CHAPTER 4
REACTIONS IN AQUEOUS SOLUTIONS

PROBLEM-SOLVING STRATEGIES AND TUTORIAL SOLUTIONS

TYPES OF PROBLEMS

Problem Type 1: Applying Solubility Rules.

Problem Type 2: Writing Molecular, Ionic, and Net Ionic Equations.

Problem Type 3: Acid-Base Reactions.
- **(a)** Identifying Brønsted acids and bases.
- **(b)** Writing acid/base reactions.

Problem Type 4: Oxidation-Reduction Reactions.
- **(a)** Assigning oxidation numbers.
- **(b)** Writing oxidation/reduction half-reactions.
- **(c)** Using an activity series.

Problem Type 5: Concentration of Solutions.

Problem Type 6: Dilution of Solutions.

Problem Type 7: Gravimetric Analysis.

Problem Type 8: Acid-Base Titrations.

Problem Type 9: Redox Titrations.

PROBLEM TYPE 1: APPLYING SOLUBILITY RULES

Ionic compounds are classified as "soluble", "slightly soluble", or "insoluble". Table 4.2 of your text provides solubility rules that will help you determine how a given compound behaves in aqueous solution.

EXAMPLE 4.1

According to the solubility rules, which of the following compounds are soluble in water?

(a) $MgCO_3$ (b) $AgNO_3$ (c) $MgCl_2$ (d) $Ca_3(PO_4)_2$ (e) KOH

Strategy: Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations, the ammonium ion, and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, refer to Table 4.2 of the text.

Solution:

(a) $MgCO_3$ is *insoluble* (Most ionic compounds containing carbonate ions are *insoluble*).

(b) $AgNO_3$ is *soluble* (All ionic compounds containing nitrate ions are *soluble*).

(c) $MgCl_2$ is *soluble* (Most ionic compounds containing chloride ions are *soluble*).

(d) $Ca_3(PO_4)_2$ is *insoluble* (Most ionic compounds containing phosphate ions are *insoluble*).

(e) KOH is *soluble* (All ionic compounds containing alkali metal ions are *soluble*).

PRACTICE EXERCISE

1. Predict whether the following ionic compounds are soluble or insoluble in water.

   (a) $NaNO_3$ **(b)** AgCl **(c)** $Ba(OH)_2$ **(d)** $CaCO_3$

Text Problems: 4.18, **4.20**, 4.24

PROBLEM TYPE 2: WRITING MOLECULAR, IONIC, AND NET IONIC EQUATIONS

In a *molecular equation*, the formulas are written as though all species existed as molecules or whole units. However, a molecular equation does not accurately describe what actually happens at the microscopic level. To better describe the reaction in solution, the equation should show the dissociation of dissolved ionic compounds into ions. An *ionic equation* shows dissolved ionic compounds in terms of their free ions. A *net ionic equation* shows only the species that actually take part in the reaction.

EXAMPLE 4.2

Write balanced molecular, ionic, and net ionic equations for the reaction that occurs when a $BaCl_2$ solution is mixed with a Na_2SO_4 solution.

Strategy: Recall that an *ionic equation* shows dissolved ionic compounds in terms of their free ions. A *net ionic equation* shows only the species that actually take part in the reaction. What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of $BaCl_2$ and Na_2SO_4? What happens when the cations encounter the anions in solution?

Solution: In solution, $BaCl_2$ dissociates into Ba^{2+} and Cl^- ions and Na_2SO_4 dissociates into Na^+ and SO_4^{2-} ions. According to Table 4.2 of the text, barium ions (Ba^{2+}) and sulfate ions (SO_4^{2-}) will form an insoluble compound, barium sulfate ($BaSO_4$), while the other product, NaCl, is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:

$$BaCl_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2NaCl(aq)$$

The *ionic equation* should show dissolved ionic compounds in terms of their free ions.

$$Ba^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + 2Na^+(aq) + 2Cl^-(aq)$$

As you write out the ionic equation above, you should notice that some ions (Na^+ and Cl^-) are not involved in the overall reaction. These ions are called *spectator ions*. Since the spectator ions appear on both sides of the equation and are unchanged in the chemical reaction, they can be canceled from both sides of the equation. A *net ionic equation* shows only the species that actually take part in the reaction.

Cancel the spectator ions to write the *net ionic equation*.

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

Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

Tip: To help pick out the spectator ions, think about spectators at a sporting event. The spectators are at the stadium, watching the action, but they do *not* participate in the game.

PRACTICE EXERCISE

2. Write the balanced molecular, ionic, and net ionic equations for the following reaction:

$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow$$

Text Problem: 4.22

PROBLEM TYPE 3: ACID-BASE REACTIONS

A. Identifying Brønsted acids and bases

A **Brønsted acid** is a proton donor, and a **Brønsted base** is a proton acceptor. To identify a Brønsted acid, you should look for a substance that contains hydrogen. The formula of inorganic acids will begin with H. For example, consider HCl (hydrochloric acid), HNO_2 (nitrous acid), and H_3PO_4 (phosphoric acid). Carboxylic acids contain the carboxyl group, –COOH. The hydrogen from the carboxyl group can be donated. Examples of carboxylic acids are CH_3COOH (acetic acid) and HCOOH (formic acid).

To identify a Brønsted base, you should look for soluble hydroxide salts. The hydroxide ion (OH^-) will accept a proton to form H_2O. Also look for weak bases, which are amines. Ammonia (NH_3) is an example. Finally, look for anions from acids. These negatives ions can accept a proton (H^+). Some examples are $H_2PO_4^{2-}$, NO_2^-, and HCO_3^-.

EXAMPLE 4.3

Identify each of the following species as a Brønsted acid, base, or both: (a) HNO_3, (b) $Ba(OH)_2$, (c) SO_4^{2-}, (d) $CH_3CH_2CH_2COOH$, (e) HPO_4^{2-}.

Strategy: What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions or soluble hydroxide salts.

Solution:

(a) Brønsted acid. The formula of this compound starts with H; this indicates that it is probably an acid.
(b) Brønsted base. This is a soluble hydroxide salt.
(c) Brønsted base. This negative ion can accept a proton; therefore, it is a base.
(d) Brønsted acid. This is a carboxylic acid. It contains a carboxyl group, –COOH.
(e) Both a Brønsted acid and base. This ion has a proton (H^+) that it can donate. It also has a negative charge and therefore can accept a proton.

PRACTICE EXERCISE

3. Identify each of the following species as a Brønsted acid, base, or both.

(a) CH_3CH_2COOH **(b)** HF **(c)** KOH **(d)** HCO_3^-

Text Problem: 4.32

B. Writing Acid-Base Reactions

An acid-base reaction is called a **neutralization reaction**. The typical products of an acid-base reaction are a salt and water.

acid + base ⟶ salt + water

Let's consider a generic acid, HA, reacted with a generic base, MOH.

$$\mathrm{HA + MOH \longrightarrow MA(salt) + H_2O}$$

The H^+ from the acid combines with OH^- from the base to produce water. The anion from the acid, A^-, combines with the metal cation from the base, M^+, to form the salt, MA.

EXAMPLE 4.4

Complete and balance the following equations and write the corresponding ionic and net ionic equations:

(a) $\mathbf{HBr(\mathit{aq}) + Ba(OH)_2(\mathit{aq}) \longrightarrow}$

(b) $\mathbf{HCOOH(\mathit{aq}) + NaOH(\mathit{aq}) \longrightarrow}$

Strategy: Recall that strong acids and strong bases are strong electrolytes. They are completely ionized in solution. An *ionic equation* will show strong acids and strong bases in terms of their free ions. Weak acids and weak bases are weak electrolytes. They only ionize to a small extent in solution. Weak acids and weak bases are shown as molecules in ionic and net ionic equations. A *net ionic equation* shows only the species that actually take part in the reaction.

(a)

Solution: HBr is a strong acid. It completely ionizes to H^+ and Br^- ions. $Ba(OH)_2$ is a strong base. It completely ionizes to Ba^{2+} and OH^- ions. Since HBr is an acid, it donates an H^+ to the base, OH^-, producing water. The other product is the salt, $BaBr_2$, which is soluble and remains in solution. The balanced molecular equation is:

$$\mathrm{2HBr}(aq) + \mathrm{Ba(OH)_2}(aq) \longrightarrow \mathrm{BaBr_2}(aq) + \mathrm{2H_2O}(l)$$

The ionic and net ionic equations are:

$$\mathrm{2H^+}(aq) + \mathrm{2Br^-}(aq) + \mathrm{Ba^{2+}}(aq) + \mathrm{2OH^-}(aq) \longrightarrow \mathrm{Ba^{2+}}(aq) + \mathrm{2Br^-}(aq) + \mathrm{2H_2O}(l)$$

$$\mathrm{2H^+}(aq) + \mathrm{2OH^-}(aq) \longrightarrow \mathrm{2H_2O}(l) \quad \text{or} \quad \mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}(l)$$

(b)

Solution: HCOOH is a weak acid. It will be shown as a molecule in the ionic equation. NaOH is a strong base. It completely ionizes to Na^+ and OH^- ions. Since HCOOH is an acid, it donates an H^+ to the base, OH^-, producing water. The other product is the salt, HCOONa, which is soluble and remains in solution. The balanced molecular equation is:

$$\mathrm{HCOOH}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{HCOONa}(aq) + \mathrm{H_2O}(l)$$

The ionic and net ionic equations are:

$$\mathrm{HCOOH}(aq) + \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{HCOO^-}(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{HCOOH}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{HCOO^-}(aq) + \mathrm{H_2O}(l)$$

PRACTICE EXERCISE

4. Write the balanced molecular, ionic, and net ionic equations for the following acid-base reaction:

$$\mathrm{HNO_2}(aq) + \mathrm{Ba(OH)_2}(aq) \longrightarrow$$

Text Problem: 4.34

PROBLEM TYPE 4: OXIDATION-REDUCTION REACTIONS

A. Assigning oxidation numbers

Oxidation numbers are assigned to reactants and products in oxidation-reduction (redox) reactions to keep track of electrons. An oxidation number refers to the number of charges an atom would have in a molecule (or an ionic compound) if electrons were transferred completely.

Rules for assigning oxidation numbers are in Section 4.4 of your text. These rules will be used in the following example.

To assign oxidation numbers you should refer to the following *two* steps:

Step 1: Use the rules in Section 4.4 to assign oxidation numbers to as many atoms as possible.

Step 2: Often times, one atom does not follow any rules outlined in Section 4.4. To assign an oxidation number to this atom, follow rule 6 of the text. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of the oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.

EXAMPLE 4.5

Assign oxidation numbers to all the atoms in the following compounds and ion:
(a) Na_2SO_4, (b) CuCl, (c) SO_3^{2-}

Strategy: In general, we follow the rules listed in Section 4.4 of the text for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1 in ionic compounds, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of −2 in their compounds.

Solution:

(a) Na always has an oxidation number of +1 (Rule 2). The oxidation number of oxygen in most compounds is −2 (Rule 3).

You can now assign an oxidation number to S based on Na having a +1 oxidation number and O having a −2 oxidation number. This is a neutral ionic compound, so the sum of the oxidation numbers of all the atoms must be zero.

$$2(\text{oxi. no. Na}) + (\text{oxi. no. S}) + 4(\text{oxi. no. O}) = 0$$

$$2(+1) + (\text{oxi. no. S}) + 4(-2) = 0$$

$$\mathbf{(oxi.\ no.\ S)} = 8 - 2 = \mathbf{+6}$$

(b) An oxidation number of −1 can be assigned to Cl (Rule 5).

You can now assign an oxidation number to Cu. This is a neutral ionic compound.

$$(\text{oxi. no. Cu}) + (\text{oxi. no. Cl}) = 0$$
$$(\text{oxi. no. Cu}) + (-1) = 0$$

$$\mathbf{(oxi.\ no.\ Cu)} = \mathbf{+1}$$

(c) An oxidation number of −2 can be assigned to oxygen (Rule 3).

