs to Group 2A.

An **alkane** is a saturated hydrocarbon, *i.e.*, a hydrocarbon that contains no multiple bonds.

An **alkene** is a hydrocarbon that contains carbon-carbon double bonds.

An **alkyl group** is an organic group formed by removing one hydrogen atom from an alkane

Allotropes are different crystalline forms of the same element that have different properties. Graphite and diamond are allotropes of carbon.

Alpha decay is the emission of an alpha particle. It is common among the heavy isotopes because it is the best way to reduce mass.

An **alpha particle** is a helium nucleus.

An **amide** is an amine attached to a carbonyl.

An **amine** is an ammonia molecule in which one or more of the hydrogen atoms have been replaced with other groups.

An **amino acid** is a compound that contains both amine and carboxylic acid functional groups.

Amorphous solids have ordered arrangements of particles over short distances only. This is referred to as local order.

The **ampere (A)** is the SI unit for electrical current. $1\text{ A} = 1\text{ C/s}$.

An **amphiprotic** substance is able to function as either an acid or a base.

An **analyte** is a substance that is being analyzed

The **angstrom (Å)** is 10^{-10} m . It is commonly used for bond lengths because most bond lengths are between 1 and 2 Å.

Angular momentum (L) is a property of a rotating object. It is equal to the mass of the object times its velocity times its distance from the center of rotation; *i.e.*, $L = mvr$.

The **angular momentum quantum number (l)** is an integer between 0 and $n-1$ that defines the shape of an atomic orbital.

An **anion** is a negatively charged ion.

The **anode compartment or electrode** is where oxidation occurs in an electrochemical cell.

Antibonding interactions occur in molecular orbitals when the atomic orbitals on adjacent atoms used to construct the molecular orbital have opposite phases.

An **antibonding MO** is one in which the number of antibonding interactions exceeds the number of bonding interactions.

An **antiferromagnetic** substance is not magnetic because all of its electron spins are paired.

An **Arrhenius acid** is a substance that contains H atoms and produces H^{1+} ions in water.

An **Arrhenius base** is a substance that contains OH and produces OH^{1-} ions in water.

The **Arrhenius equation** relates a rate constant to the temperature and activation energy of the reaction: $k = Ae^{-E_a/RT}$ or $\ln k = \ln A - E_a/RT$

An **Arrhenius plot** is a plot of $\ln k$ (rate constant) versus $1/T$. The slope is $-E_a/R$ and the intercept is $\ln A$ (the pre-exponential).

Atoms are the building blocks of matter. Elements consist of only one type of atom.

Atomic mass or atomic weight is the average mass of the atoms of an element relative to that of carbon-12, which is assigned a relative mass of exactly 12.

The **atomic mass unit (amu)** is a unit of mass that is $1/12$ the mass of a single atom of carbon-12.

The **atomic number (Z)** is the number of protons in the nucleus. It identifies the atom.

The **atomization energy (ΔH_{atom})** is the energy required to break all of the bonds in a molecule in the gas phase to produce the atoms.

Autoionization of water is the reaction of water with itself: $2H_2O \rightarrow H_3O^{1+} + OH^{1-}$.

Avogadro's law states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Avogadro's number is 6.02×10^{23} . It is the number of items in a mole.

B

The **band gap** is the energy separation between the valence and conduction bands of a metallic or covalent solid.

The **band or belt of stability** is the region of a plot of the number of neutrons versus the number of protons in a nucleus in which the stable nuclei fall.

Band theory is an extension of MO theory to metals. A very large number of atomic orbitals in a metal combine to form a very large number of molecular orbitals. The resulting molecular orbitals are so close in energy that they form an energy band.

A **barometer** is a device used to determine atmospheric (or barometric) pressure.

A **base pair** consists of two complementary, N-containing bases whose structures maximize H-bonding between them. Guanine and cytosine are base pairs as are adenine and thymine. Base pairs hold the two strands of DNA together.

A **basic salt** is one in which the basicity of the anion exceeds the acidity of the cation.

Basic solutions are solutions in which $[H_3O^{1+}] < [OH^{1-}]$. A basic solution has a $pH > 7.0$ at $25^\circ C$.

A **battery** is a galvanic cell or a collection of galvanic cells. Batteries harness the free energy changes in redox reactions.

Beer's Law: The absorbance (A) of a solution equals the product of its molar absorptivity (ϵ), its molar concentration (c), and the path length (l) of the cell in which its absorbance is measured; $A = \epsilon lc$.

Belt of stability See band of stability.

Beta decay is the ejection from the nucleus of an electron produced by the decay of a neutron. β -decay reduces the neutron/proton ratio, so it is common among nuclei that lie above the band of stability.

A **beta particle (β)** is a high energy electron.

A **bimolecular** process is one that involves two molecules.

Binary compounds are composed of only two elements; Al_2O_3 is a binary compound because it contains only Al and O.

The **binding energy** is the energy that holds the nucleus together. It is related to the mass defect by $\Delta E = \Delta mc^2$.

Blackbody radiation is the light emitted by a solid when it is heated.

A **body-centered cubic (bcc)** unit cell is one in which the particles that lie on the corners are also in the body center.

The **boiling point** is the temperature at which the vapor pressure equals the external pressure. If the external pressure is 1 atm, then the temperature is called the **normal boiling point**.

Boiling point elevation (ΔT_b) is the increase in the boiling point caused by the addition of a non-volatile solute to a solvent.

The **boiling point elevation constant** (k_b) is the proportionality constant that relates the boiling point elevation of a solution to its colligative molality. $\Delta t_b = k_b m_c$.

The **bond angle** is the angle formed by two bonds to an atom.

The **bond dipole** is a measure of bond polarity. It is represented by an arrow pointing from the less electronegative atom toward the more electronegative atom.

The **bond energy** or **bond dissociation energy** is the amount of energy required to break one mole of bonds *in the gas phase*.

The **bond length** is the distance between two bound nuclei.

The **bond order** is the number of shared pairs in a bond. As the bond order increases, the length of the bond decreases and its strength increases. The bond order in a diatomic molecule is also equal to $1/2$ the difference between the number of its bonding and antibonding electrons.

The **bonding electrons** are the shared electrons in a covalent bond.

A **bonding interaction** occurs in a molecular orbital when the phases of the atomic orbitals of two adjacent atoms are the same.

A **bonding MO** is a molecular orbital in which the number of bonding interactions exceeds the number of antibonding interactions.

Boyle's law states that the pressure-volume product of a fixed amount of gas at constant temperature is constant. $PV = k(n,T)$.

A **branched chain hydrocarbon** contains a chain of carbons atoms in which at least one carbon is bound to three or four other carbon atoms.

A **Brønsted acid** is a proton donor.

A **Brønsted base** is a proton acceptor.

A **buffer** is a solution that contains a weak acid and its conjugate base in appreciable and comparable amounts. Buffers reduce pH changes brought about by the addition of strong acids and bases.

The **buffer capacity** is the amount of strong acid or base on which a buffer can act.

The **buffer range** is the pH range over which a buffer can function.

A **bulk property** is a property of a material (such as a pure solid or liquid) as opposed to individual atoms or molecules. Bulk properties are different than the atomic or molecular properties of its components due to the interactions between the components.

