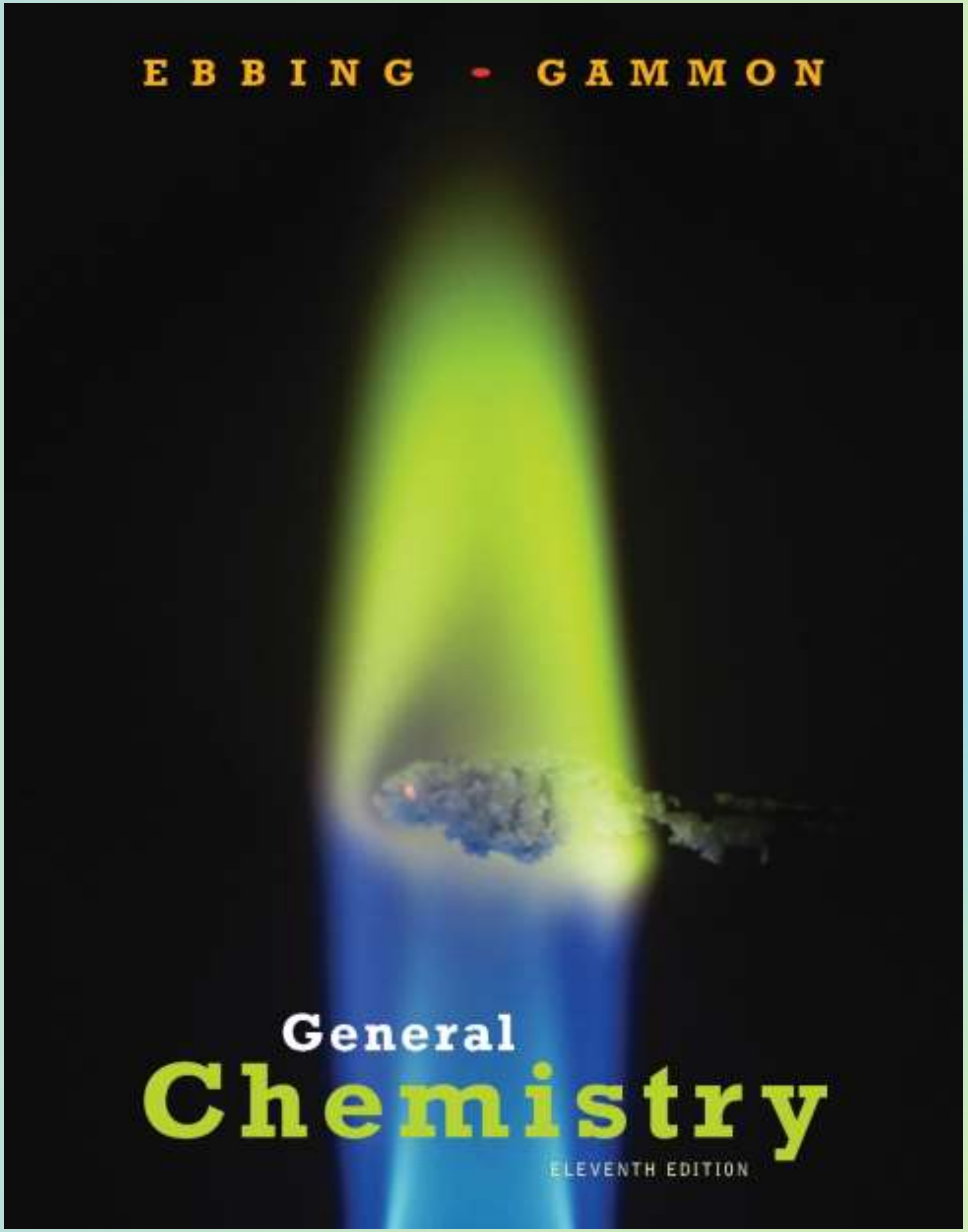
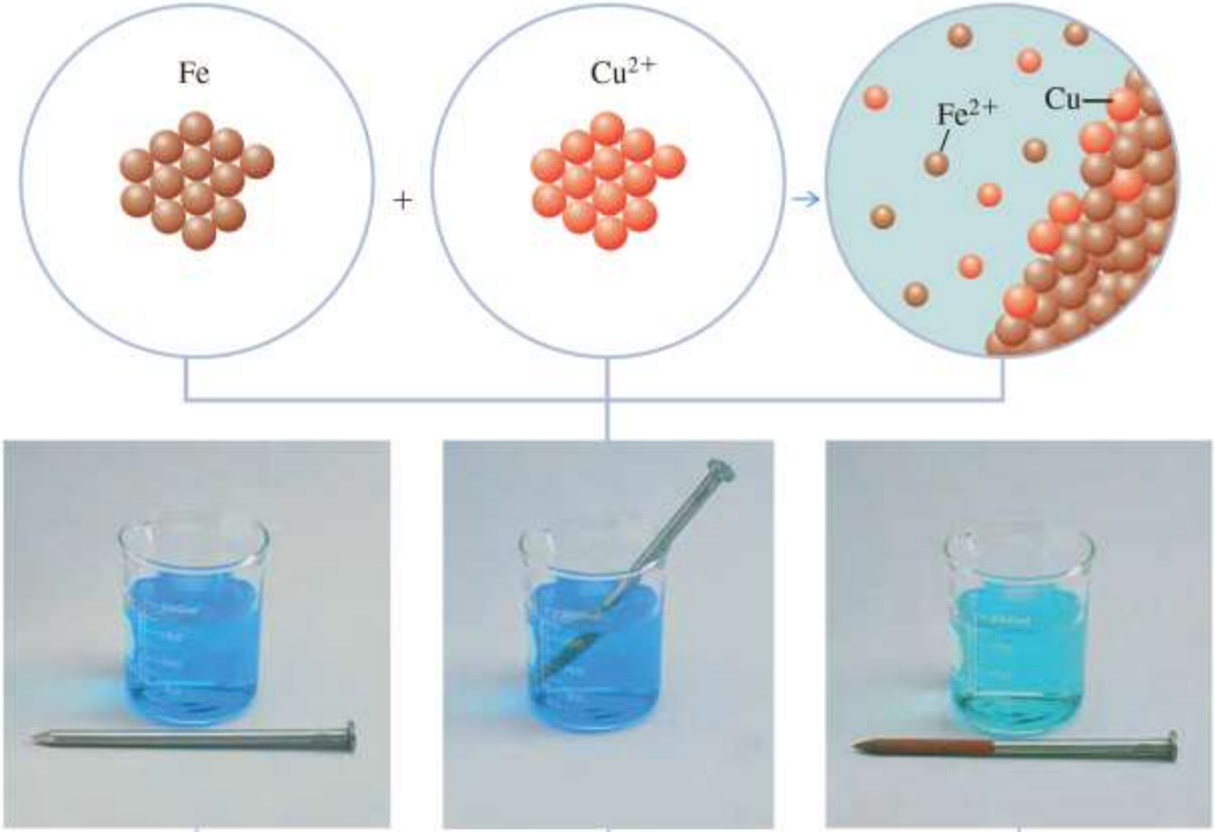