You can now assign an oxidation number to S. SO_3^{2-} is a polyatomic ion. The sum of the oxidation numbers of all elements in the ion must be equal to the net charge of the ion, in this case −2.

$$(\text{oxi. no. S}) + 3(\text{oxi. no. O}) = -2$$
$$(\text{oxi. no. S}) + 3(-2) = -2$$

$$\mathbf{(oxi.\ no.\ S)} = -2 + 6 = \mathbf{+4}$$

PRACTICE EXERCISE

5. Assign oxidation numbers to the underlined atoms in the following molecules or ions:

(a) $\underline{C}O_3^{2-}$ (b) $\underline{Cu}Cl_2$ (c) $\underline{Ti}O_2$ (d) $\underline{N}O_3^-$

Text Problems: 4.46, 4.48, 4.50

B. Writing oxidation-reduction half-reactions

Strategy: In order to break a redox reaction down into an oxidation half-reaction and a reduction half-reaction, you must first assign oxidation numbers to all the atoms in the reaction. In this way, you can determine which element is oxidized (loses electrons) and which element is reduced (gains electrons).

EXAMPLE 4.6

For the following redox reaction, break down the reaction into its half-reactions.

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

Solution: Reactants, the oxidation number of Al is 0 (Rule 1), and the oxidation number of O in a compound is –2 (Rule 3). Solve for the oxidation number of Fe in Fe_2O_3. This is a neutral ionic compound.

$$2(\text{oxi. no. Fe}) + 3(\text{oxi. no. O}) = 0$$
$$2(\text{oxi. no. Fe}) + 3(-2) = 0$$
$$2(\text{oxi. no. Fe}) = +6$$
$$\mathbf{(oxi.\ no.\ Fe) = +3}$$

Products, the oxidation number of Fe is 0 (Rule 1), and the oxidation number of O in a compound is –2 (Rule 3). Solve for the oxidation number of Al in Al_2O_3. This is a neutral ionic compound.

$$2(\text{oxi. no. Al}) + 3(\text{oxi. no. O}) = 0$$
$$2(\text{oxi. no. Al}) + 3(-2) = 0$$
$$2(\text{oxi. no. Al}) = +6$$
$$\mathbf{(oxi.\ no.\ Al) = +3}$$

$$Al \longrightarrow Al^{3+} + 3e^- \quad \text{(oxidation half-reaction, } 3e^- \text{ lost)}$$
$$Fe^{3+} + 3e^- \longrightarrow Fe \quad \text{(reduction half-reaction, } 3e^- \text{ gained)}$$

Tip: When a species is oxidized, the oxidation number will *increase*. In this example, the oxidation number of Al *increased* from 0 to +3. When a species is reduced, the oxidation number will *decrease*. In this example, the oxidation number of Fe *decreased* from +3 to 0.

PRACTICE EXERCISE

6. The nickel-cadmium (nicad) battery, a popular rechargeable "dry cell" used in battery-operated tools, uses the following redox reaction to generate electricity:

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Assign oxidation numbers to all the atoms and ions, identify the substances that are oxidized and reduced, and write oxidation and reduction half-reactions.

Text Problem: 4.44

C. Using an activity series

An activity series is used to predict whether a metal or hydrogen displacement reaction will occur (see Figure 4.16 of the text). An activity series can be described as a convenient summary of the results of many possible displacement reactions.

(1) Hydrogen displacement. Any metal above hydrogen in the activity series will displace it from water or from an acid. Metals below hydrogen will *not* react with either water or an acid.

(2) Metal displacement. Any metal will react with a compound containing any metal ion listed below it.

EXAMPLE 4.7

Predict the outcome of the reactions represented by the following equations by using the activity series, and balance the equations.

Strategy: *Hydrogen displacement*: Any metal above hydrogen in the activity series will displace it from water or from an acid. Metals below hydrogen will *not* react with either water or an acid.

Solution:

(a) $Mg(s) + HCl(aq) \longrightarrow$

Since Mg is above hydrogen in the activity series, it will displace hydrogen from the acid.

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

(b) $Au(s) + H_2O(l) \longrightarrow$

Since Au (gold) is below hydrogen in the activity series, it will *not* react with water. You probably already knew this.

$$Au(s) + H_2O(l) \longrightarrow \text{No reaction}$$

Strategy: *Metal displacement*: Any metal will react with a compound containing any metal ion listed below it.

Solution:

(c) $Cu(s) + NiCl_2(aq) \longrightarrow$

In this case Ni^{2+} is listed *above* Cu in the activity series. No reaction will occur.

$$Cu(s) + NiCl_2(aq) \longrightarrow \text{No reaction}$$

PRACTICE EXERCISE

7. Predict the outcome of the following reactions using the activity series. If a reaction occurs, balance the equation.
   (a) $Al(s) + HCl(aq) \longrightarrow$
   (b) $Au(s) + KCl(aq) \longrightarrow$

Text Problems: 4.52, 4.54

PROBLEM TYPE 5: CONCENTRATION OF SOLUTIONS

Solutions are characterized by their concentration, that is, the amount of solute dissolved in a given quantity of solvent. One of the most common units of concentration in chemistry is **molarity (*M*)**. Molarity is the number of moles of solute in 1 liter of solution:

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

Sometimes, it is useful to rearrange the above equation to the following form:

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

EXAMPLE 4.8

What is the molarity of a solution made by dissolving 32.1 g of KNO_3 in enough water to make 500 mL of solution?

Strategy: Since the definition of molarity is moles solute per liters of solution, we need to convert grams of solute to moles of solute and convert mL of solution to L of solution.

Solution:

$\mathcal{M}(KNO_3) = 101.1$ g/mol

$$?\text{ moles solute} = 32.1\,\cancel{g}\,KNO_3 \times \frac{1\text{ mol }KNO_3}{101.1\,\cancel{g}\,KNO_3} = 0.318\text{ mol }KNO_3$$

$$?\text{ liters of solution} = 500\,\cancel{mL}\text{ solution} \times \frac{1\text{ L}}{1000\,\cancel{mL}} = 0.500\text{ L solution}$$

Substitute the above values into the molarity equation.

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

$$M = \frac{0.318\text{ mol }KNO_3}{0.500\text{ L solution}} = \mathbf{0.636\ \mathit{M}}$$

This is normally written 0.636 M KNO_3.

PRACTICE EXERCISE

8. An aqueous nutrient solution is prepared by adding 50.23 g of KNO_3 (molar mass = 101.1 g/mol) to enough water to fill a 40.0 L container. What is the molarity of the KNO_3 solution?

EXAMPLE 4.9

How many moles of solute are in 2.50×10^2 mL of 0.100 M KCl?

Strategy: Since the problem asks for moles of solute, you must solve the equation algebraically for moles of solute.

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

Substitute the molarity and liters of solution into the above equation to solve for moles solute.

Solution:

$2.50 \times 10^2\text{ mL} = 0.250\text{ L}$

$$\textbf{? moles KCl solute} = \frac{0.100\text{ moles solute}}{1\,\cancel{L}\text{ solution}} \times 0.250\,\cancel{L}\text{ solution} = \mathbf{0.0250\ mol}$$

PRACTICE EXERCISE

9. You need to prepare 1.00 L of a 0.500 M NaCl solution. What mass of NaCl (in g) must you weigh out to prepare this solution?

Text Problems: 4.60, 4.62, 4.64, 4.66

PROBLEM TYPE 6: DILUTION OF SOLUTIONS

Dilution refers to the procedure for preparing a less-concentrated solution from a more-concentrated one. The key to solving a dilution problem is to realize that

moles of solute *before* dilution = moles of solute *after* dilution

In Problem Type 5 above, we discussed how to calculate moles of solute from the molarity and the volume of solution.

moles solute = (molarity) × (volume of solution (in L))

Thus,

moles of solute *before* dilution (initial) = moles of solute *after* dilution (final)

$$\boldsymbol{M_{\text{initial}}V_{\text{initial}} = M_{\text{final}}V_{\text{final}}}$$

EXAMPLE 4.10

What volume of a concentrated (12.0 *M*) hydrochloric acid stock solution is needed to prepare 8.00×10^2 mL of 0.120 *M* HCl?

Strategy: Recognize that the problem asks for the initial volume of stock solution needed to prepare the dilute solution. Solve the above equation algebraically for V_{initial}, then substitute in the appropriate values from the problem.

Solution: We prepare for the calculation by tabulating our data.

$M_i = 12.0\ M$ $\qquad M_f = 0.120\ M$

$V_i = ?$ $\qquad V_f = 8.00 \times 10^2$ mL

$$V_{\text{initial}} = \frac{M_{\text{final}}V_{\text{final}}}{M_{\text{initial}}}$$

$$V_{\textbf{initial}} = \frac{(0.120\ \cancel{M})(8.00 \times 10^2\ \text{mL})}{12.0\ \cancel{M}} = \mathbf{8.00\ mL}$$

Tip: The units of V_{initial} and V_{final} can be milliliters or liters for a dilution problem as long as they are the same. Be consistent. Also, make sure to check whether your results seem reasonable. Be sure that $M_{\text{initial}} > M_{\text{final}}$ and $V_{\text{final}} > V_{\text{initial}}$.

PRACTICE EXERCISE

10. A 20.0 mL sample of 0.127 *M* $Ca(NO_3)_2$ is diluted to 5.00 L. What is the molarity of the resulting solution?

Text Problems: 4.70, 4.72, 4.74

PROBLEM TYPE 7: GRAVIMETRIC ANALYSIS

Gravimetric analysis is an analytical technique based on the measurement of mass. The type of gravimetric analysis discussed in your text involves the formation, isolation, and mass determination of a precipitate. This procedure is applicable only to reactions that go to completion, or have nearly a 100 percent yield. Thus, the precipitate must be insoluble rather than slightly soluble. See Section 4.6 of your text for further discussion of this technique.

The typical problem involves determining the mass percent of an element in one of the reactants. The element (ion) of interest is completely precipitated from solution. Use the following approach to solve this type of problem.

Step 1: From the measured mass of precipitate, calculate the mass of the element of interest in the precipitate. This is the same amount of the element that was present in the original sample.

Step 2: Calculate the mass percent of the element of interest in the original sample. See Problem Type 4A, Chapter 3.

> **Tip:** Try to be flexible when solving problems. Some gravimetric analysis problems may ask you to calculate the *molar concentration* of the component of interest in the sample, rather than mass percent. For this type of problem, you must modify your approach by converting grams of the component of interest to moles, then dividing by the volume of solution in liters.

EXAMPLE 4.11
A 0.7469 g sample of an ionic compound containing Pb ions is dissolved in water and treated with excess Na_2SO_4. If the mass of $PbSO_4$ that precipitates is 0.6839 g, what is the percent by mass of Pb in the original sample?

Strategy: We want to calculate the mass % of Pb in the original compound. Let's start with the definition of mass %.

want to calculate need to find

$$\text{mass \% Pb} = \frac{\text{mass Pb}}{\text{mass of sample}} \times 100\%$$

given

The mass of the sample is given in the problem (0.7469 g). Therefore we need to find the mass of Pb in the original sample. We assume the precipitation is quantitative, that is, that all of the lead in the sample has been precipitated as lead sulfate. From the mass of $PbSO_4$ produced, we can calculate the mass of Pb. There is 1 mole of Pb in 1 mole of $PbSO_4$.

Solution: First, we calculate the mass of Pb in 0.6839 g of the $PbSO_4$ precipitate. The molar mass of $PbSO_4$ is 303.27 g/mol.

$$\textbf{? mass of Pb} = 0.6839\,\cancel{\text{g}}\,\text{PbSO}_4 \times \frac{1\,\cancel{\text{mol}}\,\text{PbSO}_4}{303.27\,\cancel{\text{g}}\,\text{PbSO}_4} \times \frac{1\,\cancel{\text{mol}}\,\text{Pb}}{1\,\cancel{\text{mol}}\,\text{PbSO}_4} \times \frac{207.2\text{ g Pb}}{1\,\cancel{\text{mol}}\,\text{Pb}} = \textbf{0.4673 g Pb}$$

Next, we calculate the mass percent of Pb in the unknown compound.

$$\textbf{\%Pb by mass} = \frac{0.4673\text{ g}}{0.7469\text{ g}} \times 100\% = \textbf{62.57\%}$$

PRACTICE EXERCISE

11. The concentration of Pb^{2+} ions in tap water could be determined by adding excess sodium sulfate solution to water. Excess sodium sulfate solution is added to 0.250 L of tap water. Write the net ionic equation and calculate the molar concentration of Pb^{2+} in the water sample if 0.01685 g of solid $PbSO_4$ is formed.