C

The **calorie (cal)** is the heat required to raise 1 g of water 1 °C. 1 cal = 4.184 J. The dietary calorie (Cal) is actually a kilocalorie (kcal).

A **calorimeter** is a piece of equipment used to determine the amount of heat released or absorbed during a reaction.

A **carbonyl** contains the C=O group.

A **carboxyl group** is the combination of a carbonyl (C=O) and a hydroxyl (O-H) group. Molecules with carboxyl groups are called carboxylic acids (RCOOH), and the deprotonated ions are called carboxylates (RCOO¹⁻).

A **catalyst** is a substance that speeds up a reaction but is unchanged by it.

The **cathode compartment or electrode** is where reduction occurs in an electrochemical cell.

A **cathode ray** is light emitted from the cathode (negative electrode) of a gas discharge tube.

A **cation** is a positively charged ion.

The **cell potential** is the potential difference between the cathode and anode of an electrochemical cell.
 $\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cathode}} - \mathcal{E}_{\text{anode}}$

The **Celsius (or centigrade) scale** is the temperature scale based on the freezing (0 °C) and boiling points (100 °C) of water.

A **chain reaction** is a reaction in which a product initiates more reaction.

Charles' law states that the volume of a fixed amount of gas at constant pressure is proportional to its absolute temperature. $V = k(n,P)T$

A **chemical property** is a property of a substance that requires the substance to change into another substance. Hydrogen and oxygen react to produce water is a chemical property of hydrogen.

Chemistry is that branch of science that deals with matter and the changes it undergoes.

A **cis** configuration is one in which two groups are on the same side of a bond or atom.

Cohesive forces are forces between like molecules (compare with adhesive force).

The **colligative concentration** is the concentration of all solute particles in a solution. The colligative concentration of a solute equals its concentration times its van't Hoff factor.

Colligative properties are those properties of a solution that depend upon the concentration, but not the identity, of the solute particles.

The **collision frequency** is the number of collisions per unit volume per unit time, which normally has units of (moles of collisions)/(liter·s).

Combustion is a reaction with oxygen.

A **common ion** is an ion that appears in an equilibrium but has at least two sources.

A **complex ion** is an ion in which a central metal is surrounded by molecular or anionic ligands.

A **compound** is a pure substance that consists of more than one element.

The **concentration** of a solute is the amount of solute divided by the volume in which it is contained.

A **concentration cell** is an electrochemical cell in which the two compartments differ only in their concentrations. The cell potential depends upon the concentration difference.

Condensation is the process of converting a vapor into its liquid.

Condensation polymers are formed by condensation reactions.

A **condensation reaction** is a reaction in which two reactants combine to form two products (one of which is often a small molecule such as water or an alcohol).

The **conduction band** is the lowest energy unfilled band in a solid that has no partially filled bands. Electrons in a conduction band are free to move throughout the metal due to the presence of unfilled orbitals. Thus, electrons can conduct electricity only when they are in the conduction band.

A **conductor** is a substance that conducts electricity at all temperatures. Its conduction decreases slightly with increasing temperature.

A **conjugate acid-base pair** is a Brønsted acid and base that differ by one proton only.

Connectivity is the manner in which the atoms in a molecule are connected.

Constitutional isomers are compounds with the same formula but different connectivities.

A **continuous chain hydrocarbon** is a chain of carbon atoms in which no carbon is bound to more than two other carbon atoms.

A **continuous spectrum** is a spectrum in which all wavelengths of light in the region are present. Thus, they merge into one another continuously. A rainbow is a continuous spectrum of visible light.

A **coordinate covalent bond** is a bond in which both bonding electrons are contributed by the same atom. The bonds formed in Lewis acid-base reactions are coordinate covalent because both bonding electrons always come from the base.

The **coordination number** of a particle is the number of its nearest neighbors in a crystal or in a compound.

Core electrons are the tightly bound electrons that are unaffected by chemical reactions. They reside in filled sublevels and form a spherical shell of negative charge around the nucleus that affects the amount of nuclear charge that the outermost electrons experience.

Corrosion is the natural oxidation of a metal.

The **coulomb (C)** is the SI unit of electrical charge. The charge on one electron is 1.602×10^{-19} C.

Coulomb's law states that two charged particles experience a force that is proportional to the product of their charges and varies inversely with the dielectric of the medium and the square of the distance that separates them. Negative forces are attractive, while positive forces are repulsive.

A **counter ion** is an ion that accompanies a desired ion

in order to maintain the electrical neutrality of the compound that contains the desired ion. Counter ions are spectator ions in net chemical equations.

A **covalent bond** results when electrons are shared. It can be viewed as the attraction of the bonding electrons for the bound nuclei.

The **covalent radius** of an atom X is equal to one-half of the distance between the X atoms in X_2 .

The **critical mass** is the minimum mass of a radioactive material required to maintain a chain reaction.

The **critical point** is the temperature and pressure beyond which the liquid cannot exist. Substances beyond their critical point are supercritical fluids.

The **critical pressure** is the pressure required to liquefy a gas at its critical temperature.

The **critical temperature** is the highest temperature at which a gas can be liquefied.

A **crystal orbital** is to a crystal what a molecular orbital is to a molecule.

Crystalline solids are solids with well defined and ordered repeat units. The order, which exists throughout the crystal, is said to be long range order.

D

Degrees of freedom are the basic set of motions (translations, rotations, and vibrations) that a molecule undergoes. The kinetic energy of a molecule is distributed amongst its degrees of freedom. A molecule with N atoms has 3N degrees of freedom.

Delocalized electrons or bonds are spread over several atoms.

Density is the mass to volume ratio of a substance or solution. $d = m/V$

The **density of states** is the number of allowed energy states in a region of energy.

Deposition is the process in which a vapor is converted into its solid.

A **detergent** is a substance that has both a hydrophobic region that interacts well with nonpolar molecules such as grease, and a hydrophilic region that interacts well with polar molecules such as water.

Diamagnetism is the tendency of certain atoms not to be attracted by a magnetic field. It is an atomic property associated with atoms that have no unpaired electrons.

Diatomic molecules contain two and only two atoms.

The **dielectric constant** (ϵ) is a number that relates the ability of a medium to shield two charged particles from one another. A medium with a high dielectric constant shields the charges better than one with a low constant.

A **dipole** consists of two electrical poles, one positive and one negative. Bonds dipoles arise between atoms of different electronegativities. A molecular dipole is the vector sum of its bond dipoles.

Dipole-dipole or dipolar forces are the inter-molecular forces that result from the interaction of the oppositely charged poles of two polar molecules.

Dispersion forces are forces between molecules that result from the interaction of temporary or induced dipoles. Dispersion forces increase approximately with molecular size.

The **dissociation constant** is the equilibrium constant for the dissociation of a complex ion into its component ions and/or molecules. Also see acid dissociation constant.

The **dissociation or bond energy** is the energy required to break one mole of bonds in the gas phase.

Dissolution is the process in which an ionic substance dissolves in water to produce ions.

A **donor orbital** is the orbital on the reducing agent that contains the electrons to be transferred in a redox reaction.

The **double helix** is the structure adopted by DNA. It consists of a pair of intertwined polynucleotide strands held together by hydrogen bonding between base pairs.