Chemical Reactions

4.5 Oxidation–Reduction Reactions

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$



Iron nail and copper(II) sulfate solution, which has a blue color.

Fe reacts with Cu^{2+}(*aq*) to yield Fe^{2+}(*aq*) and Cu(*s*). The molecular view above the pictures depicts the net ionic equation; water and the sulfate anion have been omitted.

The copper metal forms a coating on the nail.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s)$$

The net ionic equation is:

$$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$$

- **Oxidation Numbers**

an **oxidation–reduction reaction** (or **redox reaction**) is *a reaction in which electrons are transferred between species or in which atoms change oxidation number.*

Formerly, the term *oxidation* meant "reaction with oxygen."

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$

$$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$$

➢ Oxidation-Number Rules:

Table 4.5 Rules for Assigning Oxidation Numbers

Rule	Applies to	Statement
1	Elements	The oxidation number of an atom in an element is zero.
2	Monatomic ions	The oxidation number of an atom in a monatomic ion equals the charge on the ion.
3	Oxygen	The oxidation number of oxygen is −2 in most of its compounds. (An exception is O in H_2O_2 and other peroxides, where the oxidation number is −1.)
4	Hydrogen	The oxidation number of hydrogen is +1 in most of its compounds. (The oxidation number of hydrogen is −1 in binary compounds with a metal, such as CaH_2.)
5	Halogens	The oxidation number of fluorine is −1 in all of its compounds. Each of the other halogens (Cl, Br, I) has an oxidation number of −1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
6	Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation numbers of the atoms in a polyatomic ion equals the charge on the ion.