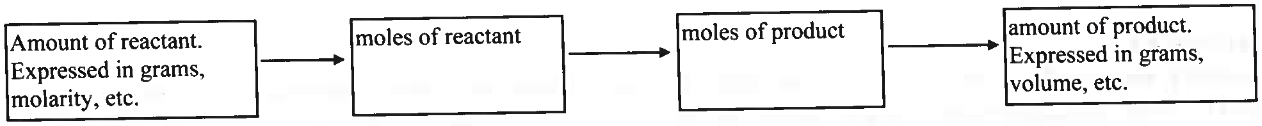
Text Problems: 4.78, 4.80

PROBLEM TYPE 8: ACID-BASE TITRATIONS

You must try to convince yourself that a titration problem follows the same thought process as the stoichiometry problems discussed in Chapter 3. The difference is that for acid and base solutions, you will typically be given the molarity rather than grams of substance.

Remember, you cannot directly compare grams of one substance to grams of another. Similarly, you typically cannot compare molarity or volume of one substance to that of another. Therefore, you must convert to *moles* of one substance, and then apply the correct mole ratio from the balanced chemical equation to convert to *moles* of the other substance.

A typical approach to a stoichiometry problem is outlined below.



EXAMPLE 4.12

What volume of 0.900 *M* HCl is required to completely neutralize 50.0 mL of a 0.500 *M* $Ba(OH)_2$ solution?

Strategy: We know the molarity of the HCl solution, and we want to calculate the volume of the HCl solution.

$$\overset{\text{given}}{M}\text{ of HCl} = \frac{\overset{\text{need to find}}{\text{mol HCl}}}{\underset{\text{want to calculate}}{\text{L of HCl soln}}}$$

If we can determine the moles of HCl, we can then use the definition of molarity to calculate the volume of HCl needed. From the volume and molarity of $Ba(OH)_2$, we can calculate moles of $Ba(OH)_2$. Then, using the mole ratio from the balanced equation, we can calculate moles of HCl.

Solution: In order to have the correct mole ratio to solve the problem, you must start with a balanced chemical equation.

$$2HCl(aq) + Ba(OH)_2(aq) \longrightarrow BaCl_2(aq) + 2H_2O(l)$$

From the molarity and volume of the $Ba(OH)_2$ solution, you can calculate moles of $Ba(OH)_2$. Then, using the mole ratio from the balanced equation above, you can calculate moles of HCl.

50.0 mL = 0.0500 L

$$?\text{ mol HCl} = 0.0500\,\cancel{\text{L}} \times \frac{0.500\text{ m}\cancel{\text{ol}}\text{ Ba(OH)}_2}{1\,\cancel{\text{L}}\text{ of solution}} \times \frac{2\text{ mol HCl}}{1\text{ m}\cancel{\text{ol}}\text{ Ba(OH)}_2} = 0.0500\text{ mol HCl}$$

Thus, 0.0500 mol of HCl are required to neutralize 50.0 mL of 0.500 *M* $Ba(OH)_2$.

Solve the molarity equation algebraically for liters of solution. Then, substitute in the moles of HCl and molarity of HCl to solve for volume of HCl.

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

$$\textbf{volume of HCl} = \frac{0.0500\text{ m}\cancel{\text{ol}}\text{ HCl}}{0.900\text{ m}\cancel{\text{ol}}/\text{L}} = \textbf{0.0556 L} = \textbf{55.6 mL}$$

PRACTICE EXERCISE

12. The distinctive odor of vinegar is due to acetic acid, CH_3COOH. Acetic acid reacts with sodium hydroxide in the following fashion:

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow H_2O(l) + CH_3COONa(aq)$$

If 2.50 mL of vinegar requires 34.9 mL of 0.0960 *M* NaOH to reach the equivalence point in a titration, how many grams of acetic acid are in the 2.50 mL sample?

Text Problems: 4.86, **4.88**

PROBLEM TYPE 9: REDOX TITRATIONS

Redox titration problems are solved in a similar manner to acid-base titration problems. A redox reaction is an *electron transfer* reaction; whereas an acid-base reaction is typically a *proton* transfer reaction. In a redox titration, an oxidizing agent is titrated against a reducing agent.

EXAMPLE 4.13

A 20.32 mL volume of 0.2002 M $KMnO_4$ solution is needed to oxidize 10.00 mL of an oxalic acid ($H_2C_2O_4$) solution. What is the concentration of the oxalic acid solution? The net ionic equation is:

$$\mathbf{2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

Strategy: We want to calculate the molarity of the oxalic acid solution. From the molarity and volume of $KMnO_4$, we can calculate moles of $KMnO_4$. Then, using the mole ratio from the balanced equation, we can calculate moles of $H_2C_2O_4$. From the moles and volume of oxalic acid, we can calculate the molarity?

Solution: The balanced equation is given in the problem. From the molarity and volume of the $KMnO_4$ solution, you can calculate moles of MnO_4^-. Then, using the mole ratio from the balanced equation above, you can calculate moles of $C_2O_4^{2-}$.

20.32 mL = 0.02032 L

$$0.02032\,\cancel{L}\text{ soln} \times \frac{0.2002\ \cancel{mol}\ MnO_4^{2-}}{1\,\cancel{L}\text{ soln}} \times \frac{5\text{ mol }C_2O_4^{2-}}{2\ \cancel{mol}\ MnO_4^{2-}} = \mathbf{0.01017\ mol\ C_2O_4^{2-}}$$

The mole ratio between $C_2O_4^{2-}$ and oxalic acid, $H_2C_2O_4$, is 1:1; therefore, the number of moles of oxalic acid is 0.01017 mole.

We can now calculate the molarity of the oxalic acid solution from the moles of oxalic acid and the volume of the solution.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{0.01017\text{ mol oxalic acid}}{10.00 \times 10^{-3}\text{ L soln}} = \mathbf{1.017\ \mathit{M}\ oxalic\ acid}$$

PRACTICE EXERCISE

13. Fe metal reacts with hydrochloric acid to produce Fe^{2+} ions and hydrogen gas. It takes 55.6 mL of 1.15 M HCl to completely react with a piece of Fe. What is the mass of the Fe? The balanced equation is:

$$Fe(s) + 2H^+(aq) + 2Cl^-(aq) \longrightarrow Fe^{2+}(aq) + H_2(g) + 2Cl^-(aq)$$

Text Problems: **4.92**, 4.94, 4.96, 4.98

ANSWERS TO PRACTICE EXERCISES

1. **(a)** soluble **(b)** insoluble **(c)** soluble **(d)** insoluble

2. $CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow 2NaCl(aq) + CaCO_3(s)$

$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \longrightarrow 2Na^+(aq) + 2Cl^-(aq) + CaCO_3(s)$

$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$

3. **(a)** acid **(b)** acid **(c)** base **(d)** both

4. $2HNO_2(aq) + Ba(OH)_2(aq) \longrightarrow Ba(NO_2)_2(aq) + 2H_2O(l)$

$2HNO_2(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow Ba^{2+}(aq) + 2NO_2^-(aq) + 2H_2O(l)$

$2HNO_2(aq) + 2OH^-(aq) \longrightarrow 2NO_2^-(aq) + 2H_2O(l)$

5. **(a)** +4 **(b)** +2 **(c)** +4 **(d)** +5

6. The oxidation numbers of the atoms and ions are:

$$Cd^0(s) + Ni^{4+}O_2^{2-}(s) + 2H_2^{+}O^{2-}(l) \longrightarrow Cd^{2+}(OH)_2^-(s) + Ni^{2+}(OH)_2^-(s)$$

$Cd^0(s)$ is oxidized, and Ni^{4+} is reduced. The oxidation and reduction half-reactions are:

$$Cd \longrightarrow Cd^{2+} + 2e^-$$
$$Ni^{4+} + 2e^- \longrightarrow Ni^{2+}$$

7. **(a)** $2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$ **(b)** No reaction

8. 0.0124 *M* **9.** 29.22 g NaCl **10.** 5.08×10^{-4} *M*

11. $Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$

$[Pb^{2+}] = 2.222 \times 10^{-4}\ M$

12. 0.201 g acetic acid **13.** 1.79 g Fe

SOLUTIONS TO SELECTED TEXT PROBLEMS

4.8 When NaCl dissolves in water it dissociates into Na^+ and Cl^- ions. When the ions are hydrated, the water molecules will be oriented so that the negative end of the water dipole interacts with the positive sodium ion, and the positive end of the water dipole interacts with the negative chloride ion. The negative end of the water dipole is near the oxygen atom, and the positive end of the water dipole is near the hydrogen atoms. The diagram that best represents the hydration of NaCl when dissolved in water is choice **(c)**.

4.10 Ionic compounds, strong acids, and strong bases (metal hydroxides) are strong electrolytes (completely broken up into ions of the compound). Weak acids and weak bases are weak electrolytes. Molecular substances other than acids or bases are nonelectrolytes.

(a) strong electrolyte (ionic)
(b) nonelectrolyte
(c) weak electrolyte (weak base)
(d) strong electrolyte (strong base)

4.12 **(a)** Solid NaCl does not conduct. The ions are locked in a rigid lattice structure.

(b) Molten NaCl conducts. The ions can move around in the liquid state.

(c) Aqueous NaCl conducts. NaCl dissociates completely to $Na^+(aq)$ and $Cl^-(aq)$ in water.

4.14 Since HCl dissolved in water conducts electricity, then HCl(*aq*) must actually exists as $H^+(aq)$ cations and $Cl^-(aq)$ anions. Since HCl dissolved in benzene solvent does not conduct electricity, then we must assume that the HCl molecules in benzene solvent do not ionize, but rather exist as un-ionized molecules.

4.18 Refer to Table 4.2 of the text to solve this problem. $Mg(OH)_2$ is insoluble in water. It will precipitate from solution. KCl is soluble in water and will remain as K^+ and Cl^- ions in solution. Diagram **(b)** best represents the mixture.

4.20 Applying solubility rules, Problem Type 1.

Strategy: Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations, the ammonium ion, and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, refer to Table 4.2 of the text.

Solution:

(a) $CaCO_3$ is **insoluble**. Most carbonate compounds are insoluble.
(b) $ZnSO_4$ is **soluble**. Most sulfate compounds are soluble.
(c) $Hg(NO_3)_2$ is **soluble**. All nitrate compounds are soluble.
(d) $HgSO_4$ is **insoluble**. Most sulfate compounds are soluble, but those containing Ag^+, Ca^{2+}, Ba^{2+}, Hg^{2+}, and Pb^{2+} are insoluble.
(e) NH_4ClO_4 is **soluble**. All ammonium compounds are soluble.

4.22 Writing Molecular, Ionic, and Net Ionic Equations, Problem Type 2.

(a)

Strategy: Recall that an *ionic equation* shows dissolved ionic compounds in terms of their free ions. A *net ionic equation* shows only the species that actually take part in the reaction. What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of Na_2S and $ZnCl_2$? What happens when the cations encounter the anions in solution?

Solution: In solution, Na_2S dissociates into Na^+ and S^{2-} ions and $ZnCl_2$ dissociates into Zn^{2+} and Cl^- ions. According to Table 4.2 of the text, zinc ions (Zn^{2+}) and sulfide ions (S^{2-}) will form an insoluble compound, zinc sulfide (ZnS), while the other product, NaCl, is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:

$$Na_2S(aq) + ZnCl_2(aq) \longrightarrow ZnS(s) + 2NaCl(aq)$$

The ionic and net ionic equations are:

Ionic: $2Na^+(aq) + S^{2-}(aq) + Zn^{2+}(aq) + 2Cl^-(aq) \longrightarrow ZnS(s) + 2Na^+(aq) + 2Cl^-(aq)$

Net ionic: $Zn^{2+}(aq) + S^{2-}(aq) \longrightarrow ZnS(s)$

Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

(b)
Strategy: What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of K_3PO_4 and $Sr(NO_3)_2$? What happens when the cations encounter the anions in solution?