Dynamic equilibria are attained when two competing processes occur at equal rates. Contrast to a static equilibrium where the competing processes stop.

E

Effective nuclear charge (Z_{eff}) is the nuclear charge experienced by an electron in an atom. It is less than the nuclear charge due to shielding by the other electrons.

An **electrical current** is the rate at which charge flows through a circuit. A current of one ampere is a rate of one Coulomb of charge per second.

An **electrochemical cell** is a device used to extract the free energy change of a spontaneous redox reaction (see Galvanic cells) or to inject the energy required to drive a redox reaction that is not spontaneous (see electrolytic cells).

Electrochemistry is the combination of electrical conduction through a circuit and electron transfer reactions.

An **electrode** is a metal that provides a surface at which electrons can be transferred between an electrical circuit and a reactant in a redox reaction.

Electrodes are active if they participate in the reaction and passive if they do not.

Electrolysis is a non-spontaneous redox reaction that is driven uphill in free energy by the application of an external electrical potential.

An **electrolyte** is a material that produces ions when dissolved in water. Electrolytes can be weak or strong depending upon the extent to which they produce ions. Substances that dissolve in water as molecules rather than ions are called non-electrolytes.

An **electrolytic cell** is an electrochemical cell that converts electrical potential energy into chemical potential energy. See electrolysis.

Electrolytic conduction is conduction of electricity through a solution as a result of the migration of ions in the solution.

Electromagnetic radiation is an electric and a magnetic field oscillating perpendicular to one another that travels through space in the form of radio waves, microwaves, infrared waves, visible light, ultraviolet light, *etc.*

An **electron** is the basic quantity of negative charge. It carries a charge of -1.602×10^{-19} C and has a mass of 5×10^{-4} amu.

Electron capture is the capture of a core electron by the nucleus. It converts a proton into a neutron.

The **electron configuration** of an atom is a listing of the sublevels that are occupied and the number of electrons in them.

Electron density is the probability of finding an electron in a particular region of space. The electron density is high in regions where the probability of finding an electron is high.

Electronegativity (χ) is a relative measure of the ability of an atom to attract bonding electrons to itself. Atoms with high electronegativities have unfilled orbitals that are low in energy.

An **electronic transition** is the changing of the energy of an electron from one quantum state to another.

An **element** is a pure substance that cannot be broken down into a simpler substance by chemical means.

The **elemental composition** of a compound is a listing of the relative masses, usually expressed as percents, of the elements in the compound.

An **elementary reaction** is a reaction that occurs in one step.

Emission is the ejection of a photon by an atom or a molecule. The energy of the atom or molecule decreases by the energy of the photon ($h\nu$).

An **empirical or simplest formula** is a chemical formula that indicates only the smallest whole number ratio of the atoms present in the compound.

Enantiomers are two molecules that are non-superimposable mirror images of one another.

An **endothermic** process absorbs heat.

The **end point** is the point at which an indicator changes color. The end point should be nearly the same as the equivalence point.

Energetics is a combination of thermodynamics and kinetics.

Energy is the capacity to do work or to transfer heat.

An **energy band** is a region of allowed energy in a metal in which there is no separation between adjacent energy levels.

The **energy of interaction** is the energy of two interacting particles relative to the energy of the

two particles when they are not interacting. Energies of interaction in chemistry result from the electrostatic interactions.

The **enthalpy or heat of combustion** is the heat absorbed when one mole of a substance reacts with oxygen. Heats of combustion are negative because they are exothermic.

The **enthalpy or heat of reaction** is the heat absorbed by a reaction run at constant temperature and pressure. A negative heat of reaction simply means that the heat is given off not absorbed.

Entropy is the thermodynamic measure the number of ways in which a system can distribute its energy. It is often related to the disorder in the system.

An **enzyme** is a biological compound (usually a protein) that acts as a catalyst.

The **equilibrium constant (K)** is the value of the reaction quotient (Q) when equilibrium activities are used.

The **equivalence point** is the point in a titration at which stoichiometric amounts of reactants are present.

Esters are compounds with the general formula RCOOR' , *i.e.*, two groups connected by a carboxyl group.

Esterification is a condensation reaction between a carboxylic acid and an alcohol to produce an ester and water.

Evaporation is the conversion of a liquid to its vapor.

An **excited state** is an allowed state that is not the lowest energy state.

An **exothermic** process gives off heat.

Exponential decay is a decrease in concentration that goes as e^{-x} . First order reactions undergo exponential decay: $[A] = [A]_0 e^{-kt}$.

An **extensive property** is one that depends upon the amount of material. Mass and volume are extensive properties. Also see intensive property.

An **extensive reaction** is one with a large equilibrium constant. If a reaction is extensive, then the equilibrium concentration of least one of the reactants will be very small.

F

A **face centered cubic (*fcc*)** unit cell is one in which the atoms that are located in the corners are also found in the centers of the faces.

The **factor label method** is a method that uses the labels (units) of the factors to determine the order and manner in which the factors should be used to convert one quantity into another.

Family See group.

The **Faraday (\mathcal{F})** is the charge of one mole of electrons. $1\mathcal{F} = 96,485 \text{ C/mol}$.

A **fatty acid** is a carboxylic acid with a long hydrocarbon chain.

The **Fermi level** the highest occupied energy level in a band.

A **ferrimagnet** is a magnetic material whose particles have opposing but unequal spins.

A **ferromagnet** is a magnetic material whose particles have aligned spins.

Ferromagnetism is a bulk magnetism in a material (such as iron) resulting from the alignment of the spins of adjacent atoms in the same direction.

The **first law of thermodynamics** states that energy is neither created nor destroyed in any process.

Fission is the process in which a heavy nucleus splits into lighter nuclei.

Formal charge is the charge an atom would have if the bonds were completely covalent, *i.e.*, if its bonding electrons were assigned equally between the atoms in each bond.

The **formation constant (K_f)** is the equilibrium constant for the formation of a complex ion. For example, $\text{Ag}^+ + 2\text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^+$.

Free energy is the energy that is required to drive a non-spontaneous process. The negative of the free energy is the amount of work that can be extracted from a spontaneous process.

The **freezing point depression (ΔT_f)** is the decrease in the freezing point of a liquid caused by the addition of a non-volatile solute.

The **frequency** of a light wave is the number of oscillations per second that the wave undergoes.

A **functional group** is a group of connected atoms within a molecule that has a specific reactivity.

Fusion is the state change from a solid to a liquid or the combination of two lighter nuclei to produce a heavier one.

G

A **galvanic cell** is a spontaneous electrochemical cell. Galvanic cells convert chemical potential energy into electrical potential energy.

Geometric isomers are stereoisomers that differ because two groups can be on the same side (*cis* isomer) or on the opposite side (*trans* isomer) of some structural feature.

Gibbs free energy (ΔG) is the change in free energy at constant temperature and pressure.

The **ground state** is the state of an atom or molecule that has the lowest energy.

A **group (or family)** is a vertical column in the periodic table. The elements in a group have similar properties

H

A **half-cell** is that portion of an electrochemical cell in which one half-reaction takes place.

The **half-life ($t_{1/2}$)** is the time required for one-half of a reactant to disappear.