Examples:

SO_2:

$HClO_4$:

ClO_3^-:

$K_2Cr_2O_7$:

MnO_4^-:

➢ Describing Oxidation–Reduction Reactions

$$\overset{0}{\mathrm{Fe}}(s) + \overset{+2}{\mathrm{Cu}}{}^{2+}(aq) \longrightarrow \overset{+2}{\mathrm{Fe}}{}^{2+}(aq) + \overset{0}{\mathrm{Cu}}(s)$$

We can write this reaction in terms of two half-reactions

$$\overset{0}{\mathrm{Fe}}(s) \longrightarrow \overset{+2}{\mathrm{Fe}}{}^{2+}(aq) + 2e^- \qquad \text{(electrons lost by Fe)}$$

$$\overset{+2}{\mathrm{Cu}}{}^{2+}(aq) + 2e^- \longrightarrow \overset{0}{\mathrm{Cu}}(s) \qquad \text{(electrons gained by } \mathrm{Cu}^{2+}\text{)}$$

oxidation

$$\underset{\substack{\text{reducing}\\\text{agent}}}{\overset{0}{\mathrm{Fe}}(s)} + \underset{\substack{\text{oxidizing}\\\text{agent}}}{\overset{+2}{\mathrm{Cu}}{}^{2+}(aq)} \longrightarrow \overset{+2}{\mathrm{Fe}}{}^{2+}(aq) + \overset{0}{\mathrm{Cu}}(s)$$

reduction

➢ Some Common Oxidation–Reduction Reactions

1. Combination reaction
2. Decomposition reaction
3. Displacement reaction
4. Combustion reaction

1. **Combination Reactions** is *a reaction in which two substances combine to form a third substance*

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

✓ Not all combination reactions are oxidation- reduction reactions

$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

2. **Decomposition Reactions** is *a reaction in which a single compound reacts to give two or more substances*

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

$$2KClO_3(s) \xrightarrow[MnO_2]{\Delta} 2KCl(s) + 3O_2(g)$$

- ✓ Not all decomposition reactions are oxidation-reduction reactions

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

3. **Displacement reaction** (also called a **single-replacement reaction**) is *a reaction in which an element reacts with a compound, displacing another element from it.*

- ✓ involve an element and one of its compounds →must be oxidation–reduction reactions.

$$Cu(s) + 2AgNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2Ag(s)$$

Net ionic rxn. $$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

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

Net ionic rxn.

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

- ✓ metals listed at the top are the strongest reducing agents (they lose electrons easily)
- ✓ A free element reacts with the monatomic ion of another element if the free element is above the other element in the activity series
- ✓ The highlighted elements react slowly with liquid water, but readily with steam, to give H_2

$$2K(s) + 2H^+(aq) \longrightarrow 2K^+(aq) + H_2(g)$$

Table 4.6 Activity Series of the Elements

React vigorously with acidic solutions and water to give H_2	Li K Ba Ca Na
React with acids to give H_2	Mg Al Zn Cr Fe Cd Co Ni Sn Pb
Do not react with acids to give H_2*	H_2 Cu Hg Ag Au

4. **Combustion reaction** is *a reaction in which a substance reacts with oxygen, usually with the rapid release of heat to produce a flame.*

✓ The products include one or more oxides. Oxygen changes oxidation number from 0 to -2, so combustions are oxidation-reduction reactions.

$$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(g)$$

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

4.6 Balancing Simple Oxidation-Reduction Equations

(Q) Apply the half-reaction method to balance the following equation: $Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$

$$\overset{0}{Mg}(s) + \overset{0}{N}_2(g) \longrightarrow \overset{+2}{Mg}_3\overset{-3}{N}_2(s)$$

$$Mg \longrightarrow Mg^{2+} + 2e^- \qquad \text{(balanced oxidation half-reaction)}$$

$$N_2 + 6e^- \longrightarrow 2N^{3-} \qquad \text{(balanced reduction half-reaction)}$$

$$3 \times (Mg \longrightarrow Mg^{2+} + 2e^-)$$

$$1 \times (N_2 + 6e^- \longrightarrow 2N^{3-})$$

$$3Mg + N_2 + \cancel{6e^-} \longrightarrow 3Mg^{2+} + 2N^{3-} + \cancel{6e^-}$$

$$\mathbf{3Mg + N_2 \longrightarrow 3Mg^{2+} + 2N^{3-}}$$

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

4.66 Balance the following oxidation–reduction reactions by the half-reaction method.

a. $FeI_3(aq) + Mg(s) \rightarrow Fe(s) + MgI_2(aq)$

$Mg \rightarrow Mg^{2+} + 2e^-$ (oxidation half-reaction)