Solution: In solution, K_3PO_4 dissociates into K^+ and PO_4^{3-} ions and $Sr(NO_3)_2$ dissociates into Sr^{2+} and NO_3^- ions. According to Table 4.2 of the text, strontium ions (Sr^{2+}) and phosphate ions (PO_4^{3-}) will form an insoluble compound, strontium phosphate [$Sr_3(PO_4)_2$], while the other product, KNO_3, is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:

$$2K_3PO_4(aq) + 3Sr(NO_3)_2(aq) \longrightarrow Sr_3(PO_4)_2(s) + 6KNO_3(aq)$$

The ionic and net ionic equations are:

Ionic: $6K^+(aq) + 2PO_4^{3-}(aq) + 3Sr^{2+}(aq) + 6NO_3^-(aq) \longrightarrow Sr_3(PO_4)_2(s) + 6K^+(aq) + 6NO_3^-(aq)$

Net ionic: $3Sr^{2+}(aq) + 2PO_4^{3-}(aq) \longrightarrow Sr_3(PO_4)_2(s)$

Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

(c)
Strategy: What happens when ionic compounds dissolve in water? What ions are formed from the dissociation of $Mg(NO_3)_2$ and NaOH? What happens when the cations encounter the anions in solution?

Solution: In solution, $Mg(NO_3)_2$ dissociates into Mg^{2+} and NO_3^- ions and NaOH dissociates into Na^+ and OH^- ions. According to Table 4.2 of the text, magnesium ions (Mg^{2+}) and hydroxide ions (OH^-) will form an insoluble compound, magnesium hydroxide [$Mg(OH)_2$], while the other product, $NaNO_3$, is soluble and remains in solution. This is a precipitation reaction. The balanced molecular equation is:

$$Mg(NO_3)_2(aq) + 2NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2NaNO_3(aq)$$

The ionic and net ionic equations are:

Ionic: $Mg^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s) + 2Na^+(aq) + 2NO_3^-(aq)$

Net ionic: $Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$

Check: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side, and the number of positive and negative charges on the left-hand side of the equation is the same.

4.24 (a) Add chloride ions. KCl is soluble, but AgCl is not.

(b) Add hydroxide ions. $Ba(OH)_2$ is soluble, but $Pb(OH)_2$ is insoluble.

(c) Add carbonate ions. $(NH_4)_2CO_3$ is soluble, but $CaCO_3$ is insoluble.

(d) Add sulfate ions. $CuSO_4$ is soluble, but $BaSO_4$ is insoluble.

4.32 Identifying Brønsted acids and bases, Problem Type 3A.

Strategy: What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

Solution:

(a) PO_4^{3-} in water can accept a proton to become HPO_4^{2-}, and is thus a **Brønsted base.**

(b) ClO_2^- in water can accept a proton to become $HClO_2$, and is thus a **Brønsted base.**

(c) NH_4^+ dissolved in water can donate a proton H^+, thus behaving as a **Brønsted acid.**

(d) HCO_3^- can either accept a proton to become H_2CO_3, thus behaving as a **Brønsted base.** Or, HCO_3^- can donate a proton to yield H^+ and CO_3^{2-}, thus behaving as a **Brønsted acid.**

Comment: The HCO_3^- species is said to be *amphoteric* because it possesses both acidic and basic properties.

4.34 Writing acid-base reactions, Problem Type 3B.

Strategy: Recall that strong acids and strong bases are strong electrolytes. They are completely ionized in solution. An *ionic equation* will show strong acids and strong bases in terms of their free ions. Weak acids and weak bases are weak electrolytes. They only ionize to a small extent in solution. Weak acids and weak bases are shown as molecules in ionic and net ionic equations. A *net ionic equation* shows only the species that actually take part in the reaction.

(a)

Solution: CH_3COOH is a weak acid. It will be shown as a molecule in the ionic equation. KOH is a strong base. It completely ionizes to K^+ and OH^- ions. Since CH_3COOH is an acid, it donates an H^+ to the base, OH^-, producing water. The other product is the salt, CH_3COOK, which is soluble and remains in solution. The balanced molecular equation is:

$$CH_3COOH(aq) + KOH(aq) \longrightarrow CH_3COOK(aq) + H_2O(l)$$

The ionic and net ionic equations are:

Ionic: $CH_3COOH(aq) + K^+(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + K^+(aq) + H_2O(l)$

Net ionic: $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$

(b)

Solution: H_2CO_3 is a weak acid. It will be shown as a molecule in the ionic equation. NaOH is a strong base. It completely ionizes to Na^+ and OH^- ions. Since H_2CO_3 is an acid, it donates an H^+ to the base, OH^-, producing water. The other product is the salt, Na_2CO_3, which is soluble and remains in solution. The balanced molecular equation is:

$$H_2CO_3(aq) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + 2H_2O(l)$$

The ionic and net ionic equations are:

Ionic: $H_2CO_3(aq) + 2Na^+(aq) + 2OH^-(aq) \longrightarrow 2Na^+(aq) + CO_3^{2-}(aq) + 2H_2O(l)$

Net ionic: $H_2CO_3(aq) + 2OH^-(aq) \longrightarrow CO_3^{2-}(aq) + 2H_2O(l)$

(c)

Solution: HNO_3 is a strong acid. It completely ionizes to H^+ and NO_3^- ions. $Ba(OH)_2$ is a strong base. It completely ionizes to Ba^{2+} and OH^- ions. Since HNO_3 is an acid, it donates an H^+ to the base, OH^-, producing water. The other product is the salt, $Ba(NO_3)_2$, which is soluble and remains in solution. The balanced molecular equation is:

$$2HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

The ionic and net ionic equations are:

Ionic: $2H^+(aq) + 2NO_3^-(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow Ba^{2+}(aq) + 2NO_3^-(aq) + 2H_2O(l)$

Net ionic: $2H^+(aq) + 2OH^-(aq) \longrightarrow 2H_2O(l)$ or $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

4.44 Writing oxidation/reduction half-reactions, Problem Type 4B.

Strategy: In order to break a redox reaction down into an oxidation half-reaction and a reduction half-reaction, you should first assign oxidation numbers to all the atoms in the reaction. In this way, you can determine which element is oxidized (loses electrons) and which element is reduced (gains electrons).

Solution: In each part, the reducing agent is the reactant in the first half-reaction and the oxidizing agent is the reactant in the second half-reaction. The coefficients in each half-reaction have been reduced to smallest whole numbers.

(a) The product is an ionic compound whose ions are Fe^{3+} and O^{2-}.

$$Fe \longrightarrow Fe^{3+} + 3e^-$$
$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

O_2 is the oxidizing agent; Fe is the reducing agent.

(b) Na^+ does not change in this reaction. It is a "spectator ion."

$$2Br^- \longrightarrow Br_2 + 2e^-$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

Cl_2 is the oxidizing agent; Br^- is the reducing agent.

(c) Assume SiF_4 is made up of Si^{4+} and F^-.

$$Si \longrightarrow Si^{4+} + 4e^-$$
$$F_2 + 2e^- \longrightarrow 2F^-$$

F_2 is the oxidizing agent; Si is the reducing agent.

(d) Assume HCl is made up of H^+ and Cl^-.

$$H_2 \longrightarrow 2H^+ + 2e^-$$
$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$

Cl_2 is the oxidizing agent; H_2 is the reducing agent.

4.46 Assigning oxidation numbers, Problem Type 4A.

Strategy: In general, we follow the rules listed in Section 4.4 of the text for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1 in ionic compounds, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of −2 in their compounds.

Solution: All the compounds listed are neutral compounds, so the oxidation numbers must sum to zero (Rule 6, Section 4.4 of the text).

Let the oxidation number of P = x.

(a) $x + 1 + (3)(-2) = 0,\ \mathbf{x = +5}$

(b) $x + (3)(+1) + (2)(-2) = 0,\ \mathbf{x = +1}$

(c) $x + (3)(+1) + (3)(-2) = 0,\ \mathbf{x = +3}$

(d) $x + (3)(+1) + (4)(-2) = 0,\ \mathbf{x = +5}$

(e) $2x + (4)(+1) + (7)(-2) = 0,\ 2x = 10,\ \mathbf{x = +5}$

(f) $3x + (5)(+1) + (10)(-2) = 0,\ 3x = 15,\ \mathbf{x = +5}$

The molecules in part (a), (e), and (f) can be made by strongly heating the compound in part (d). Are these oxidation-reduction reactions?

Check: In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species, in this case zero?

4.48 All are free elements, so all have an oxidation number of **zero**.

4.50 **(a)** N: −3 **(b)** O: −1/2 **(c)** C: −1 **(d)** C: +4

(e) C: +3 **(f)** O: −2 **(g)** B: +3 **(h)** W: +6

4.52 Using an activity series, Problem Type 4C.

Strategy: *Hydrogen displacement*: Any metal above hydrogen in the activity series will displace it from water or from an acid. Metals below hydrogen will *not* react with either water or an acid.

Solution: Only **(b)** Li and **(d)** Ca are above hydrogen in the activity series, so they are the only metals in this problem that will react with water.

4.54 **(a)** $Cu(s) + HCl(aq) \rightarrow$ no reaction, since $Cu(s)$ is less reactive than the hydrogen from acids.

(b) $I_2(s) + NaBr(aq) \rightarrow$ no reaction, since $I_2(s)$ is less reactive than $Br_2(l)$.

(c) $Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$, since $Mg(s)$ is more reactive than $Cu(s)$.

Net ionic equation: $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

(d) $Cl_2(g) + 2KBr(aq) \rightarrow Br_2(l) + 2KCl(aq)$, since $Cl_2(g)$ is more reactive than $Br_2(l)$

Net ionic equation: $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$

4.56 **(a)** Combination reaction
(b) Decomposition reaction
(c) Displacement reaction
(d) Disproportionation reaction

4.60 Concentration of Solutions, Problem Type 5.

Strategy: How many moles of $NaNO_3$ does 250 mL of a 0.707 *M* solution contain? How would you convert moles to grams?

Solution: From the molarity (0.707 *M*), we can calculate the moles of $NaNO_3$ needed to prepare 250 mL of solution.

$$\text{Moles } NaNO_3 = \frac{0.707 \text{ mol } NaNO_3}{1000 \cancel{\text{mL}} \text{ soln}} \times 250 \cancel{\text{mL}} \text{ soln} = 0.177 \text{ mol}$$

Next, we use the molar mass of $NaNO_3$ as a conversion factor to convert from moles to grams.

$\mathcal{M}(NaNO_3) = 85.00$ g/mol.

$$0.177 \cancel{\text{mol}}\, NaNO_3 \times \frac{85.00 \text{ g } NaNO_3}{1 \cancel{\text{mol}}\, NaNO_3} = 15.0 \text{ g } NaNO_3$$

To make the solution, **dissolve 15.0 g of $NaNO_3$ in enough water to make 250 mL of solution.**

Check: As a ball-park estimate, the mass should be given by [molarity (mol/L) × volume (L) = moles × molar mass (g/mol) = grams]. Let's round the molarity to 1 *M* and the molar mass to 80 g, because we are simply making an estimate. This gives: [1 mol/L × (1/4)L × 80 g = 20 g]. This is close to our answer of 15.0 g.