A **half-reaction** is half of a redox reaction. They represent the electron gain or loss by showing the electrons explicitly. $\text{Ox} + n\text{e}^{1-} \rightarrow \text{Red}$ is the general form of a reduction half-reaction.

A **halogen** is an element that belongs to Group 7A. The common halogens are fluorine, chlorine, bromine, and iodine. The elemental halogens are diatomic.

Hard water contains Mg^{2+} and Ca^{2+} , which form insoluble salts with soaps.

Heat (q) is that form of energy that is transferred as a result of a temperature difference. By definition, q is the heat absorbed by the system, and $-q$ is the heat released by the system.

The **heat capacity (C)** of an object is the amount of heat required to raise the temperature of the object by 1°C or 1 K .

Heat of combustion (ΔH_{comb}) is the heat absorbed when one mole of a substance reacts with oxygen.

Heat of formation (ΔH_f) is the enthalpy change resulting when one mole of a substance is formed from its elements in their standard states.

Heat of fusion (ΔH_{fus}) is the heat required to melt one mole of a substance at its melting point.

Heat of sublimation (ΔH_{sub}) is the heat required to convert one mole of a solid into its gas.

Heat of vaporization (ΔH_{vap}) is the amount of heat required to convert one mole of a liquid into its gas.

The **Henderson-Hasselbalch equation** is used to calculate the pH of a buffer solution.

$$\text{pH} = \text{pK}_a + \log\left(\frac{n_b}{n_a}\right)$$

Hess' law of heat summation states that if a process can be expressed as the sum of several steps, then the enthalpy change of the process is the sum of the enthalpy changes of the steps.

A **heterogeneous catalyst** is in a different phase than the reactants. Typically it is a solid for gas or solution reactions.

A **heterogeneous mixture** is one whose composition varies as in a mixture of water and oil.

A **high spin metal** is one in which the splitting of the d orbitals is small enough that the d electrons remain unpaired in the higher energy set rather than pairing in the lower energy set.

Homo is the abbreviation for the highest occupied molecular orbital.

A **homogeneous catalyst** is in the same phase as the reactants.

A **homogeneous mixture** is a mixture whose composition is the same throughout, *i.e.*, one in which the concentration of each component is the same regardless of the volume that is sampled. Homogeneous mixtures are called solutions.

A **homonuclear diatomic molecule** is one in which the two atoms are the same.

Hund's rule states that the number of electrons with identical spin is maximized when filling the orbitals of a sublevel.

A **hybrid orbital** is an orbital constructed by mixing two atomic orbitals on the same atom. They are used to explain bonding in the valence bond model.

Hybridization is the process by which hybrid orbitals are produced from atomic orbitals.

A **hydrate** is a compound with a characteristic number of water molecules associated with it.

Hydration is the process in which a solute particle interacts with the surrounding water molecules.

A **hydrocarbon** is a compound that contains only carbon and hydrogen.

Hydrogenation is the addition of hydrogen to a compound.

The **hydrogen bond** is an especially strong dipolar interaction that occurs in compounds containing a hydrogen atom attached to N, O, or F.

The **hydronium ion** (H_3O^{1+}) is the conjugate acid of water. Therefore, it is the strongest acid that can be present in aqueous solutions.

A **hydrophilic** molecule interacts well with water.

A **hydrophobic** molecule is excluded from water because it does not interact well with water.

The **hydrophobic effect** is the tendency of water to exclude hydrophobic molecules by establishing an ice-like structure around them.

A **hypothesis** is a proposed explanation of an observation. If a hypothesis proves successful in explaining many other experiments, it becomes a theory, but if it fails to explain a test, it is discarded or modified.

I

An **ideal gas** is a hypothetical gas composed of molecules that do not interact with one another.

The **ideal gas law** is the relationship between the pressure (P), volume (V), temperature (T) and number of moles (n) of an ideal gas. $PV = nRT$.

Ideal gases obey the ideal gas law at all T and P, while real gases deviate at high P and low T.

An **indicator** is a compound that changes color within a small pH range. The pH at which the indicator changes color is called the end point.

An **induced dipole** is a molecular dipole in one molecule caused by the asymmetric charge distribution in a neighboring molecule.

The **instantaneous rate** of a reaction is the rate at a specified time. It is equal to the slope of the concentration vs. time plot at the specified time.

An **insulator** is a substance that does not conduct electricity at reasonable temperatures because its band gap is too large.

An **integrated rate law** expresses the concentration of a reactant as a function of time.

An **intensive property** is independent of sample size. Color and density are intensive properties.

An **intermediate** in a chemical reaction is a substance that is formed and then consumed in the reaction. Intermediates do not appear in the net chemical equation for the reaction.

Intermolecular interactions are between different molecules. Dipolar and dispersion forces are intermolecular interactions.

Intramolecular interactions are within a molecule. Chemical bonds are intramolecular interactions.

An **ion** is a charged chemical species.

The **ion product** (Q_{ip}) is the reaction quotient for the reaction in which a solid dissolves as its ions in solution. $Q_{ip} = K_{sp}$ at equilibrium.

The **ion product constant of water** (K_w) is the equilibrium constant for the reaction $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{1+} + \text{OH}^{1-}$. $K_w = [\text{H}_3\text{O}^{1+}][\text{OH}^{1-}]$, which has a value of 1.0×10^{-14} at 25°C .

An **ionic bond** is an electrostatic (Coulombic) force between oppositely charged ions.

The **ionic radius** of an ion is determined from the distances between it and adjacent ions in an ionic crystal. The distance between the two adjacent ions equals the sum of their ionic radii.

The **ionization energy** is the energy required to remove an electron from an atom or molecule.

Ionizing radiation is high energy radiation that can remove electrons from a substance. X-rays are ionizing radiation.

Two substances are **isoelectronic** if they have the same number of electrons.

Isomers are different molecules with the same formula.

Isotopes are atoms with the same atomic number but different mass numbers, *i.e.*, isotopes have the same number of protons but different numbers of neutrons.

J

The **joule (J)** is the SI unit of energy.

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$$

K

Kaolinite clays are composed of silicate and aluminate layers (aluminosilicates). They are the main component of china clay.

The **kelvin (K)** is the SI unit of temperature. $K = ^\circ\text{C} + 273.15$.

Kinetics is the study of reaction rates and mechanisms.

Kinetic energy ($KE = \frac{1}{2}mv^2$) is energy of motion. Anything in motion has the capacity to do work on another object by simply colliding with it.

Kinetic-molecular theory is the model used to explain the ideal gas law. One of its postulates is that the average kinetic energy of the molecules in a gas is directly proportional to the absolute temperature of the gas.

The **kinetic region** of a reaction is the period of the reaction in which concentrations are changing.

L

A crystal **lattice** is the arrangement of the particles in a crystal. Each particle lies on a lattice site.

A **law** is a statement that summarizes many observations.

The **law of combining volumes** states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

The **law of conservation of energy** is stated by the first law of thermodynamics; $\Delta E_{\text{univ}} = 0$.

The **law of conservation of mass** states that the total mass of reactants and products remains constant during a chemical reaction; *i.e.*, mass is neither created nor destroyed in a chemical reaction.

The **law of definite or constant proportions** states that the elements of a compound are always present in definite proportions by mass.

