Reactions in Aqueous Solution

OVERVIEW OF THE CHAPTER

4.1, 4.3 Aqueous Solution: Electrolytes, Acids, and Bases

Review: Solutions (1.2), nomenclature of acids, bases, and salts (2.8).

Learning Goals: You should be able to:
1. Identify substances as nonelectrolytes, strong electrolytes, or weak electrolytes.
2. Characterize electrolytes and predict what ions form when electrolytes dissociate or ionize.
3. Identify substances as acids, bases, or salts.

4.2 Precipitation Reactions: Ionic Equations

Learning Goals: You should be able to:
1. Use solubility rules to predict whether a precipitate forms when two different salt solutions are mixed.
2. Predict the products of metathesis reactions (including both neutralization and precipitation reactions) and write balanced chemical equations for them.
3. Write molecular and net ionic equations for reactions in aqueous solutions.

4.4 Oxidation and Reduction: Oxidation Numbers and Activity Series

Learning Goals: You should be able to:
1. Determine whether a chemical reaction involves oxidation and reduction.
2. Assign oxidation numbers to atoms in molecules and ions.
3. Use the activity series to predict whether a reaction will occur when a metal is added to an aqueous solution of either a metal salt or an acid, and write the balanced molecular and net ionic equations for the reaction.

4.5 Concentrations of Solutions

Learning Goals: You should be able to:
1. Calculate molarity, solution volume, or number of moles of solute given any two of these quantities.
2. Describe how to quantitatively use a concentrated solution to prepare a solution of lesser concentration.

4.6 Solution Stoichiometry

Review: Stoichiometry of chemical reactions (3.6), limiting reactants (3.7).

Learning Goals: You should be able to:
1. Calculate the volume of a solution required to react with a volume of a different solution using molarity and the stoichiometry of the reaction.
2. Calculate the amount of a substance required to react with a given volume of a solution using molarity and the stoichiometry of the reaction.
3. Calculate the concentration or mass of solute in a sample from titration data.
Chapter 4

TOPIC SUMMARIES AND EXERCISES

Aqueous Solution: Electrolytes, Acids, and Bases (4.1, 4.3)

In Chapter 2 of the textbook, we learned that a solution is a homogeneous mixture. Key definitions include:

- A solution contains a solvent and solute(s).
- The solvent is the substance in a mixture that maintains its physical state and usually is in the greatest amount.
- Whatever else is dissolved in the solution is called a solute. A solute may or may not maintain its physical state.

An electrolyte is a substance that causes a solution to be a better electrical conductor than the pure solvent. This occurs when the solute forms ions in the solution. The different types of electrolytes are summarized as follows:

1. **Strong electrolytes**: Effectively ionize or dissociate 100% in a solvent. Examples are most ionic compounds (salts) and strong acids and bases.
2. **Weak electrolytes**: Incompletely ionize or dissociate (<100%) in a solvent. Examples are weak acids and bases.
3. **Nonelectrolytes**: These do not ionize or dissociate in a solvent. Sugar and alcohol (ethanol) are two examples.

Do not confuse solubility with whether a substance is a weak or strong electrolyte.

- Solubility refers to the quantity of a solute dissolved in a stated amount of solvent.
- The form of a solute in solution determines whether it is an electrolyte. BaSO₄ is only very slightly soluble in water. However, essentially all of the dissolved BaSO₄ exists in solution as Ba²⁺(aq) and SO₄²⁻(aq); therefore, it is a strong electrolyte. Unless otherwise noted we will assume insoluble (slightly soluble) salts are strong electrolytes in water.

Acids, bases, and salts are commonly encountered in your general chemistry course. Therefore, it is important that you become thoroughly familiar with common acids and bases and know their properties.

- **Acids** are substances that contain one or more hydrogen atoms that ionize to form H⁺(aq) in water. The chemical formulas of acids usually have the element hydrogen listed as the first element. Acids that lose only one hydrogen atom are referred to as monoprotic and those that lose two hydrogen atoms are diprotic. Two types of acids discussed are:
  1. **Strong acids**: These are strong electrolytes. Hydrochloric acid (HCl) is an example of a monoprotic acid, and sulfuric acid (H₂SO₄) is an example of a diprotic acid.
  2. **Weak acids**: These are weak electrolytes. Examples are acetic acid (HC₂H₃O₂), hydrocyanic acid (HCN), hydrofluoric acid (HF), and hydrosulfuric acid (H₂S).

- **Bases** are substances that accept H⁺ ions in chemical reactions.
  1. **Strong bases**: Metallic hydroxides that dissociate 100% in water such as NaOH.
  2. **Weak bases**: The most common one we encounter is ammonia (NH₃) and occasionally amines (RNH₂, R₂NH, and R₃N where R represents a carbon-based group—you will learn more about these in Chapter 16 of the textbook).