4.62 Since the problem asks for grams of solute (KOH), you should be thinking that you can calculate moles of solute from the molarity and volume of solution. Then, you can convert moles of solute to grams of solute.

$$\text{? moles KOH solute} = \frac{5.50 \text{ moles solute}}{1000 \cancel{\text{mL}} \text{ solution}} \times 35.0 \cancel{\text{mL}} \text{ solution} = 0.193 \text{ mol KOH}$$

The molar mass of KOH is 56.11 g/mol. Use this conversion factor to calculate grams of KOH.

$$\textbf{? grams KOH} = 0.193 \cancel{\text{mol}} \text{ KOH} \times \frac{56.108 \text{ g KOH}}{1 \cancel{\text{mol}} \text{ KOH}} = \textbf{10.8 g KOH}$$

4.64 **(a)**

$$\text{? mol } CH_3OH = 6.57 \cancel{\text{g}}\, CH_3OH \times \frac{1 \text{ mol } CH_3OH}{32.042 \cancel{\text{g}}\, CH_3OH} = 0.205 \text{ mol } CH_3OH$$

$$\boldsymbol{M} = \frac{0.205 \text{ mol } CH_3OH}{0.150 \text{ L}} = \mathbf{1.37}\ \boldsymbol{M}$$

(b)

$$\text{? mol } CaCl_2 = 10.4 \cancel{\text{g}}\, CaCl_2 \times \frac{1 \text{ mol } CaCl_2}{110.98 \cancel{\text{g}}\, CaCl_2} = 0.0937 \text{ mol } CaCl_2$$

$$\boldsymbol{M} = \frac{0.0937 \text{ mol } CaCl_2}{0.220 \text{ L}} = \mathbf{0.426}\ \boldsymbol{M}$$

(c) $$? \text{ mol } C_{10}H_8 = 7.82\,\cancel{\text{g}}\,C_{10}H_8 \times \frac{1 \text{ mol } C_{10}H_8}{128.16\,\cancel{\text{g}}\,C_{10}H_8} = 0.0610 \text{ mol } C_{10}H_8$$

$$M = \frac{0.0610 \text{ mol } C_{10}H_8}{0.0852 \text{ L}} = \mathbf{0.716}\ \boldsymbol{M}$$

4.66 A 250 mL sample of 0.100 M solution contains 0.0250 mol of solute (mol = $M \times$ L). The computation in each case is the same:

(a) $$0.0250\,\cancel{\text{mol}}\text{ CsI} \times \frac{259.8 \text{ g CsI}}{1\,\cancel{\text{mol}}\text{ CsI}} = \mathbf{6.50\ g\ CsI}$$

(b) $$0.0250\,\cancel{\text{mol}}\,H_2SO_4 \times \frac{98.086 \text{ g } H_2SO_4}{1\,\cancel{\text{mol}}\,H_2SO_4} = \mathbf{2.45\ g\ H_2SO_4}$$

(c) $$0.0250\,\cancel{\text{mol}}\,Na_2CO_3 \times \frac{105.99 \text{ g } Na_2CO_3}{1\,\cancel{\text{mol}}\,Na_2CO_3} = \mathbf{2.65\ g\ Na_2CO_3}$$

(d) $$0.0250\,\cancel{\text{mol}}\,K_2Cr_2O_7 \times \frac{294.2 \text{ g } K_2Cr_2O_7}{1\,\cancel{\text{mol}}\,K_2Cr_2O_7} = \mathbf{7.36\ g\ K_2Cr_2O_7}$$

(e) $$0.0250\,\cancel{\text{mol}}\,KMnO_4 \times \frac{158.04 \text{ g } KMnO_4}{1\,\cancel{\text{mol}}\,KMnO_4} = \mathbf{3.95\ g\ KMnO_4}$$

4.70 Dilution of Solutions, Problem Type 6.

Strategy: Because the volume of the final solution is greater than the original solution, this is a dilution process. Keep in mind that in a dilution, the concentration of the solution decreases, but the number of moles of the solute remains the same.

Solution: We prepare for the calculation by tabulating our data.

$M_i = 0.866\ M$ $M_f = ?$

$V_i = 25.0 \text{ mL}$ $V_f = 500 \text{ mL}$

We substitute the data into Equation (4.3) of the text.

$$M_iV_i = M_fV_f$$

$$(0.866\ M)(25.0 \text{ mL}) = M_f(500 \text{ mL})$$

$$\boldsymbol{M_f} = \frac{(0.866\ M)(25.0\,\cancel{\text{mL}})}{500\,\cancel{\text{mL}}} = \mathbf{0.0433}\ \boldsymbol{M}$$

4.72 You need to calculate the final volume of the dilute solution. Then, you can subtract 505 mL from this volume to calculate the amount of water that should be added.

$$V_{\text{final}} = \frac{M_{\text{initial}}V_{\text{initial}}}{M_{\text{final}}} = \frac{(0.125\,\cancel{M})(505 \text{ mL})}{(0.100\,\cancel{M})} = 631 \text{ mL}$$

$$(631 - 505) \text{ mL} = \mathbf{126\ mL\ of\ water}$$

4.74 Moles of calcium nitrate in the first solution:

$$\frac{0.568\text{ mol}}{1000\ \cancel{\text{mL}}\text{ soln}} \times 46.2\ \cancel{\text{mL}}\text{ soln} = 0.0262\text{ mol Ca(NO}_3)_2$$

Moles of calcium nitrate in the second solution:

$$\frac{1.396\text{ mol}}{1000\ \cancel{\text{mL}}\text{ soln}} \times 80.5\ \cancel{\text{mL}}\text{ soln} = 0.112\text{ mol Ca(NO}_3)_2$$

The volume of the combined solutions = 46.2 mL + 80.5 mL = 126.7 mL. The concentration of the final solution is:

$$M = \frac{(0.0262 + 0.112)\text{mol}}{0.1267\text{ L}} = \mathbf{1.09}\ \boldsymbol{M}$$

4.78 Gravimetric Analysis, Problem Type 7.

Strategy: We want to calculate the mass % of Ba in the original compound. Let's start with the definition of mass %.

$$\overset{\text{want to calculate}}{\text{mass \% Ba}} = \frac{\overset{\text{need to find}}{\text{mass Ba}}}{\underset{\text{given}}{\text{mass of sample}}} \times 100\%$$

The mass of the sample is given in the problem (0.6760 g). Therefore we need to find the mass of Ba in the original sample. We assume the precipitation is quantitative, that is, that all of the barium in the sample has been precipitated as barium sulfate. From the mass of $BaSO_4$ produced, we can calculate the mass of Ba. There is 1 mole of Ba in 1 mole of $BaSO_4$.

Solution: First, we calculate the mass of Ba in 0.4105 g of the $BaSO_4$ precipitate. The molar mass of $BaSO_4$ is 233.4 g/mol.

$$\begin{aligned}?\text{ mass of Ba} &= 0.4105\ \cancel{\text{g}}\ \text{BaSO}_4 \times \frac{1\ \cancel{\text{mol}}\ \text{BaSO}_4}{233.37\ \cancel{\text{g}}\ \text{BaSO}_4} \times \frac{1\ \cancel{\text{mol}}\ \text{Ba}}{1\ \cancel{\text{mol}}\ \text{BaSO}_4} \times \frac{137.3\text{ g Ba}}{1\ \cancel{\text{mol}}\ \text{Ba}}\\ &= 0.2415\text{ g Ba}\end{aligned}$$

Next, we calculate the mass percent of Ba in the unknown compound.

$$\textbf{\%Ba by mass} = \frac{0.2415\ \cancel{\text{g}}}{0.6760\ \cancel{\text{g}}} \times 100\% = \mathbf{35.72\%}$$

4.80 The net ionic equation is: $Cu^{2+}(aq) + S^{2-}(aq) \longrightarrow CuS(s)$

The answer sought is the molar concentration of Cu^{2+}, that is, moles of Cu^{2+} ions per liter of solution. The factor-label method is used to convert, in order:

g of CuS → moles CuS → moles Cu^{2+} → moles Cu^{2+} per liter soln

$$[\mathbf{Cu^{2+}}] = 0.0177\ \cancel{\text{g}}\ \text{CuS} \times \frac{1\ \cancel{\text{mol}}\ \text{CuS}}{95.62\ \cancel{\text{g}}\ \text{CuS}} \times \frac{1\text{ mol Cu}^{2+}}{1\ \cancel{\text{mol}}\ \text{CuS}} \times \frac{1}{0.800\text{ L}} = \mathbf{2.31 \times 10^{-4}}\ \boldsymbol{M}$$

4.86 The reaction between HCl and NaOH is:

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

We know the volume of the NaOH solution, and we want to calculate the molarity of the NaOH solution.

$$\overset{\text{want to calculate}}{M \text{ of NaOH}} = \frac{\overset{\text{need to find}}{\text{mol NaOH}}}{\underset{\text{given}}{\text{L of NaOH soln}}}$$

If we can determine the moles of NaOH in the solution, we can then calculate the molarity of the solution. From the volume and molarity of HCl, we can calculate moles of HCl. Then, using the mole ratio from the balanced equation, we can calculate moles of NaOH.

$$?\ \text{mol NaOH} = 17.4\ \cancel{\text{mL}}\ \text{HCl} \times \frac{0.312\ \cancel{\text{mol}}\ \text{HCl}}{1000\ \cancel{\text{mL}}\ \text{soln}} \times \frac{1\ \text{mol NaOH}}{1\ \cancel{\text{mol}}\ \text{HCl}} = 5.43 \times 10^{-3}\ \text{mol NaOH}$$

From the moles and volume of NaOH, we calculate the molarity of the NaOH solution.

$$\boldsymbol{M}\ \textbf{of NaOH} = \frac{\text{mol NaOH}}{\text{L of NaOH soln}} = \frac{5.43 \times 10^{-3}\ \text{mol NaOH}}{25.0 \times 10^{-3}\ \text{L soln}} = \mathbf{0.217}\ \boldsymbol{M}$$

4.88 Acid-Base Titrations, Problem Type 8.

Strategy: We know the molarity of the HCl solution, and we want to calculate the volume of the HCl solution.

$$\overset{\text{given}}{M \text{ of HCl}} = \frac{\overset{\text{need to find}}{\text{mol HCl}}}{\underset{\text{want to calculate}}{\text{L of HCl soln}}}$$

If we can determine the moles of HCl, we can then use the definition of molarity to calculate the volume of HCl needed. From the volume and molarity of NaOH or Ba(OH)_2, we can calculate moles of NaOH or Ba(OH)_2. Then, using the mole ratio from the balanced equation, we can calculate moles of HCl.

Solution:

(a) In order to have the correct mole ratio to solve the problem, you must start with a balanced chemical equation.

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

$$?\ \text{mol HCl} = 10.0\ \cancel{\text{mL}} \times \frac{0.300\ \cancel{\text{mol}}\ \text{NaOH}}{1000\ \cancel{\text{mL}}\ \text{of solution}} \times \frac{1\ \text{mol HCl}}{1\ \cancel{\text{mol}}\ \text{NaOH}} = 3.00 \times 10^{-3}\ \text{mol HCl}$$

From the molarity and moles of HCl, we calculate volume of HCl required to neutralize the NaOH.

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

$$\textbf{volume of HCl} = \frac{3.00 \times 10^{-3}\ \cancel{\text{mol}}\ \text{HCl}}{0.500\ \cancel{\text{mol}}/\text{L}} = \mathbf{6.00 \times 10^{-3}\ L = 6.00\ mL}$$

(b) This problem is similar to part (a). The difference is that the mole ratio between acid and base is 2:1.

$$2\text{HCl}(aq) + \text{Ba(OH)}_2(aq) \longrightarrow \text{BaCl}_2(aq) + 2\text{H}_2\text{O}(l)$$

$$?\ \text{mol HCl} = 10.0\ \cancel{\text{mL}} \times \frac{0.200\ \cancel{\text{mol}}\ \text{Ba(OH)}_2}{1000\ \cancel{\text{mL}}\ \text{of solution}} \times \frac{2\ \text{mol HCl}}{1\ \cancel{\text{mol}}\ \text{Ba(OH)}_2} = 4.00 \times 10^{-3}\ \text{mol HCl}$$

$$\textbf{volume of HCl} = \frac{4.00 \times 10^{-3}\ \cancel{\text{mol}}\ \text{HCl}}{0.500\ \cancel{\text{mol}}/\text{L}} = \mathbf{8.00 \times 10^{-3}\ L = 8.00\ mL}$$

4.92 Redox Titrations, Problem Type 9.

Strategy: We want to calculate the grams of SO_2 in the sample of air. From the molarity and volume of $KMnO_4$, we can calculate moles of $KMnO_4$. Then, using the mole ratio from the balanced equation, we can calculate moles of SO_2. How do we convert from moles of SO_2 to grams of SO_2?