The **law of multiple proportions** states that the masses of one element that combine with a fixed mass of another element in different compounds of the same elements are in a ratio of small whole numbers.

Le Châtelier's principle states that a system at equilibrium will respond to a stress in such a way as to minimize the effect of the stress.

A **level** or shell is an allowed energy designated by the principal quantum number n .

The **leveling effect** of a solvent requires that no acid in a solvent can be stronger than the conjugate acid of the solvent and no base can be stronger than the conjugate base of the solvent. Thus, hydronium ion is the strongest acid that can exist in water and hydroxide ion is the strongest base.

A **Lewis acid** is a substance with a low lying, empty orbital that can be used to form a covalent bond to a Lewis base. Lewis acidic sites are characterized by less than four electron regions.

A **Lewis acid-base reaction** is the conversion of a lone pair on a Lewis base and the empty orbital on a Lewis acid into a covalent bond between the acid and the base.

A **Lewis base** is a substance with a lone pair that can be shared with a Lewis acid to form a covalent bond between the acid and the base.

A **Lewis structure** is a representation of a molecule that shows all of the valence electrons. The non-bonding electrons are represented as dots, but the bonding pairs are usually shown as lines.

The **Lewis symbol** shows the atom's valence electrons as dots in four regions around an atom.

A **ligand** is a molecule or ion that is attached to a metal.

The **ligand field splitting energy** (Δ) is the energy difference between the sets of d-orbitals in an atom. It results from the electrostatic field of the ligands, *i.e.*, the ligand field.

The **limiting reactant** is that reactant whose amount limits the amount of product that can be obtained in a reaction, *i.e.*, the reactant that is totally consumed.

A **line spectrum** is a spectrum in which only certain wavelengths (lines) are present. Atomic spectra are line spectra.

A **liquid junction** is a device that allows ion migration between the electrodes of an electro-chemical cell to complete the electrical circuit.

A **load** is a device in a galvanic cell that utilizes the free energy given off by the transferred electrons.

A **lone pair** is a pair of nonbonding valence electrons.

A **low-spin metal** is a metal in which the d electrons pair in the lower energy set of orbitals before occupying the higher energy set.

The **lumo** is the lowest unoccupied molecular orbital.

M

The **magnetic quantum number** (m_l) is an integer between $-l$ and $+l$ that specifies the directional character of an atomic orbital.

A **main group element** is an element in one of the groups designated as 'A' in the periodic table. Other elements are either transition or inner transition elements.

A **manometer** is a device used to determine the pressure of a gas.

The **mass fraction** of a substance in a mixture is the mass of the substance divided by the mass of the mixture. Mass fractions represent the fraction of the whole, so they are less than one. However, they can be expressed as fractions of 100, in which case they are called mass percents.

The **mass defect** (Δm) is the difference between the mass of a nucleus and the sum of the masses of its neutrons and protons.

Mass-energy is a term used to show that mass and energy are interchangeable ($E = mc^2$).

The **mass number** (A) is the number of protons plus the number of neutrons in the nucleus.

The **mechanical surroundings** is that portion of the surroundings that exchanges energy with the system in the form of work.

The **melting point** is the temperature at which the solid and liquid states are in equilibrium.

A **meniscus** is the curved shape of the top of a liquid.

A **metal** is a material that is shiny, malleable, and a good conductor of electricity. Elements that are metals lie on the left side of the periodic chart and represent about 80% of the elements.

A **metallic bond** is one delocalized over the entire metal. The large number of atoms involved in a typical metallic bond is so large that the bonding electrons occupy bands of energy.

Metalloids have properties intermediate between the metals and nonmetals. The eight metalloids are shiny and brittle. They are not good conductors of heat or electricity (they are semiconductors).

A **micelle** is spherical arrangement of detergent molecules in which the heads form a polar outer shell and the tails form a hydrophobic liquid center.

Micro (μ) is the SI prefix for 10^{-6} , a millionth.

Milli (**m**) is the SI prefix for 10^{-3} , a thousandth.

Two liquids are **miscible** if they are soluble in one another in all proportions.

The **molality (m)** of a solute is the number of moles of solute present in 1 kg of solvent.

The **molar absorptivity (ϵ)** is the absorbance of a 1 M solution in a 1 cm cell.

The **molarity (M)** of a solute is the number of moles of solute present in a liter of solution.

The **molar mass (M_m)** is the mass of one mole of substance. It is equal to the atomic or molecular mass (weight) expressed in grams.

The **mole (mol)** is 6.02×10^{23} items. It is the number of molecules or atoms in a sample of a compound or element that has a mass equal to its molecular or atomic mass expressed in grams.

The **mole fraction (X)** of a substance in a mixture is the number of moles of that substance divided by the number of moles of all components of the mixture.

A **molecular dipole** is equal to the product of the charges on the two poles of a polar molecule and the distance between them. It is represented by an arrow pointing from the center of positive charge toward the center of negative charge.

The **molecular formula** of a compound shows the actual numbers of atoms present in the molecule. Contrast with the simplest or empirical formula that shows only the smallest integers that are in the same ratio as in the molecular formula.

Molecularity is the number of reacting molecules in an elementary reaction.

The **molecular mass or weight** is the relative mass of a molecule relative to the mass of a carbon-12 atom.

Molecular orbital theory is a bonding theory in which bonds are formed from the combination of several atomic orbitals on several atoms.

Molecular weight See molecular mass

A **molecule** is an independent particle that consists of two or more chemically bound atoms.

A **monatomic ion** is derived from a single atom.

A **monomer** is a single unit building block that can be bound to other monomers to form larger molecules. Linking two monomers produces a dimer, linking three produces a trimer, and linking many produces a polymer.

N

Nano (n) is the SI prefix for 10^{-9} , a billionth.

Nanotechnology is science and engineering of systems on the nanoscale (1-50 nm).

The **Nernst equation** relates a cell's potential to its standard potential and its reaction quotient.

$$E_{\text{cell}} = E^{\circ} - \left(\frac{RT}{nF} \right) \ln Q$$

A **net chemical equation** shows only those substances that are changed during the reaction.

In a **network covalent solid**, all of the atoms are bound covalently with no discernable molecules.

A **neutral salt** is a compound in which the acid and base strengths of the cation and anion are equal.

In **neutral solutions**, $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$. The pH of a neutral solution is 7.0 at 25 °C.

In **neutralization reactions**, an acid reacts with a base to produce water and a salt.

A **neutron** is a subatomic particle found in the nucleus. It has no charge and a mass of ~1 amu.

A **noble gas** is an element that belongs to Group 8A. The noble gases are helium, neon, argon, krypton, xenon, and radon.

A **nodal plane** is a plane of zero electron density that lies between regions of opposite algebraic sign in an orbital. A p orbital and a π orbital each contain a single nodal plane.

A **nonbonding MO** has an equal number of bonding and antibonding interactions.

A **nonelectrolyte** is a substance whose aqueous solution does not conduct electricity. Electricity is not conducted because the electrolyte produces no ions in solution.

Non-ionizing radiation, such as visible light, does not have sufficient energy to ionize matter.

Nonmetals are elements on the right side of the periodic table. They can be gases, liquids, or solids and are dull, brittle, and poor conductors of electricity. Nonmetals react with one another to form covalent compounds or with metals to form ionic compounds.