**Neutralization** is a reaction in which an acid reacts with a base to form water and a salt (contains cation of base and anion of acid). For example:

\[
\text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water}
\]

\[
\text{HBr(aq)} + \text{KOH(aq)} \rightarrow \text{H}_2\text{O(l)} + \text{KBr(aq)}
\]

Means a substance is dissolved in water

Means water is liquid and in this example it is also the solvent

54 Copyright © 2015 Pearson Education, Inc.
EXERCISE 1 Identifying types of electrolytes

Classify each of the following as a strong electrolyte, weak electrolyte, or nonelectrolyte in water: HBr; H₂S; NH₃; Ba(OH)₂; KCl; C₂H₆; I₂.

SOLUTION: Analyze: We are given the formulas of seven substances and asked to predict what type of electrolyte each is in water.

Plan: We can use Tables 4.2 and 4.3 in the textbook to help us.

Solve: Ba(OH)₂ and KCl are ionic (salts) and therefore they are strong electrolytes. You can use Table 4.2 to determine if a H₂X compound is an acid. HBr is a strong acid and thus a strong electrolyte. H₂S is a weak acid and thus a weak electrolyte (it is not listed as a strong acid, thus we can reasonably conclude it is a weak acid). NH₃ is listed as a weak base and thus is a weak electrolyte. C₂H₆ and I₂ are not found in the tables; however, both are molecular substances because they do not contain metals. They are not listed as acids or bases and therefore this suggests they are nonelectrolytes.

Comment: It is important to learn the information contained in Tables 4.2 and 4.3 of the textbook. This may require using flash cards or other learning techniques. This information is frequently used in answering questions.

EXERCISE 2 Identifying acids and bases and describing their reactions in water

(a) Identify each of the following as an acid or base and write its reaction with water: HF(g); H₂SO₄(ℓ); NaOH(s); Ba(OH)₂(s). (b) Write the neutralization reaction between Ba(OH)₂(s) and HNO₃(aq).

SOLUTION: Analyze: (a) We are asked to determine whether the substances are acids and bases and then write an equation that shows how they react with water. (b) We are given two substances and asked to write a neutralization reaction.

Plan: (a) Acids typically have a hydrogen atom listed as the first element in their chemical formulas and most strong bases contain one or more hydroxide units. The ammonium ion is a weak acid, but it does not have a hydrogen listed first in their chemical formula. Ammonia is a weak base and shows no hydroxide units. (b) A neutralization reaction between an acid and base yields a salt and water.

Solve: (a) Using the approach in the Plan, we obtain the following identities and reactions:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type</th>
<th>Reaction with Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>Acid</td>
<td>HF(g) → H⁺(aq) + F⁻(aq)</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Acid (diprotic)</td>
<td>H₂SO₄(ℓ) → H⁺(aq) + HSO₄⁻(aq)</td>
</tr>
<tr>
<td>NaOH</td>
<td>Base</td>
<td>NaOH(s) → Na⁺(aq) + OH⁻(aq)</td>
</tr>
<tr>
<td>Ba(OH)₂</td>
<td>Base</td>
<td>Ba(OH)₂(s) → Ba²⁺(aq) + 2 OH⁻(aq)</td>
</tr>
</tbody>
</table>

A single arrow is used to show a reaction that goes to completion and a double arrow shows one that is at equilibrium. (b) Using the approach in the Plan, gives:

\[
2\text{HNO}_3(aq) + \text{Ba(OH)}_2(s) \rightarrow 2\text{H}_2\text{O}(l) + \text{Ba(NO}_3)_2(aq)
\]

Precipitation Reactions: Ionic Equations (4.2)

Section 4.2 of this chapter introduces reactions in water that result in the formation of a solid substance, a precipitate. One of the goals of this section is to learn which ionic substances are soluble and insoluble in water. A table of solubilities is given in Table 4.1 in the textbook. Note that all salts containing an alkali metal (group 1A), a nitrate ion (NO₃⁻), an acetate ion (C₂H₃O₂⁻), or an ammonium ion (NH₄⁺) are soluble in water. The other rules are easier to remember if we know these.

Another goal in this section of the textbook is to predict whether a precipitate forms when two aqueous solutions containing ionic substances are mixed together. How do we do this?
Chapter 4

1. If we are given only the reactants, we can carry out an exchange reaction (metathesis reaction) as follows:

\[
\begin{align*}
\text{Y replaces X in AX} & \\
AX + BY & \rightarrow AY + BX \\
\text{X replaces Y in BY}
\end{align*}
\]

2. Identify the phase of each reactant. Soluble substances are assigned an aqueous phase \((aq)\). Insoluble substances in water are assigned a solid phase \((s)\). Use solubility rules to help you identify soluble and insoluble substances in the products.

3. Balance the chemical equation.

Net ionic equations show only ions, solids, gases, and weak or nonelectrolytes involved in chemical reactions. We construct these from molecular equations, which show all reactants and products in a "molecular" form, even if they are salts.

- An example of a molecular equation is \(\text{HNO}_3(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq)\).

- To form a net ionic equation from a molecular equation, rewrite the molecular equation so that all soluble strong electrolytes are written in their ion form in solution. Non-electrolytes, weak electrolytes, gases, and insoluble salts are not changed. Eliminate all ions common to both reactants and products; these are termed spectator ions. The prior example of a molecular equation becomes

\[
\text{H}^+(aq) + \text{NO}_3^-(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)
\]

**HNO_3** is a strong electrolyte.

\(\text{NH}_3\) is a weak electrolyte and is not altered.