Solution: The balanced equation is given in the problem.

$$5\text{SO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \longrightarrow 5\text{SO}_4^{2-} + 2\text{Mn}^{2+} + 4\text{H}^+$$

The moles of $KMnO_4$ required for the titration are:

$$\frac{0.00800\ \text{mol KMnO}_4}{1000\ \cancel{\text{mL}}\ \text{soln}} \times 7.37\ \cancel{\text{mL}} = 5.90 \times 10^{-5}\ \text{mol KMnO}_4$$

We use the mole ratio from the balanced equation and the molar mass of SO_2 as conversion factors to convert to grams of SO_2.

$$(5.90 \times 10^{-5}\ \cancel{\text{mol}}\ \text{KMnO}_4) \times \frac{5\ \cancel{\text{mol}}\ \text{SO}_2}{2\ \cancel{\text{mol}}\ \text{KMnO}_4} \times \frac{64.07\ \text{g SO}_2}{1\ \cancel{\text{mol}}\ \text{SO}_2} = \mathbf{9.45 \times 10^{-3}\ g\ SO_2}$$

4.94 The balanced equation is given in the problem.

$$2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \longrightarrow 5\text{O}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$

First, calculate the moles of potassium permanganate in 36.44 mL of solution.

$$\frac{0.01652\ \text{mol KMnO}_4}{1000\ \cancel{\text{mL}}\ \text{soln}} \times 36.44\ \cancel{\text{mL}} = 6.020 \times 10^{-4}\ \text{mol KMnO}_4$$

Next, calculate the moles of hydrogen peroxide using the mole ratio from the balanced equation.

$$(6.020 \times 10^{-4}\ \cancel{\text{mol}}\ \text{KMnO}_4) \times \frac{5\ \text{mol H}_2\text{O}_2}{2\ \cancel{\text{mol}}\ \text{KMnO}_4} = 1.505 \times 10^{-3}\ \text{mol H}_2\text{O}_2$$

Finally, calculate the molarity of the H_2O_2 solution. The volume of the solution is 0.02500 L.

$$\textbf{Molarity of } \mathbf{H_2O_2} = \frac{1.505\times10^{-3}\text{ mol } H_2O_2}{0.02500\text{ L}} = \mathbf{0.06020}\ \boldsymbol{M}$$

4.96 From the reaction of oxalic acid with NaOH, the moles of oxalic acid in 15.0 mL of solution can be determined. Then, using this number of moles and other information given, the volume of the $KMnO_4$ solution needed to react with a second sample of oxalic acid can be calculated.

First, calculate the moles of oxalic acid in the solution. $H_2C_2O_4(aq) + 2NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2H_2O(l)$

$$0.0252\,\cancel{\text{L}}\times\frac{0.149\,\cancel{\text{mol}}\text{ NaOH}}{1\,\cancel{\text{L}}\text{ soln}}\times\frac{1\text{ mol } H_2C_2O_4}{2\,\cancel{\text{mol}}\text{ NaOH}} = 1.88\times10^{-3}\text{ mol } H_2C_2O_4$$

Because we are reacting a second sample of equal volume (15.0 mL), the moles of oxalic acid will also be 1.88×10^{-3} mole in this second sample. The balanced equation for the reaction between oxalic acid and $KMnO_4$ is:

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Let's calculate the moles of $KMnO_4$ first, and then we will determine the volume of $KMnO_4$ needed to react with the 15.0 mL sample of oxalic acid.

$$(1.88\times10^{-3}\,\cancel{\text{mol}}\ H_2C_2O_4)\times\frac{2\text{ mol } KMnO_4}{5\,\cancel{\text{mol}}\ H_2C_2O_4} = 7.52\times10^{-4}\text{ mol } KMnO_4$$

Using Equation (4.2) of the text:

$$M = \frac{n}{V}$$

$$V_{KMnO_4} = \frac{n}{M} = \frac{7.52\times10^{-4}\text{ mol}}{0.122\text{ mol/L}} = \mathbf{0.00616\ L = 6.16\ mL}$$

4.98 The balanced equation is:

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$\text{mol } MnO_4^- = \frac{9.56\times10^{-4}\text{ mol } MnO_4^-}{1000\,\cancel{\text{mL}}\text{ of soln}}\times 24.2\,\cancel{\text{mL}} = 2.31\times10^{-5}\text{ mol } MnO_4^-$$

Using the mole ratio from the balanced equation, we can calculate the mass of Ca^{2+} in the 10.0 mL sample of blood.

$$(2.31\times10^{-5}\,\cancel{\text{mol}}\ MnO_4^-)\times\frac{5\,\cancel{\text{mol}}\ C_2O_4^{2-}}{2\,\cancel{\text{mol}}\ MnO_4^-}\times\frac{1\,\cancel{\text{mol}}\ Ca^{2+}}{1\,\cancel{\text{mol}}\ C_2O_4^{2-}}\times\frac{40.08\text{ g } Ca^{2+}}{1\,\cancel{\text{mol}}\ Ca^{2+}} = 2.31\times10^{-3}\text{ g } Ca^{2+}$$

Converting to mg/mL:

$$\frac{2.31\times10^{-3}\,\cancel{\text{g}}\ Ca^{2+}}{10.0\text{ mL of blood}}\times\frac{1\text{ mg}}{0.001\,\cancel{\text{g}}} = \mathbf{0.231\ mg\ Ca^{2+}/mL\ of\ blood}$$

4.100 First, the gases could be tested to see if they supported combustion. O_2 would support combustion, CO_2 would not. Second, if CO_2 is bubbled through a solution of calcium hydroxide [$Ca(OH)_2$], a white precipitate of $CaCO_3$ forms. No reaction occurs when O_2 is bubbled through a calcium hydroxide solution.

4.102 Starting with a balanced chemical equation:

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

From the mass of Mg, you can calculate moles of Mg. Then, using the mole ratio from the balanced equation above, you can calculate moles of HCl reacted.

$$4.47\,\cancel{g}\,Mg \times \frac{1\,\cancel{mol}\,Mg}{24.31\,\cancel{g}\,Mg} \times \frac{2\text{ mol HCl}}{1\,\cancel{mol}\,Mg} = 0.368\text{ mol HCl reacted}$$

Next we can calculate the number of moles of HCl in the original solution.

$$\frac{2.00\,\cancel{mol}\,HCl}{1000\,\cancel{mL}\text{ soln}} \times (5.00 \times 10^2\,\cancel{mL}) = 1.00\text{ mol HCl}$$

$$\text{Moles HCl remaining} = 1.00\text{ mol} - 0.368\text{ mol} = 0.632\text{ mol HCl}$$

$$\textbf{conc. of HCl after reaction} = \frac{\text{mol HCl}}{\text{L soln}} = \frac{0.632\text{ mol HCl}}{0.500\text{ L}} = 1.26\text{ mol/L} = \mathbf{1.26}\ \boldsymbol{M}$$

4.104 The balanced equation is:

$$2HCl(aq) + Na_2CO_3(s) \longrightarrow CO_2(g) + H_2O(l) + 2NaCl(aq)$$

The mole ratio from the balanced equation is 2 moles HCl : 1 mole Na_2CO_3. The moles of HCl needed to react with 0.256 g of Na_2CO_3 are:

$$0.256\,\cancel{g}\,Na_2CO_3 \times \frac{1\,\cancel{mol}\,Na_2CO_3}{105.99\,\cancel{g}\,Na_2CO_3} \times \frac{2\text{ mol HCl}}{1\,\cancel{mol}\,Na_2CO_3} = 4.83 \times 10^{-3}\text{ mol HCl}$$

$$\textbf{Molarity HCl} = \frac{\text{moles HCl}}{\text{L soln}} = \frac{4.83 \times 10^{-3}\text{ mol HCl}}{0.0283\text{ L soln}} = 0.171\text{ mol/L} = \mathbf{0.171}\ \boldsymbol{M}$$

4.106 Starting with a balanced chemical equation:

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$$

From the molarity and volume of the NaOH solution, you can calculate moles of NaOH. Then, using the mole ratio from the balanced equation above, you can calculate moles of CH_3COOH.

$$5.75\,\cancel{mL}\text{ solution} \times \frac{1.00\,\cancel{mol}\,NaOH}{1000\,\cancel{mL}\text{ of solution}} \times \frac{1\text{ mol }CH_3COOH}{1\,\cancel{mol}\,NaOH} = 5.75 \times 10^{-3}\text{ mol }CH_3COOH$$

$$\textbf{Molarity CH}_3\textbf{COOH} = \frac{5.75 \times 10^{-3}\text{ mol }CH_3COOH}{0.0500\text{ L}} = \mathbf{0.115}\ \boldsymbol{M}$$

4.108 The balanced equation is:

$$\text{Zn}(s) + 2\text{AgNO}_3(aq) \longrightarrow \text{Zn(NO}_3)_2(aq) + 2\text{Ag}(s)$$

Let x = mass of Ag produced. We can find the mass of Zn reacted in terms of the amount of Ag produced.

$$x\ \cancel{\text{g}}\ \text{Ag} \times \frac{1\ \cancel{\text{mol}}\ \text{Ag}}{107.9\ \cancel{\text{g}}\ \text{Ag}} \times \frac{1\ \cancel{\text{mol}}\ \text{Zn}}{2\ \cancel{\text{mol}}\ \text{Ag}} \times \frac{65.39\ \text{g Zn}}{1\ \cancel{\text{mol}}\ \text{Zn}} = 0.303x\ \text{g Zn reacted}$$

The mass of Zn remaining will be:

$$2.50\ \text{g} - \text{amount of Zn reacted} = 2.50\ \text{g Zn} - 0.303x\ \text{g Zn}$$

The final mass of the strip, 3.37 g, equals the mass of Ag produced + the mass of Zn remaining.

$$3.37\ \text{g} = x\ \text{g Ag} + (2.50\ \text{g Zn} - 0.303\,x\ \text{g Zn})$$

$$\boldsymbol{x = 1.25\ \textbf{g} = \textbf{mass of Ag produced}}$$

$$\textbf{mass of Zn remaining} = 3.37\ \text{g} - 1.25\ \text{g} = \textbf{2.12 g Zn}$$

or

$$\textbf{mass of Zn remaining} = 2.50\ \text{g Zn} - 0.303x\ \text{g Zn} = 2.50\ \text{g} - (0.303)(1.25\ \text{g}) = \textbf{2.12 g Zn}$$

4.110 The balanced equation is: $\text{HNO}_3(aq) + \text{NaOH}(aq) \longrightarrow \text{NaNO}_3(aq) + \text{H}_2\text{O}(l)$

$$\text{mol HNO}_3 = \frac{0.211\ \text{mol HNO}_3}{1000\ \cancel{\text{mL}}\ \text{soln}} \times 10.7\ \cancel{\text{mL}}\ \text{soln} = 2.26 \times 10^{-3}\ \text{mol HNO}_3$$

$$\text{mol NaOH} = \frac{0.258\ \text{mol NaOH}}{1000\ \cancel{\text{mL}}\ \text{soln}} \times 16.3\ \cancel{\text{mL}}\ \text{soln} = 4.21 \times 10^{-3}\ \text{mol NaOH}$$

Since the mole ratio from the balanced equation is 1 mole NaOH : 1 mole HNO_3, then 2.26×10^{-3} mol HNO_3 will react with 2.26×10^{-3} mol NaOH.

$$\text{mol NaOH remaining} = (4.21 \times 10^{-3}\ \text{mol}) - (2.26 \times 10^{-3}\ \text{mol}) = 1.95 \times 10^{-3}\ \text{mol NaOH}$$

$$10.7\ \text{mL} + 16.3\ \text{mL} = 27.0\ \text{mL} = 0.0270\ \text{L}$$

$$\textbf{molarity NaOH} = \frac{1.95 \times 10^{-3}\ \text{mol NaOH}}{0.0270\ \text{L}} = \boldsymbol{0.0722\ M}$$

4.112 The balanced equations for the two reactions are:

$$\text{X}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{XSO}_4(aq) + \text{H}_2(g)$$

$$\text{H}_2\text{SO}_4(aq) + 2\text{NaOH}(aq) \longrightarrow \text{Na}_2\text{SO}_4(aq) + 2\text{H}_2\text{O}(l)$$

First, let's find the number of moles of excess acid from the reaction with NaOH.

$$0.0334\ \cancel{\text{L}} \times \frac{0.500\ \cancel{\text{mol}}\ \text{NaOH}}{1\ \cancel{\text{L}}\ \text{soln}} \times \frac{1\ \text{mol H}_2\text{SO}_4}{2\ \cancel{\text{mol}}\ \text{NaOH}} = 8.35 \times 10^{-3}\ \text{mol H}_2\text{SO}_4$$

The original number of moles of acid was:

$$0.100\,\cancel{L} \times \frac{0.500 \text{ mol } H_2SO_4}{1\,\cancel{L} \text{ soln}} = 0.0500 \text{ mol } H_2SO_4$$

The amount of sulfuric acid that reacted with the metal, X, is

$$(0.0500 \text{ mol } H_2SO_4) - (8.35 \times 10^{-3} \text{ mol } H_2SO_4) = 0.0417 \text{ mol } H_2SO_4.$$

Since the mole ratio from the balanced equation is 1 mole X : 1 mole H_2SO_4, then the amount of X that reacted is 0.0417 mol X.

$$\textbf{molar mass X} = \frac{1.00 \text{ g X}}{0.0417 \text{ mol X}} = \textbf{24.0 g/mol}$$

The element is **magnesium**.