$Fe^{3+} + 3e^- \rightarrow Fe$ (reduction half-reaction)

$$3 \times (Mg \rightarrow Mg^{2+} + 2e^-)$$

$$\underline{2 \times (Fe^{3+} + 3e^- \rightarrow Fe)}$$

$$2Fe^{3+} + 3Mg + \cancel{6e^-} \rightarrow 2Fe + 3Mg^{2+} + \cancel{6e^-}$$

$$2Fe^{3+} + 3Mg \rightarrow 2Fe + 3Mg^{2+}$$

$$2FeI_3(aq) + 3Mg(s) \rightarrow 2Fe(s) + 3MgI_2(aq)$$

4.7 Molar Concentration

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

(Q) A sample of $NaNO_3$ weighing 0.38 g is placed in a 50.0 mL volumetric flask. The flask is then filled with water to the mark on the neck. What is the molarity of the resulting solution?

$$\text{Molarity} = \frac{4.4\underline{7} \times 10^{-3} \text{ mol NaNO}_3}{50.0 \times 10^{-3} \text{ L soln}} = \mathbf{0.089\ \mathit{M}\ NaNO_3}$$

4.8 Diluting Solutions

$$M_i \times V_i = M_f \times V_f$$

(Q)You are given a solution of 14.8 *M* NH_3. How many milliliters of this solution do you require to give 100.0 mL of 1.00 *M* NH_3 ?

$$V_i = \frac{1.00\ \cancel{M} \times 100.0 \text{ mL}}{14.8\ \cancel{M}} = \mathbf{6.76\ mL}$$

✓ Number of moles does not change

(Q) What is the molar concentration of Na^+ in a solution made by dissolving 1.59 g of Na_2CO_3 (molar mass = 106g/mol) in 100 mL H_2O?

4.9 Gravimetric Analysis

is *a type of quantitative analysis in which the amount of a species in a material is determined by converting the species to a product that can be isolated completely and weighed*.

(Q) A 1.000-L sample of polluted water was analyzed for lead(II) ion, Pb^{2+}, by adding an excess of sodium sulfate to it. The mass of lead(II) sulfate that precipitated was 229.8 mg. What is the mass of lead in a liter of the water? Give the answer as milligrams of lead per liter of solution.

✓ Solution: mass percentage of Pb in $PbSO_4$

$$\% \text{ Pb} = \frac{207.2 \text{ g/mol}}{303.3 \text{ g/mol}} \times 100\% = 68.32\%$$

Amount Pb in sample = 229.8 mg $PbSO_4$ X 0.6832 = 157.0 mg Pb

The water sample contains **157.0 mg Pb per liter.**

Exercise 4.14 You are given a sample of limestone, which is mostly $CaCO_3$, to determine the mass percentage of Ca in the rock. You dissolve the limestone in hydrochloric acid, which gives a solution of calcium chloride. Then you precipitate the calcium ion in solution by adding sodium oxalate, $Na_2C_2O_4$. The precipitate is calcium oxalate, CaC_2O_4. You find that a sample of limestone weighing 128.3 mg gives 140.2 mg of CaC_2O_4. What is the mass percentage of calcium in the limestone?

There are two different reactions taking place in forming the CaC_2O_4 (molar mass 128.10 g/mol) precipitate. These are

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

$$CaCl_2(aq) + Na_2C_2O_4(aq) \rightarrow CaC_2O_4(s) + 2NaCl(aq)$$

The overall stoichiometry of the reactions is one mol $CaCO_3$/one mol CaC_2O_4. Also note that each $CaCO_3$ contains one Ca atom, so this gives an overall conversion factor of one mol Ca/one mol CaC_2O_4.

The mass of Ca can now be calculated.

$$0.1402 \text{ g } CaC_2O_4 \times \frac{1 \text{ mol } CaC_2O_4}{128.10 \text{ g } CaC_2O_4} \times \frac{1 \text{ mol Ca}}{1 \text{ mol } CaC_2O_4} \times \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} = 0.0438\underline{6}6 \text{ g Ca}$$

Now, calculate the percentage of calcium in the 128.3 mg (0.1283 g) limestone:

$$\frac{0.0438\underline{6}6 \text{ g Ca}}{0.1283 \text{ g limestone}} \times 100\% = 34.1\underline{9}0 = 34.19\%$$

4.85 Copper has compounds with copper(I) ion or copper(II) ion. A compound of copper and chlorine was treated with a solution of silver nitrate, $AgNO_3$, to convert the chloride ion in the compound to a precipitate of AgCl. A 59.40-mg sample of the copper compound gave 86.00 mg AgCl.

a. Calculate the percentage of chlorine in the copper compound.

b. Decide whether the formula of the compound is CuCl or $CuCl_2$.