\(\text{NH}_4\text{NO}_3\) is a strong electrolyte. The nitrate ion is a spectator ion.

- The ionic reaction that remains after removing spectator ions is the net ionic equation:

\[
\text{H}^+(aq) + \text{NH}_3(aq) \rightarrow \text{NH}_4^+(aq)
\]

**Exercise 3** Using solubility rules

Identify the following salts as soluble or insoluble in water: (a) \(\text{Fe(NO}_3)_3\); (b) \(\text{PbCl}_2\); (c) \(\text{CaBr}_2\); (d) \(\text{BaSO}_4\); (e) \(\text{Na}_2\text{SO}_4\).

**Solution:** Analyze: We are asked to identify the solubility of several salts in water based on having learned the rules of solubility.

**Plan:** We can apply the rules of solubility and our knowledge of the properties of salts to answering the question.

**Solve:** (a) Soluble. All nitrate salts are soluble; (b) Insoluble. This is one of the three exceptions to the rule that chloride salts are soluble. AgCl, HgCl, and PbCl are insoluble. (c) Soluble. All bromide salts are soluble except AgBr, HgBr, PbBr, and HgBr; (d) Insoluble. BaSO is one of the exceptions to the rule that sulfate salts are soluble; (e) Soluble. All alkali metal salts are soluble.

**Exercise 4** Writing net ionic equations I

Write a net ionic equation for the following reaction:

\[
\text{NaCl(aq)} + \text{AgNO}_3(aq) \rightarrow \text{AgCl(s)} + \text{NaNO}_3(aq)
\]

**Solution:** Analyze: We are asked to write a net ionic equation having been given a molecular equation.

**Plan:** Rewrite the molecular equation so that soluble, strong electrolytes are in their ion form in water. Eliminate any spectator ions and write the net ionic equation:

**Solve:**

\[
\text{Na}^+(aq) + \text{Cl}^-(aq) + \text{Ag}^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{AgCl(s)} + \text{Na}^+(aq) + \text{NO}_3^-(aq)
\]

AgCl is an insoluble salt and remains in a combined form. All other species are strong electrolytes. \(\text{Na}^+\) and \(\text{NO}_3^-\) ions are spectator ions. The net ionic equation is

\[
\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl(s)}
\]

**Check:** The number of each type of atom is the same on both sides of the arrow and the charges balance (zero on both sides of the arrow). No spectator ions are shown. Chemical formulas are correct.
**Exercise 5  Writing net ionic equations II**

Complete the following reactions and write net ionic equations for them.

(a) \( \text{Pb(NO}_3\text{)}_2(aq) + \text{KBr}(aq) \rightarrow \) 
(b) \( \text{NiCl}_2(aq) + \text{Na}_3\text{PO}_4(aq) \rightarrow \)

**Solution:** Analyze: We are given reactants in each problem and asked to complete the reactions and also write net ionic equations.

**Plan:** First, determine the nature of the reactants. Are they salts? If they are both salts, then we can predict the products by doing a double displacement of the ions. Next, we identify the phases of the products. Use Table 4.3 in the textbook to help you identify insoluble salts. To write a net ionic equation, separate all soluble, strong electrolytes in the molecular equation into their component ions and then eliminate spectator ions. Note that both conditions, soluble and strong, must be met, not just one.

**Solve:** (a) \( \text{Pb(NO}_3\text{)}_2(aq) + 2\text{KBr}(aq) \rightarrow \text{PbBr}_2(s) + 2\text{KNO}_3(aq) \)

\( \text{PbBr}_2 \) is an insoluble salt; \( \text{KNO}_3 \) is a strong electrolyte and a soluble salt.

\( \text{Pb}^{2+}(aq) + 2\text{NO}_3^-(aq) + 2\text{K}^+(aq) + 2\text{Br}^-(aq) \rightarrow \text{PbBr}_2(s) + 2\text{K}^+(aq) + 2\text{NO}_3^-(aq) \)

**Net ionic equation:**

\( \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq) \rightarrow \text{PbBr}_2(s) \)

(b) \( \text{3NiCl}_2(aq) + 2\text{Na}_3\text{PO}_4(aq) \rightarrow \text{Ni}_3\text{(PO}_4\text{)}_2(s) + 6\text{NaCl}(aq) \)

\( \text{Ni}_3\text{(PO}_4\text{)}_2 \) is an insoluble salt; \( \text{NaCl} \) is a strong electrolyte and a soluble salt.

\( 3\text{Ni}^{2+}(aq) + 6\text{Cl}^-(aq) + 6\text{Na}^+(aq) + 2\text{PO}_4^{3-}(aq) \rightarrow \text{Ni}_3\text{(PO}_4\text{)}_2(s) + 6\text{Na}^+(aq) + 6\text{Cl}^-(aq) \)

**Net ionic equation:**

\( 3\text{Ni}^{2+}(aq) + 2\text{PO}_4^{3-}(aq) \rightarrow \text{Ni}_3\text{(PO}_4\text{)}_2(s) \)

**Check:** The number of each type of atom is the same on both sides of the arrow and the charges balance (zero on both sides of the arrow) for each net ionic equation. All ions reacting are in a different form in the product spectator are shown. Also check that the chemical formulas are correct.