4.114 First, calculate the number of moles of glucose present.

$$\frac{0.513 \text{ mol glucose}}{1000\,\cancel{mL} \text{ soln}} \times 60.0\,\cancel{mL} = 0.0308 \text{ mol glucose}$$

$$\frac{2.33 \text{ mol glucose}}{1000\,\cancel{mL} \text{ soln}} \times 120.0\,\cancel{mL} = 0.280 \text{ mol glucose}$$

Add the moles of glucose, then divide by the total volume of the combined solutions to calculate the molarity.

60.0 mL + 120.0 mL = 180.0 mL = 0.180 L

$$\textbf{Molarity of final solution} = \frac{(0.0308 + 0.280) \text{ mol glucose}}{0.180 \text{ L}} = 1.73 \text{ mol/L} = \mathbf{1.73}\ \boldsymbol{M}$$

4.116 Iron(II) compounds can be oxidized to iron(III) compounds. The sample could be tested with a small amount of a strongly colored oxidizing agent like a $KMnO_4$ solution, which is a deep purple color. A loss of color would imply the presence of an oxidizable substance like an iron(II) salt.

4.118 Since both of the original solutions were strong electrolytes, you would expect a mixture of the two solutions to also be a strong electrolyte. However, since the light dims, the mixture must contain fewer ions than the original solution. Indeed, H^+ from the sulfuric acid reacts with the OH^- from the barium hydroxide to form water. The barium cations react with the sulfate anions to form insoluble barium sulfate.

$$2H^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow 2H_2O(l) + BaSO_4(s)$$

Thus, the reaction depletes the solution of ions and the conductivity decreases.

4.120 You could test the conductivity of the solutions. Sugar is a nonelectrolyte and an aqueous sugar solution will not conduct electricity; whereas, NaCl is a strong electrolyte when dissolved in water. Silver nitrate could be added to the solutions to see if silver chloride precipitated. In this particular case, the solutions could also be tasted.

4.122 In a redox reaction, the oxidizing agent gains one or more electrons. In doing so, the oxidation number of the element gaining the electrons must become more negative. In the case of chlorine, the −1 oxidation number is already the most negative state possible. The chloride ion *cannot* accept any more electrons; therefore, hydrochloric acid is *not* an oxidizing agent.

4.124 The reaction is too violent. This could cause the hydrogen gas produced to ignite, and an explosion could result.

4.126 The solid sodium bicarbonate would be the better choice. The hydrogen carbonate ion, HCO_3^-, behaves as a Brønsted base to accept a proton from the acid.

$$HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq) \longrightarrow H_2O(l) + CO_2(g)$$

The heat generated during the reaction of hydrogen carbonate with the acid causes the carbonic acid, H_2CO_3, that was formed to decompose to water and carbon dioxide.

The reaction of the spilled sulfuric acid with sodium hydroxide would produce sodium sulfate, Na_2SO_4, and water. There is a possibility that the Na_2SO_4 could precipitate. Also, the sulfate ion, SO_4^{2-} is a weak base; therefore, the "neutralized" solution would actually be *basic*.

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

Also, NaOH is a caustic substance and therefore is not safe to use in this manner.

4.128 **(a)** Table salt, NaCl, is very soluble in water and is a strong electrolyte. Addition of $AgNO_3$ will precipitate AgCl.

(b) Table sugar or sucrose, $C_{12}H_{22}O_{11}$, is soluble in water and is a nonelectrolyte.

(c) Aqueous acetic acid, CH_3COOH, the primary ingredient of vinegar, is a weak electrolyte. It exhibits all of the properties of acids (Section 4.3).

(d) Baking soda, $NaHCO_3$, is a water-soluble strong electrolyte. It reacts with acid to release CO_2 gas. Addition of $Ca(OH)_2$ results in the precipitation of $CaCO_3$.

(e) Washing soda, $Na_2CO_3 \cdot 10H_2O$, is a water-soluble strong electrolyte. It reacts with acids to release CO_2 gas. Addition of a soluble alkaline-earth salt will precipitate the alkaline-earth carbonate. Aqueous washing soda is also slightly basic (Section 4.3).

(f) Boric acid, H_3BO_3, is weak electrolyte and a weak acid.

(g) Epsom salt, $MgSO_4 \cdot 7H_2O$, is a water-soluble strong electrolyte. Addition of $Ba(NO_3)_2$ results in the precipitation of $BaSO_4$. Addition of hydroxide precipitates $Mg(OH)_2$.

(h) Sodium hydroxide, NaOH, is a strong electrolyte and a strong base. Addition of $Ca(NO_3)_2$ results in the precipitation of $Ca(OH)_2$.

(i) Ammonia, NH_3, is a sharp-odored gas that when dissolved in water is a weak electrolyte and a weak base. NH_3 in the gas phase reacts with HCl gas to produce solid NH_4Cl.

(j) Milk of magnesia, $Mg(OH)_2$, is an insoluble, strong base that reacts with acids. The resulting magnesium salt may be soluble or insoluble.

(k) $CaCO_3$ is an insoluble salt that reacts with acid to release CO_2 gas. $CaCO_3$ is discussed in the Chemistry in Action essays entitled, "An Undesirable Precipitation Reaction" and "Metal from the Sea" in Chapter 4.

With the exception of NH_3 and vinegar, all the compounds in this problem are white solids.

4.130 We carry an additional significant figure throughout this calculation to minimize rounding errors. The balanced equation for the reaction is:

$$\text{XCl}(aq) + \text{AgNO}_3(aq) \longrightarrow \text{AgCl}(s) + \text{XNO}_3(aq) \qquad \text{where X = Na, or K}$$

From the amount of AgCl produced, we can calculate the moles of XCl reacted (X = Na, or K).

$$1.913\ \cancel{\text{g}}\ \text{AgCl} \times \frac{1\ \cancel{\text{mol}}\ \text{AgCl}}{143.35\ \cancel{\text{g}}\ \text{AgCl}} \times \frac{1\ \text{mol XCl}}{1\ \cancel{\text{mol}}\ \text{AgCl}} = 0.013345\ \text{mol XCl}$$

Let x = number of moles NaCl. Then, the number of moles of KCl = 0.013345 mol − x. The sum of the NaCl and KCl masses must equal the mass of the mixture, 0.8870 g. We can write:

$$\text{mass NaCl} + \text{mass KCl} = 0.8870\ \text{g}$$

$$\left[x\ \cancel{\text{mol}}\ \text{NaCl} \times \frac{58.44\ \text{g NaCl}}{1\ \cancel{\text{mol}}\ \text{NaCl}}\right] + \left[(0.013345 - x)\cancel{\text{mol}}\ \text{KCl} \times \frac{74.55\ \text{g KCl}}{1\ \cancel{\text{mol}}\ \text{KCl}}\right] = 0.8870\ \text{g}$$

$$x = 6.6958 \times 10^{-3} = \text{moles NaCl}$$

$$\text{mol KCl} = 0.013345 - x = 0.013345\ \text{mol} - (6.6958 \times 10^{-3}\ \text{mol}) = 6.6492 \times 10^{-3}\ \text{mol KCl}$$

Converting moles to grams:

$$\text{mass NaCl} = (6.6958 \times 10^{-3}\ \cancel{\text{mol}}\ \text{NaCl}) \times \frac{58.44\ \text{g NaCl}}{1\ \cancel{\text{mol}}\ \text{NaCl}} = 0.3913\ \text{g NaCl}$$

$$\text{mass KCl} = (6.6492 \times 10^{-3}\ \cancel{\text{mol}}\ \text{KCl}) \times \frac{74.55\ \text{g KCl}}{1\ \cancel{\text{mol}}\ \text{KCl}} = 0.4957\ \text{g KCl}$$

The percentages by mass for each compound are:

$$\textbf{\% NaCl} = \frac{0.3913\ \text{g}}{0.8870\ \text{g}} \times 100\% = \textbf{44.11\% NaCl}$$

$$\textbf{\% KCl} = \frac{0.4957\ \text{g}}{0.8870\ \text{g}} \times 100\% = \textbf{55.89\% KCl}$$

4.132 The number of moles of oxalic acid in 5.00×10^2 mL is:

$$\frac{0.100\ \text{mol H}_2\text{C}_2\text{O}_4}{1000\ \cancel{\text{mL}}\ \text{soln}} \times (5.00 \times 10^2\ \cancel{\text{mL}}) = 0.0500\ \text{mol H}_2\text{C}_2\text{O}_4$$

The balanced equation shows a mole ratio of 1 mol Fe_2O_3 : 6 mol $H_2C_2O_4$. The mass of rust that can be removed is:

$$0.0500\ \cancel{\text{mol}}\ \text{H}_2\text{C}_2\text{O}_4 \times \frac{1\ \cancel{\text{mol}}\ \text{Fe}_2\text{O}_3}{6\ \cancel{\text{mol}}\ \text{H}_2\text{C}_2\text{O}_4} \times \frac{159.7\ \text{g Fe}_2\text{O}_3}{1\ \cancel{\text{mol}}\ \text{Fe}_2\text{O}_3} = \mathbf{1.33\ g\ Fe_2O_3}$$

4.134 The precipitation reaction is: $Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

In this problem, the relative amounts of NaBr and $CaBr_2$ are not known. However, the total amount of Br^- in the mixture can be determined from the amount of AgBr produced. Let's find the number of moles of Br^-. We carry an additional significant figure throughout this calculation to minimize rounding errors.

$$1.6930\,\cancel{g}\,\text{AgBr} \times \frac{1\,\cancel{mol}\,\text{AgBr}}{187.8\,\cancel{g}\,\text{AgBr}} \times \frac{1\text{ mol Br}^-}{1\,\cancel{mol}\,\text{AgBr}} = 9.0149 \times 10^{-3}\text{ mol Br}^-$$

The amount of Br^- comes from both NaBr and $CaBr_2$. Let x = number of moles NaBr. Then, the number of moles of $CaBr_2 = \dfrac{9.0149 \times 10^{-3}\text{ mol} - x}{2}$. The moles of $CaBr_2$ are divided by 2, because 1 mol of $CaBr_2$ produces 2 moles of Br^-. The sum of the NaBr and $CaBr_2$ masses must equal the mass of the mixture, 0.9157 g. We can write:

$$\text{mass NaBr} + \text{mass CaBr}_2 = 0.9157\text{ g}$$

$$\left[x\,\cancel{mol}\,\text{NaBr} \times \frac{102.89\text{ g NaBr}}{1\,\cancel{mol}\,\text{NaBr}}\right] + \left[\left(\frac{9.0149 \times 10^{-3} - x}{2}\right)\cancel{mol}\,\text{CaBr}_2 \times \frac{199.88\text{ g CaBr}_2}{1\,\cancel{mol}\,\text{CaBr}_2}\right] = 0.9157\text{ g}$$

$$2.95x = 0.014751$$

$$x = 5.0003 \times 10^{-3} = \text{moles NaBr}$$

Converting moles to grams:

$$\text{mass NaBr} = (5.0003 \times 10^{-3}\,\cancel{mol}\,\text{NaBr}) \times \frac{102.89\text{ g NaBr}}{1\,\cancel{mol}\,\text{NaBr}} = 0.51448\text{ g NaBr}$$

The percentage by mass of NaBr in the mixture is:

$$\textbf{\% NaBr} = \frac{0.51448\text{ g}}{0.9157\text{ g}} \times 100\% = \mathbf{56.18\%\ NaBr}$$

4.136 There are two moles of Cl^- per one mole of $CaCl_2$.

(a) $$25.3\,\cancel{g}\,\text{CaCl}_2 \times \frac{1\,\cancel{mol}\,\text{CaCl}_2}{110.98\,\cancel{g}\,\text{CaCl}_2} \times \frac{2\text{ mol Cl}^-}{1\,\cancel{mol}\,\text{CaCl}_2} = 0.456\text{ mol Cl}^-$$

$$\textbf{Molarity Cl}^- = \frac{0.456\text{ mol Cl}^-}{0.325\text{ L soln}} = 1.40\text{ mol/L} = \mathbf{1.40}\ \boldsymbol{M}$$

(b) We need to convert from mol/L to grams in 0.100 L.

$$\frac{1.40\,\cancel{mol}\,\text{Cl}^-}{1\,\cancel{L}\,\text{soln}} \times \frac{35.45\text{ g Cl}}{1\,\cancel{mol}\,\text{Cl}^-} \times 0.100\,\cancel{L}\,\text{soln} = \mathbf{4.96\ g\ Cl^-}$$

4.138 **(a)** $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$

(b) From the amount of NaOH needed to neutralize the 0.2041 g sample, we can find the amount of the 0.2041 g sample that is NH_4NO_3.