The **normal boiling point** is the temperature at which the vapor pressure of a liquid is 1 atm.

The **nuclear binding energy** is the energy required to break one mole of nuclei into their constituent nucleons.

Nuclear chemistry or radiochemistry is the study of reactions that involve changes in the nucleus.

Nuclear fission is the splitting of a heavier nucleus into lighter nuclei.

Nuclear fusion is the combination of two lighter nuclei into a heavier one.

Nucleons are the particles found in the nucleus. Protons and neutrons are nucleons.

A **nucleotide** is a unit of a nucleic acid that consists of a phosphate, a sugar, and an N-containing base. Nucleic acids are polymers built with nucleotides.

The atomic **nucleus** contains all of the positive charge, virtually all of the mass, but occupies almost none of the volume of an atom.

Nylon is a polyamide produced in the reaction of a diamine and a diester.

O

The **octet rule** states that atoms in molecules strive to obtain an octet (eight) of valence electrons by sharing the bonding electrons with other atoms.

An **orbital** is a solution to the wave equation. Electrons reside in atomic or molecular orbitals, and bonding results from the interaction of atomic orbitals of different atoms.

An **organic compound** is one that is based on carbon.

Osmosis is the net movement of solvent molecules from a dilute solution into a more concentrated one through a semipermeable membrane, *i.e.*, one that allows only solvent molecules to pass.

Osmotic pressure is the pressure caused at a semipermeable membrane bounded by solutions of different concentration. It results because solute particles cannot pass through the membrane but solvent molecules can.

Overpotential is the amount by which the applied potential for electrolysis must be increased above that predicted from half-cell potentials to carry out the electrolysis at a reasonable rate. Overpotentials are due to high activation energies.

An **oxidant** is an oxidizing agent.

Oxidation is the loss of electrons or increase in oxidation state that accompanies electron transfer.

The **oxidation state** of an atom is the charge it would have if its bonds were assumed to be ionic, *i.e.*, if its bonding electrons were assigned to the more electronegative atom in each bond.

An **oxidizing agent** is a substance that promotes oxidation in other substances. The oxidizing agent is reduced by the electron transfer.

An **oxoacid** is a Brønsted acid in which the proton is attached to an oxygen atom.

An **oxoanion** has a central atom surrounded by oxygen atoms. The central atom is usually in a high oxidation state because it is surrounded by the very electronegative oxygen atoms.

P

Packing efficiency is the fraction of the volume of the unit cell that is occupied by particles.

Paramagnetism is the tendency of certain atoms to be attracted by a magnetic field. It is an atomic property that is related to the number of unpaired electrons on the atom.

Partial ionic character See percent ionic character.

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

Parts per billion (ppb) is the number of grams of solute in 10^9 g of solution.

Parts per million (ppm) is the number of grams of solute in 10^6 g of solution.

Parts per thousand (ppt) is the number of grams of solute in 1000 g of solution.

The **pascal (Pa)** is the SI unit of pressure.

$$1\text{ Pa} = 1\text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2} = 9.9 \times 10^{-6}\text{ atm}$$

A **passive electrode** is one that does not participate in the half-reaction. For example, a platinum electrode in a $2\text{H}^{1+} + 2\text{e}^{1-} \rightarrow \text{H}_2$ half-cell is passive.

The **Pauli Exclusion Principle** states that no two electrons in an atom can have the same set of quantum numbers.

A **peptide** is an amide produced from the reaction of two amino acids.

The **percent ionic character** is a measure of the charge separation in a bond, which results from electronegativity differences between the bound atoms. A bond is considered to be ionic if it has over 50% ionic character.

The **percent yield** is the fraction of the theoretical yield, expressed as a percent, that is actually isolated in a chemical reaction.

A **period** in the periodic table is a horizontal row. The properties of the elements in a period vary gradually across the period.

The **periodic law** states that the elements exhibit a periodicity in the chemical and physical properties when they are arranged in the order of their atomic numbers.

The **periodic table or chart** is an arrangement of the elements into rows (periods) and columns (groups) such that the elements in the same group have similar properties.

pH is the negative base 10 logarithm of the hydronium ion concentration in a solution.

$$\text{pH} = -\log[\text{H}_3\text{O}^{1+}]$$

A **phase diagram** shows the state of a substance as a function of its temperature and pressure.

A **photon** is a quantum of energy in the form of electromagnetic radiation.

Photosynthesis is the process in which plants use solar energy to convert CO_2 and H_2O into carbohydrates.

A **physical property** is one that is independent of other substances. Melting point, boiling point, color, and hardness are some physical properties.

A **pi (π) bond** is formed from the side-on interaction of two p orbitals. Pi bonds have nodal planes that contain the internuclear axis.

The **pK_a** of an acid is the negative base 10 logarithm of the acid dissociation constant. $\text{pK}_a = -\log K_a$

Planck's constant (h) is the proportionality constant that relates the frequency of a photon to its energy.
 $h = 6.626 \times 10^{-34} \text{ J/s}$

A **polar covalent bond** is a covalent bond in which the

bonding electrons are NOT shared equally. Thus, the bonds are between atoms of different electronegativities.

Polar molecules have asymmetric charge distributions. The result is a molecular dipole.

The **polarizability** of an atom or molecule is a measure of the ease with which its electron cloud can be deformed.

A **polyamide** is a condensation polymer that contains many amide linkages. Nylons and peptides are polyamides.

A **polyatomic ion** is an ion, such as CO_3^{2-} , in which two or more atoms are covalently bound.

A **polyene** is an organic compound with many double bonds.

A **polymer** is a large molecule consisting of many single unit building blocks called mers.

A **polypeptide** is a polyamide produced from the reaction of many amino acids.

Polyprotic acid acids have more than one acidic proton. Examples: H_2SO_4 is a diprotic acid and H_3PO_4 is a triprotic acid.

Polyunsaturated organic compounds contain many C-C multiple bonds.

A **positron** is an elementary particle with the mass of an electron and a positive charge. It is the antimatter analog of the electron.

Positron decay is the emission of a positron from the nucleus. Positron decay increases the neutron/proton ratio, so it is common in nuclei that lie below the band of stability.

Potential energy is energy due to position. In chemistry, potential energy arises from the interaction of charged particles, and the closer they are, the stronger they interact.

A **precipitate** is a solid formed when two solutions are mixed, or the act of forming the solid. Thus, AgCl precipitates and is a precipitate when it does.

The **precision** of a number is given by the number of significant figures to which it is reported. 1.00 m is more precise than 1.0 m.

A **pre-exponential** precedes an exponential. Typically used in the Arrhenius equation: $k = A\exp\{-E_{\text{RT}}\}$, where A is the pre-exponential.

Pressure (P) is force per unit area: $P = F/A$.

Pressure-volume or PV work is done when the volume of a gas changes against an external pressure.

The **principal quantum number (n)** specifies the energy level of an electron in an atom.

A **protein** is a large polypeptide.

A **proton** is a subatomic particle found in the nucleus. It carries a +1 charge and has a mass of ~1 amu.

A **proton acceptor** is called a Brønsted base.

A **proton donor** is called a Brønsted acid.