**Exercise 6  Identifying which substance forms the most ions in solution**

Which solution contains the highest concentration of barium ions in 100 mL of water?

(a) 10.0 g of solid barium sulfate  
(b) 10.0 g of solid barium chloride  
(c) 10.0 g of solid barium phosphate  
(d) 10.0 g of solid barium carbonate

**Solution:** (b) Barium chloride is a soluble salt and a strong electrolyte. Barium sulfate, barium carbonate, and barium phosphate are insoluble in water and only a few barium ions form. Refer to Table 4.1 in the textbook.

**Oxidation and Reduction: Oxidation Numbers and Activity Series (4.4)**

Section 4.4 in the textbook introduces another type of chemical reaction: oxidation-reduction. Oxidation-reduction reactions involve the transfer of electrons. Oxidation and reduction occur together in a chemical reaction.

- **Oxidation** occurs when an atom, ion or molecule loses electrons and gains positive charge. Thus, when a Ca atom loses two electrons, it forms \( \text{Ca}^{2+} \). A substance that has lost electrons is said to be oxidized.

- **Reduction** is the gain of electrons by an atom, ion, or molecule and it loses positive charge (i.e., it becomes more negatively charged). Thus, when an oxygen atom gains two electrons, it forms \( \text{O}^{2-} \). A substance that has gained electrons is said to be reduced.
Chapter 4

The concept of oxidation number helps us determine whether a reaction involves oxidation and reduction. Oxidation numbers help us keep track of the change of electrons in reactions. The terms oxidation and reduction can also be stated as follows:

- Oxidation occurs when the oxidation number of an atom increases.
- Reduction occurs when the oxidation number of an atom decreases.

Oxidation number reflects the charge assigned to an atom in a particular bonding situation. It is also a tool that helps us keep track of electrons in a chemical reaction.* The terms oxidation number and oxidation state are closely related. An atom in an oxidation state of +2 is said to have a +2 oxidation number. An atom may have several possible oxidation states, positive and negative, depending on the identity of the atoms bonded to it.

A few general rules have been developed to aid you in assigning oxidation numbers to atoms in compounds.

1. The oxidation number of an element in its elementary or uncombined state is zero.
2. In an ionic compound, the oxidation number of a monatomic ion is the same as its charge.
3. Certain elements almost always have the same oxidation number in their compounds. These elements are:
   (a) Group 1A elements (Li, Na, K, Rb, Cs), with an oxidation number of +1;
   (b) Group 2A elements (Be, Mg, Ca, Sr, Ba), +2;
   (c) Group 3A elements (B, Al), +3;
   (d) Fluorine, chlorine, bromine, and iodine, −1 in binary compounds with metals (other states are possible when combined with nonmetals);
   (e) Hydrogen: +1 (except for metallic hydrides, where its oxidation state is −1, as in CaH₂ and NaH);
   (f) Oxygen: −2 (except in peroxide compounds, where the oxidation state is −1 (e.g., H₂O₂); in superoxide ions [O₂⁻], where it is −½; and when bonded to F [−2 in OF₂]).
4. In an ABₙ compound, the more electronegative element is assigned the negative oxidation number; the less electronegative one is assigned a positive oxidation number (e.g., in SF₄, F is assigned −1 and thus S is +4).
5. In a neutral compound, the sum of oxidation numbers of all atoms is zero; in a compound with a charge, the sum is equal to the charge of that compound.

The last part of Section 4.4 examines oxidation–reduction reactions of metals with acids and salts. These typically are displacement reactions. Many metals react with strong acids such as HCl, HNO₃, and H₂SO₄ to form a salt and H₂(g) in a displacement reaction. For example, consider the following example with the oxidation numbers shown for each element:

\[
\begin{align*}
0 & \quad +6 & \quad +2 & \quad +6 & \quad 0 \\
Zn(s) + H₂SO₄(aq) & \longrightarrow ZnSO₄(aq) + H₂(g)
\end{align*}
\]

Zn is oxidized because its oxidation number increases from 0 to +2. Hydrogen is reduced because its oxidation number decreases from +1 to 0.

Metals (M) may also displace another metal from a salt (BX where B is a different metal).

- M + BX \longrightarrow MX + B
- Displacement reactions of this type occur if the metal M is more easily oxidized than the metal B.
- For example, Zn(s) + CuSO₄(aq) \longrightarrow Cu(s) + ZnSO₄(aq)
- An activity series arranges metals in order of decreasing ease of oxidation. Refer to Table 4.5 in the textbook. A metallic element is able to displace ions of elements below it from their compounds.

*Caution: Oxidation number may be related to the charge of an atom, or it may have no relationship. For example, sulfur in Na₂S₈O₉ has an oxidation number of +2 ½, but an atom cannot have ½ an electron, only an integral number.
Reactions in Aqueous Solution

- Note in Table 4.5 that Li is the most active element, whereas Au is the least active. Li can displace all elements below it from their compounds. Au is essentially nonreactive.
- \( \text{H}_2 \) is low in the activity series. Metals above it can displace \( \text{H}^+ \) from acids to form \( \text{H}_2(g) \). Only Li, K, Ba, Ca, and Na will react with cold water; Others require steam.