First, calculate the moles of NaOH.

$$\frac{0.1023 \text{ mol NaOH}}{1000 \cancel{\text{mL}} \text{ of soln}} \times 24.42 \cancel{\text{mL}} \text{ soln} = 2.498 \times 10^{-3} \text{ mol NaOH}$$

Using the mole ratio from the balanced equation, we can calculate the amount of NH_4NO_3 that reacted.

$$(2.498 \times 10^{-3} \cancel{\text{mol}} \text{ NaOH}) \times \frac{1 \cancel{\text{mol}} \text{ NH}_4\text{NO}_3}{1 \cancel{\text{mol}} \text{ NaOH}} \times \frac{80.05 \text{ g NH}_4\text{NO}_3}{1 \cancel{\text{mol}} \text{ NH}_4\text{NO}_3} = 0.2000 \text{ g NH}_4\text{NO}_3$$

The purity of the NH_4NO_3 sample is:

$$\textbf{\% purity} = \frac{0.2000 \text{ g}}{0.2041 \text{ g}} \times 100\% = \mathbf{97.99\%}$$

4.140 Using the rules for assigning oxidation numbers given in Section 4.4, H is +1, F is −1, so the oxidation number of O must be **zero**.

4.142 The balanced equation is:

$$3CH_3CH_2OH + 2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 3CH_3COOH + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$$

From the amount of $K_2Cr_2O_7$ required to react with the blood sample, we can calculate the mass of ethanol (CH_3CH_2OH) in the 10.0 g sample of blood.

First, calculate the moles of $K_2Cr_2O_7$ reacted.

$$\frac{0.07654 \text{ mol K}_2\text{Cr}_2\text{O}_7}{1000 \cancel{\text{mL}} \text{ soln}} \times 4.23 \cancel{\text{mL}} = 3.24 \times 10^{-4} \text{ mol K}_2\text{Cr}_2\text{O}_7$$

Next, using the mole ratio from the balanced equation, we can calculate the mass of ethanol that reacted.

$$3.24 \times 10^{-4} \cancel{\text{mol}} \text{ K}_2\text{Cr}_2\text{O}_7 \times \frac{3 \cancel{\text{mol}} \text{ ethanol}}{2 \cancel{\text{mol}} \text{ K}_2\text{Cr}_2\text{O}_7} \times \frac{46.07 \text{ g ethanol}}{1 \cancel{\text{mol}} \text{ ethanol}} = 0.0224 \text{ g ethanol}$$

The percent ethanol by mass is:

$$\textbf{\% by mass ethanol} = \frac{0.0224 \text{ g}}{10.0 \text{ g}} \times 100\% = \mathbf{0.224\%}$$

This is well above the legal limit of 0.1 percent by mass ethanol in the blood. The individual should be prosecuted for drunk driving.

4.144 **(a)** $Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$

(b) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$

(c) $Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

(d) $NH_4NO_2(s) \xrightarrow{\text{heat}} N_2(g) + 2H_2O(g)$

4.146 NH_4Cl exists as NH_4^+ and Cl^-. To form NH_3 and HCl, a proton (H^+) is transferred from NH_4^+ to Cl^-. Therefore, this is a Brønsted acid-base reaction.

4.148 We carry an additional significant figure throughout this calculation to minimize rounding errors.

(a)
First Solution:

$$0.8214\ \cancel{g}\ KMnO_4 \times \frac{1\text{ mol }KMnO_4}{158.04\ \cancel{g}\ KMnO_4} = 5.1974 \times 10^{-3}\text{ mol }KMnO_4$$

$$M = \frac{\text{mol solute}}{\text{L of soln}} = \frac{5.1974 \times 10^{-3}\text{ mol }KMnO_4}{0.5000\text{ L}} = 1.0395 \times 10^{-2}\ M$$

Second Solution:

$$M_1V_1 = M_2V_2$$
$$(1.0395 \times 10^{-2}\ M)(2.000\ \cancel{mL}) = M_2(1000\ \cancel{mL})$$
$$M_2 = 2.079 \times 10^{-5}\ M$$

Third Solution:

$$M_1V_1 = M_2V_2$$
$$(2.079 \times 10^{-5}\ M)(10.00\ \cancel{mL}) = M_2(250.0\ \cancel{mL})$$
$$\mathbf{M_2 = 8.316 \times 10^{-7}\ M}$$

(b) From the molarity and volume of the final solution, we can calculate the moles of $KMnO_4$. Then, the mass can be calculated from the moles of $KMnO_4$.

$$\frac{8.316 \times 10^{-7}\text{ mol }KMnO_4}{1000\ \cancel{mL}\text{ of soln}} \times 250\ \cancel{mL} = 2.079 \times 10^{-7}\text{ mol }KMnO_4$$

$$2.079 \times 10^{-7}\ \cancel{mol}\ KMnO_4 \times \frac{158.04\text{ g }KMnO_4}{1\ \cancel{mol}\ KMnO_4} = \mathbf{3.286 \times 10^{-5}\ g\ KMnO_4}$$

This mass is too small to directly weigh accurately.

4.150 The first titration oxidizes Fe^{2+} to Fe^{3+}. This titration gives the amount of Fe^{2+} in solution. Zn metal is added to reduce all Fe^{3+} back to Fe^{2+}. The second titration oxidizes all the Fe^{2+} back to Fe^{3+}. We can find the amount of Fe^{3+} in the original solution by difference.

Titration #1: The mole ratio between Fe^{2+} and MnO_4^- is 5:1.

$$23.0\text{ mL soln} \times \frac{0.0200\text{ mol }MnO_4^-}{1000\text{ mL soln}} \times \frac{5\text{ mol }Fe^{2+}}{1\text{ mol }MnO_4^-} = 2.30 \times 10^{-3}\text{ mol }Fe^{2+}$$

$$[\mathbf{Fe^{2+}}] = \frac{\text{mol solute}}{\text{L of soln}} = \frac{2.30 \times 10^{-3}\ \text{mol Fe}^{2+}}{25.0 \times 10^{-3}\ \text{L soln}} = \mathbf{0.0920}\ \boldsymbol{M}$$

Titration #2: The mole ratio between Fe^{2+} and MnO_4^- is 5:1.

$$40.0\ \text{mL soln} \times \frac{0.0200\ \text{mol MnO}_4^-}{1000\ \text{mL soln}} \times \frac{5\ \text{mol Fe}^{2+}}{1\ \text{mol MnO}_4^-} = 4.00 \times 10^{-3}\ \text{mol Fe}^{2+}$$

In this second titration, there are more moles of Fe^{2+} in solution. This is due to Fe^{3+} in the original solution being reduced by Zn to Fe^{2+}. The number of moles of Fe^{3+} in solution is:

$$(4.00 \times 10^{-3}\ \text{mol}) - (2.30 \times 10^{-3}\ \text{mol}) = 1.70 \times 10^{-3}\ \text{mol Fe}^{3+}$$

$$[\mathbf{Fe^{3+}}] = \frac{\text{mol solute}}{\text{L of soln}} = \frac{1.70 \times 10^{-3}\ \text{mol Fe}^{3+}}{25.0 \times 10^{-3}\ \text{L soln}} = \mathbf{0.0680}\ \boldsymbol{M}$$

4.152 **(a)** The precipitation reaction is: $Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$

The acid-base reaction is: $Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$

The redox reactions are:

$$\begin{array}{l} Mg^{2+} + 2e^- \longrightarrow Mg \\ \underline{2Cl^- \longrightarrow Cl_2 + 2e^-} \\ MgCl_2 \longrightarrow Mg + Cl_2 \end{array}$$

(b) NaOH is much more expensive than CaO.

(c) Dolomite has the advantage of being an additional source of magnesium that can also be recovered.

4.154 Let's set up a table showing each reaction, the volume of solution added, and the species responsible for any electrical conductance of the solution. Note that if a substance completely dissociates into +1 ions and −1 ions in solution, its conductance unit will be twice its molarity. Similarly, if a substance completely dissociates into +2 ions and −2 ions in solution, its conductance unit will be four times its molarity.

(1) $CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$

Volume (added)	Conductance unit	
0 L, KOH	$[CH_3COOH] = 1.0\ M$, (negligible ions, weak acid)	0 unit
1 L, KOH	$[CH_3COOK] = \frac{1.0\ \text{mol}}{2.0\ \text{L}} = 0.50\ M$, (CH_3COO^-, K^+)	1 unit
2 L, KOH	$[CH_3COOK] = \frac{1.0\ \text{mol}}{3.0\ \text{L}} = \frac{1}{3} M$, $[KOH] = \frac{1.0\ \text{mol}}{3.0\ \text{L}} = \frac{1}{3} M$, (K^+, OH^-)	1.3 units

(2) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

Volume (added)	Conductance unit	
0 L, NaOH	$[HCl] = 1.0\ M, (H^+, Cl^-)$	2 units
1 L, NaOH	$[NaCl] = \frac{1.0\text{ mol}}{2.0\text{ L}} = 0.50\ M, (Na^+, Cl^-)$	1 unit
2 L, NaOH	$[NaCl] = \frac{1.0\text{ mol}}{3.0\text{ L}} = \frac{1}{3} M, [NaOH] = \frac{1.0\text{ mol}}{3.0\text{ L}} = \frac{1}{3} M, (Na^+, OH^-)$	1.3 units

(3) $BaCl_2(aq) + K_2SO_4(aq) \rightarrow BaSO_4(s) + 2KCl(aq)$

Volume (added)	Conductance unit	
0 L, $BaCl_2$	$[K_2SO_4] = 1.0\ M, (2K^+, SO_4^{2-})$	4 units
1 L, $BaCl_2$	$[KCl] = \frac{2.0\text{ mol}}{2.0\text{ L}} = 1.0\ M, (K^+, Cl^-)$	2 units
2 L, $BaCl_2$	$[KCl] = \frac{2.0\text{ mol}}{3.0\text{ L}} = \frac{2}{3} M, [BaCl_2] = \frac{1.0\text{ mol}}{3.0\text{ L}} = \frac{1}{3} M, (Ba^{2+}, 2Cl^-)$	2.7 units

(4) $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

Volume (added)	Conductance unit	
0 L, NaCl	$[AgNO_3] = 1.0\ M, (Ag^+, NO_3^-)$	2 units
1 L, NaCl	$[NaNO_3] = \frac{1.0\text{ mol}}{2.0\text{ L}} = 0.50\ M, (Na^+, NO_3^-)$	1 unit
2 L, NaCl	$[NaNO_3] = \frac{1.0\text{ mol}}{3.0\text{ L}} = \frac{1}{3} M, [NaCl] = \frac{1.0\text{ mol}}{3.0\text{ L}} = \frac{1}{3} M, (Na^+, Cl^-)$	1.3 units

(5) $CH_3COOH(aq) + NH_3(aq) \rightarrow CH_3COONH_4$

Volume (added)	Conductance unit	
0 L, CH_3COOH	$[NH_3] = 1.0\ M$, (negligible ions, weak base)	0 unit
1 L, CH_3COOH	$[CH_3COONH_4] = \frac{1.0\text{ mol}}{2.0\text{ L}} = 0.50\ M, (CH_3COO^-, NH_4^+)$	1 unit
2 L, CH_3COOH	$[CH_3COONH_4] = \frac{1.0\text{ mol}}{3.0\text{ L}} = \frac{1}{3} M$	0.67 unit

Matching this data to the diagrams shown, we find:

Diagram **(a)**: Reactions **(2)** and **(4)**
Diagram **(b)**: Reaction **(5)**
Diagram **(c)**: Reaction **(3)**
Diagram **(d)**: Reaction **(1)**