A **purely covalent bond** is a covalent bond in which the bonding electrons are shared equally. Thus, the bonds between atoms of the same electronegativity are purely covalent.

Q

A **qualitative observation** is one that does not involve numbers.

A **quantitative observation** is one that does involve numbers.

A **quantity** in the factor label method is an amount and is characterized by a single unit. For example, 3 m is a quantity, but 3 m/s is a factor.

A **quantum** is a packet of energy.

A **quantum number** is a number (usually an integer) that designates an allowed state. All atomic and molecular states (e.g., electronic, vibrational, rotational, and nuclear) are described by quantum numbers.

R

A **radioactive** nucleus is unstable and disintegrates spontaneously to another nucleus by emitting or capturing particles.

Radioactive dating is the determination of the age of a material from the amount of material involved in the radioactive decay of one of its components.

Radiochemistry See nuclear chemistry.

Radioisotopes are radioactive nuclei.

The **rate of change** of a quantity is the rate at which it changes as a function of the change in another quantity.

A **rate constant (k)** is the proportionality constant between the concentrations of the components (usually reactants) of a reaction and the rate of reaction.

The **rate-determining step (RDS)** is the elementary reaction in a mechanism that is so much slower than the other elementary reactions that it dictates the rate of the overall reaction.

The **rate law** expresses the rate of a reaction as a function of the concentrations of the substances (usually reactants) involved in the reaction.

The **rate of disappearance** is the rate at which a reactant reacts.

The **rate of formation** or **appearance** is the rate at which a product is produced.

The **rate of reaction** is the rate at which a product is produced or a reactant reacts divided by its coefficient in the chemical equation.

A **reactant order** is the exponent of the concentration of a reactant in the rate equation for a reaction.

The **reaction coordinate** is the combination of intermolecular distance, bond length and bond angle changes required to convert reactant molecules into product molecules.

A **reaction mechanism** is a series of elementary processes that leads to the overall reaction.

The **reaction order** is the sum of all of the reactant orders in a reaction.

The **reaction quotient (Q)** is expressed as the activities of the products divided by the activities of the reactants. Each activity is raised to an exponent equal to the coefficient of the substance in the balanced equation. When the activities are equilibrium activities, the reaction quotient is called the equilibrium constant.

A **redox couple** is the oxidized and reduced forms of the species involved in a half-reaction. For example, Cu^{2+}/Cu is a redox couple.

The **redox electrons** are the electrons that are transferred in a redox reaction.

Redox reactions involve an electron transfer from a reductant to an oxidant.

A **reducing agent** or **reductant** is a substance that promotes reduction in another material. It is oxidized in the process.

Reduction is the gain of electrons, which results in a decrease in oxidation state of the species being reduced.

A **residue** in a protein is one of the amino acids making up the protein.

A **resonance structure** is a Lewis structure of a molecule that differs from another Lewis structure only in the placement of electrons.

Respiration is the process whereby animals extract energy from carbohydrates.

Rotational degrees of freedom are spinning motions about an axis through the center of mass of the molecule. Linear molecules have two rotational degrees of freedom, and nonlinear molecules have three.

S

Salts are ionic compounds formed in an Arrhenius acid-base reaction. The anion of a salt is supplied by the acid, and the cation by the base.

A **salt bridge** is a liquid junction that consists of a saturated solution of a strong electrolyte, such as KCl. Ions enter and leave the bridge so as to maintain electrical neutrality in the two half-cells of an electrochemical cell.

Saturated carbons are involved in four sigma bonds.

Science is that branch of knowledge that is gained by the application of the scientific method.

The **Schrödinger equation** relates the energy of an electron to its wavefunction.

The **scientific method** is used to further scientific knowledge. It involves observation, hypothesis formulation, prediction, and testing.

The **second law of thermodynamics** states that the entropy of the universe increases in all spontaneous processes.

A **semiconductor** is a substance whose electrical conductivity increases with temperature. Semiconductors are characterized by small but nonzero band gaps.

A **semipermeable membrane** allows the passage of solvent molecules but not of solute particles.

Shell See level.

Shielding is the amount by which the nuclear charge experienced by an electron is reduced by interference from other electrons. Core electrons shield valence electrons much better than do other valence electrons because most of the electron density and charge of the core electrons lies between the valence electrons and the nucleus.

Sigma bonds are formed from the interaction of s orbitals or the end-on interaction of p or d orbitals. The electron density in a sigma bond contains the internuclear axis.

Significant figures are used to express the precision of a measurement or result.

In a **simple cubic (sc)** unit cell, the particles are found only at the corners.

The **simplest or empirical formula** is a chemical formula whose subscripts indicate only the smallest whole numbers that are in the same ratio as the actual numbers of atoms present in the molecule.

Smectic clays are also called swelling clays, they consist of a layer of aluminate octahedra sandwiched between two layers of silicate tetrahedra.

Soaps are similar to detergents except the polar head is a COO^{1-} (carboxylate) group because soaps are the salts of fatty acids.

The **solubility** of a solute is the maximum amount of the solute that can dissolve in a solvent at a given temperature.

The **solubility product constant (K_{sp})** is the equilibrium constant for the dissolution of a salt in water.

A **solute** is a component of a solution that is not the solvent.

A **solution** is a homogeneous mixture.

Solvation is the process in which the solvent molecules interact with solute particles.

The **solvent** is the substance responsible for the phase of a solution. If one of the components of a solution is a liquid, then the liquid is considered the solvent.

An **sp hybrid orbital** is one of the two orbitals obtained by mixing one s and one p orbital on an atom. The two sp hybrids are separated by 180° .

An **sp² hybrid orbital** is one of the three orbitals obtained by mixing one s and two p orbitals on an atom. The three sp² hybrids lie in plane and are separated by 120° .

An **sp³ hybrid orbital** one of the four orbitals obtained by mixing one s and three p orbitals on an atom. The four sp³ hybrids point toward the corners of a tetrahedron and are separated by 109° .

The **specific heat (s)** of a substance is the amount of heat required to raise the temperature of 1 g of the substance by 1°C .

Spectator ions are ions in solution that do not undergo reaction. When KCl(aq) is added to $\text{AgNO}_3\text{(aq)}$, the Ag^{1+} and Cl^{1-} ions react, but the K^{1+} and NO_3^{1-} ions are spectator ions. Spectator ions are brought into solution as counter ions to the ions that do react.

A **spectrum** is a display of radiant energy arranged in order of its frequency or wavelength.

The **spin quantum number (m_s)** of an electron is $+1/2$ or $-1/2$. It indicates the direction of the magnetic field produced by the electron.

A **spontaneous** process is one that takes place without intervention. $\Delta S_{\text{univ}} > 0$ for all spontaneous

processes, or $\Delta G < 0$ for spontaneous processes at constant temperature and pressure.

The **standard cell potential (\mathcal{E}°)** is the cell potential when all reactants and products are in their standard states.

The **standard enthalpy or heat of reaction (ΔH°)** is the enthalpy change for a reaction when it is carried out with all reactants and products in their standard states.

The **standard heat or enthalpy of formation (ΔH_f°)** is the heat absorbed when one mole of a substance is formed from its elements in their standard states.