**EXERCISE 7** Determining oxidation numbers

State the most common oxidation number(s) for each of the following elements and give an example of a compound in which an atom of the element has that oxidation number: (a) Li; (b) Sr; (c) Al; (d) Ag; (e) N; (f) O; (g) F; (h) Zn; (i) S; (j) H.

**SOLUTION:** Analyze: We are to determine the most common oxidation number(s) for 10 elements and write an example of a compound.

**Plan:** We can use the rules for assigning oxidation numbers to answer the question.

**Solve:** (a) +1: LiF. All atoms in group 1A have a +1 oxidation number. (b) +2: SrO. All atoms in group 2A have a +2 oxidation number. (c) +3: AlCl₃. (d) +1: AgCl or Ag₂O. (e) −3: NH₃ + 5: NaNO₃. (f) −2: CaO. (g) −1: HF. (h) +2: ZnS. (i) +6: SF₆. −2: H₂S. (j) +1: HCl −1: NaH (only with metallic elements).

**Comment:** Check that the sum of oxidation states in a compound is zero. For example, H₂S consists of hydrogen with a +1 oxidation state and sulfur with a −2 oxidation state; two hydrogen atoms are needed to balance the negative two oxidation state of sulfur. This shows that the formula is correct based on the sum of oxidation states. This should be done for every substance.

**EXERCISE 8** Determining oxidation numbers

Determine the oxidation state of nitrogen in each of the following: (a) NH₃; (b) N₂O₅; (c) NaNO₃.

**SOLUTION:** Analyze: We are asked to determine the oxidation number of nitrogen in three compounds.

**Plan:** We can apply the rules of oxidation numbers to the nonnitrogen elements in each compound. Calculate the oxidation number of nitrogen by applying the principle that the sum of oxidation numbers is zero for a neutral compound.

**Solve:** (a) The oxidation number of hydrogen is +1 when bonded to a nonmetal such as nitrogen. To calculate the oxidation number of nitrogen, we use the rule that the sum of oxidation numbers is zero for this molecular substance: \( 0 = x + 3(+1) \), where \( x \) is the oxidation number of nitrogen in the compound. Solving for the unknown oxidation number of nitrogen gives −3. (b) Oxygen typically has an oxidation number of −2 when bonded to nonmetals or metals. Again, the sum of oxidation numbers is zero: \( 0 = 2(x) + 4(−2) \). Solving for the unknown oxidation number of nitrogen gives +4. (c) Sodium is a metal and in compounds it carries a +1 ion charge; thus, its oxidation number is +1. This means that the NO₃ group must carry a −1 charge (it is the nitrate ion). Solving, we have \( −1 = x + 3(−2) \) and the unknown oxidation number of nitrogen is +5. Note that the −1 is used to the left of the equal sign because the nitrate ion carries a −1 charge.

**Comment:** Note that you must know the rules for assigning oxidation numbers of elements to do this type of problem.

**EXERCISE 9** Writing single displacement reactions of active metals

Write a balanced single displacement equation illustrating each of the following: (a) a metal displacing \( \text{H}^+ \) from \( \text{H}_2\text{O} \); (b) a metal displacing \( \text{H}^+ \) from an acid; and (c) a metal replacing copper in a copper(II) nitrate solution.

**SOLUTION:** Analyze: We are asked to write balanced single displacement reactions for three metals under different conditions. Also, we are to choose a metal that will react.

**Plan:** To answer these types of questions, we will need to find analogous reactions in the textbook or use the activity series to help us find appropriate metals and to predict products of the reaction.

**Solve:** (a) Choose a metal in the activity series that is above hydrogen. Li, K, Ba, Sr, Ca, and Na will liberate \( \text{H}_2 \) in cold water (Mg, Al, Mn, Zn, and Fe require steam). For example,
\[
\text{Mg}(s) + 2 \text{H}_2\text{O}(g) \rightarrow \text{Mg(OH)}_2(s) + \text{H}_2(g)
\]
(b) Also choose a metal that is higher in the activity series than hydrogen. For example, we can use magnesium
\[
\text{Mg}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{MgSO}_4(aq) + \text{H}_2(g)
\]
(c) Choose an element higher in the activity series than copper. For example,
\[
\text{Zn}(s) + \text{CuSO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{Cu}(s)
\]
EXERCISE 10 Using the activity series of metals to predict if a reaction occurs

Use the activity series to predict which reactions will occur.

(a) Hg(l) + MnSO₄(aq) → HgSO₄(s) + Mn(s)
(b) 2 Ag(s) + H₂SO₄(aq) → Ag₂SO₄(aq) + H₂(g)
(c) Ca(s) + 2 H₂O(l) → Ca(OH)₂(aq) + H₂(g)

SOLUTION: Analyze: We are given molecular equations and asked to use the activity series to predict if the reactions occur.