Molar mass (g/mol): AgCl=143.32; Cl=35.45; CuCl=99.0; $CuCl_2$=134.45

4.10 Volumetric Analysis

Example 4.13 Calculating the Volume of Reactant Solution Needed

(Q) Consider the following reaction:

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow 2H_2O(l) + Na_2SO_4(aq)$

Suppose a beaker contains 35.0 mL of 0.175 *M* H_2SO_4. How many milliliters of 0.250 *M* NaOH must be added to react completely with the sulfuric acid?

$$35.0 \times 10^{-3}\ \cancel{\text{L } H_2SO_4}\ \text{soln} \times \frac{0.175\ \cancel{\text{mol } H_2SO_4}}{1\ \cancel{\text{L } H_2SO_4\ \text{soln}}} \times \frac{2\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{mol } H_2SO_4}} \times \frac{1\ \text{L NaOH soln}}{0.250\ \cancel{\text{mol NaOH}}} = 4.90 \times 10^{-2}\ \text{L NaOH soln (or 49.0 mL NaOH soln)}$$

Exercise 4.15 consider the following reaction:

$$3NiSO_4(aq) + 2Na_3PO_4(aq) \rightarrow Ni_3(PO_4)_2(s) + 3Na_2SO_4(aq)$$

How many milliliters of 0.375 *M* $NiSO_4$ will react with 45.7 mL of 0.265 *M* Na_3PO_4?

Example 4.14

Calculating the Quantity of Substance in a Titrated Solution

(Q) A flask contains a solution with an unknown amount of HCl. This solution is titrated with 0.207 *M* NaOH. It takes 4.47 mL of the NaOH solution to complete the reaction. What is the mass of the HCl?

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

Solution The calculation is as follows:

$$4.47 \times 10^{-3}\ \cancel{\mathrm{L\ NaOH\ soln}} \times \frac{0.207\ \cancel{\mathrm{mol\ NaOH}}}{1\ \cancel{\mathrm{L\ NaOH\ soln}}} \times \frac{1\ \cancel{\mathrm{mol\ HCl}}}{1\ \cancel{\mathrm{mol\ NaOH}}} \times \frac{36.5\ \mathrm{g\ HCl}}{1\ \cancel{\mathrm{mol\ HCl}}}$$

$$= \mathbf{0.0338\ g\ HCl}$$

4.91 How many milliliters of 0.150 *M* H_2SO_4 are required to react with 8.20 g of $NaHCO_3$, according to the following equation?

$H_2SO_4(aq) + 2NaHCO_3(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$

Molar mass (g/mol): $NaHCO_3$= 84.01

4.111 A stock solution of potassium dichromate, $K_2Cr_2O_7$ (294.2 g/mol), is made by dissolving 84.5 g of the compound in 1.00 L of solution. How many milliliters of this solution are required to prepare 1.00 L of 0.15 *M* $K_2Cr_2O_7$?

4.113 A solution contains 6.0% (by mass) NaBr. The density of the solution is 1.046 g/cm^3. What is the molarity of NaBr (102.89 g/mol)?

4.132 Identify each of the following reactions as being a neutralization, precipitation, or reduction-oxidation reaction.

a. $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

b. $Na_2SO_4(aq) + Hg(NO_3)_2(aq) \rightarrow HgSO_4(s) + 2NaNO_3(aq)$

c. $CsOH(aq) + HClO_4(aq) \rightarrow Cs^+(aq) + 2H_2O(l) + ClO_4^-(aq)$

d. $Mg(NO_3)_2(aq) + Na_2S(aq) \rightarrow MgS(s) + 2NaNO_3(aq)$

4.135(modified) A 25-mL sample of 0.50 *M* NaOH is combined with a 75-mL sample of 0.30 *M* NaOH. What is the molarity of the resulting NaOH solution?

4.140 Potassium hydrogen phthalate (abbreviated as KHP) has the molecular formula $KHC_8H_4O_4$ and a molar mass of 204.22 g/mol. KHP has one acidic hydrogen. A solid sample of KHP is dissolved in 50 mL of water and titrated to the equivalence point with 22.90 mL of a 0.5010 *M* NaOH solution. How many grams of KHP were used in the titration?

4.74 What is the volume (in milliliters) of 0.100 *M* H_2SO_4 containing 0.949 g H_2SO_4 (98.07 g/mol)?