The **standard hydrogen electrode (SHE)** is a half-cell containing 1 M H^{1+} and 1 atm H_2 . It is used as the reference for standard reduction potentials. The standard reduction potential of the SHE is assigned a value of exactly 0 V.

The **standard reduction potential** of a redox couple is a measure of the free energy of the redox electrons relative to those in a reference couple such as the H^{1+}/H_2 couple. The more positive the standard reduction potential, the lower is the energy of the electrons.

A **standard solution** is a solution of known concentration that is used to determine an unknown concentration.

The **standard state** is a reference state used to compare thermodynamic quantities. It is 1 atm pressure for a gas, a concentration of 1 M for a solute, and the pure substance for a solid or a liquid.

A **state function** is a quantity that depends only upon the initial and final states.

A **stereocenter** in organic chemistry is a carbon atom that has four different groups attached to it.

Stereoisomers have the same connectivities but different spatial arrangements of their atoms.

The **steric factor** in kinetics represents the probability that a collision between the particles in an elementary process have the correct orientation to react.

The **stoichiometric factor** or **link** is the conversion factor in a stoichiometric calculation that converts from one substance into another. It is the ratio of subscripts in a chemical formula or the coefficients in a balanced chemical equation.

Stoichiometry is the study of the conversion from one chemical species into a chemically equivalent amount of another. The conversion is made through the use of chemical formulas or balanced chemical equations.

A **straight** or **continuous chain** is a chain of atoms in which no atom is bound to more than two other atoms in the chain.

A **strong acid** is an acid that reacts extensively with water, *i.e.*, one whose acid dissociation (ionization) constant is much greater than one. Aqueous solutions of strong acids are represented by H_3O^{1+} .

A **strong base** is a base that reacts extensively with water to produce OH^{1-} .

The **sublevel** of an electron is specified by the *n* and *l* quantum numbers. It dictates the energy, size, and shape of its orbitals.

Sublimation is the process in which a solid is converted into its vapor.

A **supercritical fluid** is the phase of matter beyond the critical point. It has some properties of the liquid and the gas, but it is neither.

The **surface tension** of a liquid is the energy required to increase its surface area by a fixed amount.

Surroundings See thermodynamic surroundings.

System See thermodynamic system.

T

Temperature is a measure of the average kinetic energy of the molecules in a system.

A **termolecular** process involves three molecules.

The **theoretical yield** is the amount of product predicted from the amount of limiting reactant and the stoichiometry of the reaction.

A **theory** is an explanation of many observations.

Thermal energy is the kinetic energy of a molecule, ion, or atom. Thermal energy depends only upon the temperature.

The **thermal surroundings** is that portion of the surroundings that exchanges heat with the system.

A **thermochemical equation** is a chemical equation that includes a thermodynamic quantity, usually ΔH or ΔG .

Thermochemistry is that branch of thermodynamics that deals with energy change in chemical reactions.

Thermodynamics is the study of energy and its transformations.

The **thermodynamic region** of a reaction is after equilibrium has been established.

The **thermodynamic surroundings** is that part of the universe that exchanges energy with the system.

A **thermodynamic system** is that part of the universe that is under investigation.

The **thermodynamic universe** is the system and its surroundings.

A **thermonuclear** reaction is a nuclear reaction that requires a large input of energy for initiation. Fusion reactions are thermonuclear.

The **third law of thermodynamics** states that the entropy of a perfect crystal at 0K is zero.

The **titrant** is the solution whose volume is determined in a titration.

In a **titration**, the volume of one solution of known concentration (the titrant) that is required to react with another solution (the analyte) is determined in order to find the concentration of the analyte.

A **titration curve** is a plot of the pH of the solution versus the volume of titrant.

The **torr** is a unit of pressure. A pressure of 1 torr supports a column of Hg to a height of 1 mm.

A **trans** configuration is one in which two groups are on opposite sides of a bond or atom.

A **transition element** or **metal** is an element (metal) in the d-block (B groups) of the periodic table.

The **transition state** is the highest energy species through which the reactants must pass in order to make the transition to the products.

Translational degrees of freedom are the straight-line motions of a particle. All straight line motion can be expressed as a sum of *x*, *y*, and *z* components, so all molecules have three translational degrees of freedom.

The **triple point** is the temperature and pressure at which the solid, liquid, and vapor states of a substance are in equilibrium.

U

The **uncertainty principle** states that it is impossible to know both the position and speed of subatomic particles to high accuracy. In order to measure one more accurately, you must lose accuracy in the other.

A **unimolecular** process involves only one particle.

A **unit cell** is the simplest arrangement of particles that generates the entire lattice when translated in all three dimensions.

Unsaturated carbon atoms are involved in less than four sigma bonds.

V

The **valence band** is the highest energy filled band containing the valence electrons of a metal.

In **valence bond theory**, bonds arise from the overlap of orbitals on adjacent atoms. The orbitals can be either atomic or hybridized.

Valence electrons are those outermost electrons that dictate the properties of the atom and are involved in chemical bonding. They reside in the outermost s sublevel and any unfilled sublevels.

Valence-shell electron-pair repulsion (VSEPR) theory is used to explain molecular shapes in terms of electron regions adopting the spatial orientation that minimizes the electron-electron repulsions between them.

The **Van't Hoff factor (*i*)** relates the colligative concentration to the concentration of the solute. For example, $m_c = im$.

The **van der Waals radius** is one-half of the distance between identical, nonbonded atoms in a crystal. Atoms that are closer than the sum of their van der Waals radii are assumed to be interacting.

Vaporization is the process by which a liquid is converted into its vapor.

The **vapor pressure** of a liquid is the pressure of its vapor in equilibrium with the liquid at a given temperature.

Vapor pressure lowering (ΔP) is amount by which the vapor pressure of a solvent is reduced by the addition of a volatile solute.

Vibrational degrees of freedom of a molecule are the relative motions of its atoms that result in small oscillating changes in bond lengths and angles.

Viscosity is the resistance of a liquid to flow.

Void space is unoccupied space.

The **volt** is the SI unit of electrical potential.
 $1 \text{ V} = 1 \text{ J}\cdot\text{C}^{-1}$.

W

The **wave function** of an electron is a function that contains all of the information about the electron.

The **wavelength (λ)** is the distance between two corresponding points on a wave.

Wave-particle duality is a term used to indicate that photons (light) and very small particles, such as electrons, behave as both particles and waves.

A **weak acid** is an acid that does not react extensively with water, *i.e.*, it is an acid with a dissociation constant that is much less than one.

A **weak base** is a substance that reacts only slightly with water to produce hydroxide ions.

A **weak electrolyte** is a substance whose aqueous solution conducts only a small current of electricity because only a small fraction of weak electrolyte molecules produce ions in water.

Work (*w*) is a force through a distance, $w = fd$. Thus, something must move, and there must be a resistance to the movement in order for work to be done. By definition, the symbol *w* is the work done ON the system, and $-w$ is the work done BY the system.

X

X-ray diffraction is a technique in which x-rays are scattered from atoms in the solid to determine the distances between the atoms and ions in the crystal.

Z

Zeolites are aluminosilicates built from tetrahedral AlO_4 and SiO_4 units bridged by oxygen atoms. They are filled with channels and pores, which provide many uses for the material.