Plan: All of the reactions are examples of displacement reactions:

M + B'X → MX + B'.

For these reactions to occur, M must be higher in the activity series than B'.

Solve: (a) Hg lies below Mn in the activity series; thus, the reaction does not occur. (b) Ag lies below hydrogen in the activity series; thus, the reaction does not occur. (c) Ca lies above hydrogen in the activity; thus, the reaction occurs.

EXERCISE 11 Determining trends in activities of metals

Manganese is more active than tin and copper. Silver is more active than platinum but less active than copper and copper is less active than tin. Which is the correct order of metals in increasing activity?

(a) Ag < Pt < Cu < Sn < Mn
(b) Pt < Ag < Cu < Mn < Sn
(c) Pt < Ag < Cu < Sn < Mn
(d) Mn < Sn < Cu < Pt < Ag

SOLUTION: (c).

Concentrations of Solutions (4.5)

The term concentration refers to the amount of a solute dissolved in a given quantity of solvent or solution.

- **Molarity (M)** is a concentration term used in chemistry.

- \[ M = \frac{\text{number of moles of solute}}{\text{volume of the solution in liters}} \]

- The previous equation can be algebraically changed to a form that is useful when calculating the number of moles of a solute in a solution.

\[ n_{\text{moles of solute}} = M_{\text{solution}} \times V_{\text{liters}} \]

- Molarity, like density, can be used as a conversion factor to change between volume and number of moles.

Solutions of known concentration may be diluted with the solvent to produce a more diluted (less concentrated) solution.

- We can use the molarity concept to solve for the molarity of a solution after it is diluted with the solvent. Note that the number of moles of solute does not change when only solvent is added to a solution. Therefore, the number of moles of solute before dilution equals the number of moles of solute after dilution. We can write the following relationships:

\[ n_i = n_f \]

The subscript \( i \) refers to the undiluted solution and the subscript \( f \) refers to the final diluted solution. If we substitute \( MV \) for \( n \) in the previous equation we have

\[ M_iV_i = M_fV_f \]

This relationship is often used in problems involving dilution. See Exercises 15 and 16.
EXERCISE 12  Calculating molarity

What is the molarity of a 100.0 mL aqueous solution of ethanol (C₂H₅O) containing 10.0 g of ethanol?

SOLUTION: Analyze: We are given the volume of an ethanol solution and the mass of ethanol in it and asked to calculate the molarity of the solution.

Plan: The definition of molarity is \( M = \frac{\text{moles of solute}}{\text{volume of solution in liters}} \)

We will need the equivalence relations between moles and grams of ethanol and between milliliters and liters:

\[
\begin{align*}
46.07 \text{ g C}_2\text{H}_5\text{O} &= 1 \text{ mol C}_2\text{H}_5\text{O} & \text{[Molar mass]} \\
1000 \text{ mL} &= 1 \text{ L} & \text{[Exact equivalence]}
\end{align*}
\]

Solve:

\[
M_{\text{C}_2\text{H}_5\text{O}} = \frac{(10.0 \text{ g C}_2\text{H}_5\text{O}) \left( \frac{1 \text{ mol C}_2\text{H}_5\text{O}}{46.07 \text{ g C}_2\text{H}_5\text{O}} \right)}{(100.0 \text{ mL}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right)} = \frac{0.217 \text{ mol C}_2\text{H}_5\text{O}}{0.1000 \text{ L}} = 2.17 \text{ M}
\]

Check: The answer is a reasonable concentration in terms of its magnitude. If it had been a very large or very small number, it is advisable to redo the problem.

EXERCISE 13  Using molarity to calculate grams of a solute

How many grams of HCl are contained in exactly 500 mL of a 0.250 M HCl solution?

SOLUTION: Analyze: We are given the molarity of a HCl solution and its volume and asked to calculate the number of grams of HCl in the solution.

Plan: HCl is the solute and the number of grams of it can be calculated if the number of moles of it is known. Use the definition of molarity to calculate the number of moles of HCl from the volume of the solution. Use the following sequence of conversions to obtain the desired unit of grams:

\[
\text{Volume HCl} \quad \rightarrow \quad \text{moles HCl} \quad \rightarrow \quad \text{grams HCl}
\]

These conversions require the following relationships:

\[
\begin{align*}
0.250 \text{ mol HCl} &= 1 \text{ L HCl solution} & \text{[From molarity definition]} \\
1000 \text{ mL} &= 1 \text{ L} & \text{[Exact equivalence]} \\
36.45 \text{ g HCl} &= 1 \text{ mol HCl} & \text{[Molar mass]}
\end{align*}
\]

Solve: Following the sequence of these conversion steps, we convert 500 mL of the solution to grams of HCl.

\[
\text{Grams HCl} = (500 \text{ mL}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.250 \text{ mol HCl}}{1 \text{ L}} \right) \left( \frac{36.45 \text{ g HCl}}{1 \text{ mol HCl}} \right)
\]

\[
= 4.56 \text{ g HCl}
\]

EXERCISE 14  Calculating the molarity of ions in a salt solution

What is the molarity of Na⁺ ions in a 0.020 M Na₃PO₄ solution?

SOLUTION: Analyze: We are given the concentration of a salt solution, sodium phosphate, and asked to determine the molarity of sodium ions in it.

Plan: We need to determine whether sodium phosphate is a weak or strong electrolyte. It is a salt and therefore a strong electrolyte in water. This means it dissociates completely into sodium and phosphate ions. Using the dissociation reaction, we can determine the molarity of sodium ions formed.

Solve: \( \text{Na}_3\text{PO}_4 \) dissociates completely in \( \text{H}_2\text{O} \) according to the reaction:

\[
\text{Na}_3\text{PO}_4 \rightarrow 3 \text{ Na}^+ + \text{PO}_4^{3-}
\]

For every 1 mol of \( \text{Na}_3\text{PO}_4 \) that ionizes, three moles of Na⁺ ions form. Thus, a 0.020 M \( \text{Na}_3\text{PO}_4 \) solution is \( 3(0.020 \text{ M}) \) or 0.060 M in Na⁺ ions.
Chapter 4

Comment: This type of problem requires us to know which substances are salts (contain metal and nonmetal) and how salts dissociate in water.

EXERCISE 15  Diluting a solution and calculating the volume required to achieve a given molarity

How many milliliters of a 6.00 M HCl solution must be used to prepare 100.0 mL of a 1.00 M HCl solution?

SOLUTION: Analyze: We are given a 6.00 M HCl solution and are asked what quantity (an aliquot or a portion) of this solution is used to prepare 100.0 mL of a 1.00 M HCl solution. This is achieved by diluting a portion of the more concentrated solution with the solvent water.

Plan: The key to understanding this type of problem is to recognize that the number of moles of HCl before dilution must equal the same number after dilution because only water (solvent) is added. The relation between the molarity of a solute before dilution \(i\) and after dilution \(f\) is

\[
\text{Moles solute}_i = \text{moles solute}_f
\]

or

\[
M_i V_i = M_f V_f
\]

The volumes may be expressed in units of milliliters or liters, providing both volumes have the same unit.

Solve: The initial volume of 6.00 M HCl required to form a 1.00 M solution by dilution is:

\[
V_i = \frac{M_f V_f}{M_i} = \frac{(1.00 \text{ M})(100.0 \text{ mL})}{6.00 \text{ M}} = 16.7 \text{ mL}
\]

Thus, 16.7 mL of 6.00 M HCl diluted to 100 mL with H\(_2\)O produces a 1.00 M HCl solution.

EXERCISE 16  Calculating the molarity of a solution after it is diluted

What is the molarity of a solution of NaOH formed by diluting 125 mL of a 3.0 M NaOH solution to exactly 500 mL?

SOLUTION: Analyze: We are given 125 mL of a 3.0 M NaOH solution and asked to calculate the molarity of the solution after it is diluted to 500 mL. Recognize that the number of moles of NaOH does not change when only solvent is added.

Plan: When the number of moles of solute does not change on dilution, we can use the relation:

\[
M_i V_i = M_f V_f
\]

to solve for the molarity of the diluted solution:

\[
M_f = M_i \left( \frac{V_i}{V_f} \right)
\]

Solve: \(M_f = (3.0 \text{ M}) \left( \frac{125 \text{ mL}}{500 \text{ mL}} \right) = 0.75 \text{ M}\)

Note: The molarity of a diluted solution must always be less than that of the initial solution because the ratio \(V_f/V_i\) is always smaller than 1.

Solution Stoichiometry (4.6)

In Section 3.6 of the textbook we learned how to use the stoichiometry of a chemical reaction to convert the amount of a substance in a chemical reaction to the amount of a different one. This requires the use of the balancing coefficients in the chemical reaction and molar mass. In Section 4.6, we learn how to use molarity and volume in solution stoichiometry and chemical analysis. A key relationship when doing solution stoichiometry problems is:

\[
n_{\text{moles of solute}} = M_{\text{solution}} \times V_{\text{liters}}
\]
A laboratory procedure for determining the concentration of a solute in a solution using a solution of known concentration is called a titration:

- **Titration** is a laboratory procedure used in chemical analyses and involves measuring precisely the volume of a solution whose molarity is known (called a standard solution) required to react with a volume of a solution whose concentration is unknown. The stoichiometry of the reaction provides information about the ratio of moles between the standard and the substance whose concentration is unknown.
- The equivalence point of a titration is when chemically equivalent, or stoichiometric, amounts of reactants have reacted. The end point is the experimentally determined condition when an indicator or other signalling device indicates that the end of the reaction has occurred.
- The stoichiometry of a reaction is important in determining the concentration of the unknown solution. For example, the reaction between sodium hydroxide and hydrochloric acid is:

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

  Note that they react in a 1:1 mole ratio. However, in the titration of sodium hydroxide with sulfuric acid

  \[ 2 \text{NaOH}(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow 2 \text{H}_2\text{O}(l) + \text{Na}_2\text{SO}_4(aq) \]

  note that the base and acid react in a 2:1 mole ratio.
- When doing problems involving titrations first write the chemical reaction to determine the stoichiometry between the standard and the unknown substance.

**Exercise 17  Determining the volume of a solution required to react with another solution**

What volume of 0.250 M HCl is required to react completely with 25.00 mL of 0.500 M NaOH?

**SOLUTION: Analyze:** We are asked to determine the volume of a 0.250 M HCl solution necessary to neutralize a specified volume of 0.500 M NaOH, 25.00 mL. This is a stoichiometry problem involving concentrations.

**Plan:** Since it is a stoichiometry problem, we should write the neutralization reaction between the acid HCl and the base NaOH. In a neutralization reaction, water and a salt form.

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

To solve this problem, we can carry out the following conversions:

**Volume** NaOH \( \rightarrow \) moles NaOH \( \rightarrow \) moles HCl \( \rightarrow \) volume HCl

We know the molarity of the solutions and from the stoichiometry of the chemical reaction that

1 mol HCl \( \approx \) 1 mol NaOH

**Solve:** We first solve for the number of moles of sodium hydroxide used in the chemical reaction from the molarity and volume of the standard solution, NaOH.

\[
M_{\text{NaOH}}V_{\text{NaOH\ solution}} = \text{moles of NaOH} \\
(0.500 \text{ M})(0.02500 \text{ L}) = 0.0125 \text{ mol NaOH}
\]

Next, convert the number of moles of NaOH to the number of moles of HCl that reacts with the NaOH using the balancing coefficients in the chemical reaction.

\[
\text{mol HCl} = (0.0125 \text{ mol NaOH}) \left( \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \right) = 0.0125 \text{ mol HCl}
\]

Finally, convert the number of moles of HCl to the volume of the initial HCl solution required in the reaction by once again using molarity.

\[
M_{\text{HCl\ solution}}V_{\text{HCl}} = \text{moles of HCl} \\
(0.250 \text{ M})V = 0.0125 \text{ mol HCl} \\
V = \frac{0.0125 \text{ mol HCl}}{0.250 \text{ M}} = 0.0500 \text{ L} = 50.0 \text{ mL HCl}
\]
Chapter 4

Alternatively, we can solve for the volume in one step by combining the individual steps as we learned in Section 3.6. This is not shown here, but you should try this approach for additional practice.

Self-Test Questions

Having reviewed key terms in Chapter 4 in the textbook, match key terms with phrases and identify statements as true or false. If a statement is false, indicate why it is incorrect.

Match each phrase with the best term:

4.1 Metals that are easily oxidized are high in this list.
4.2 A process in which an element loses electrons.
4.3 A process in which an element gains electrons.
4.4 A substance that produces hydroxide ions in water.
4.5 A substance that decreases the concentration of hydroxide ions in water.
4.6 A measure of the amount of solute in a solution.
4.7 HF is an example of this type of electrolyte in water.
4.8 HCl is an example of this type of electrolyte in water.
4.9 These substances cause an increase in the conductivity of a solvent.
4.10 The point in a titration when one volume of 0.10 M sulfuric acid reacts exactly with two volumes of 0.10 M sodium hydroxide.
4.11 A solution whose concentration is exactly known.
4.12 A method for determining concentrations that uses volume.
4.13 A dye that changes color as a function of pH.
4.14 Ions in a chemical reaction that do not undergo change.
4.15 A reaction in which weak electrolytes are shown in a molecular form and soluble strong electrolytes are not.
4.16 Strong electrolytes, weak electrolytes, and gases are left in an unionized form.
4.17 A reaction that produces salt and water.

Terms:
(a) acid (g) indicator (m) spectator ions
(b) activity series (h) molecular equations (n) standardized solution
(c) base (i) net ionic equation (o) strong electrolyte
(d) concentration (j) neutralization (p) titration
(e) electrolytes (k) oxidation (q) weak electrolytes
(f) equivalence point (l) reduction

Identify Each Statement as True or False:

4.18 The molarity of a solution containing 7.46 g of KCl in 0.500 liters of a solution is 0.200 M.
4.19 An example of a metathesis reaction is:

\[
\text{HNO}_3(aq) + \text{KOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{KNO}_3(aq)
\]

4.20 In the following precipitation reaction

\[
\text{CaCl}_2 + 2\text{AgNO}_3 \rightarrow \text{Ca(NO}_3)_2 + 2\text{AgI}
\]

the insoluble material (the precipitate) is Ca(NO_3)_2.

4.21 The term aqueous solution means water is the solvent.

4.22 Three grams of sodium metal and a large amount of liquid ammonia form a solution. Thus, sodium is the solvent.

4.23 A solution can have only one solute.

4.24 When a solution is diluted with a solvent, the number of moles of solute decreases.

4.25 Ethanol is a nonelectrolyte in water.

4.26 In a state of chemical equilibrium, the concentrations of reactants and products remain constant.

4.27 A base in water always forms hydroxide ion.

4.28 Sulfuric acid is a strong acid.

4.29 Hydroiodic acid is a weak acid.

4.30 Barium hydroxide is a weak base.

4.31 When a strong acid reacts with a strong base, a salt is produced.
4.32 The reaction of lead(II) nitrate with sodium chloride in water produces a white precipitate.
4.33 The solubility of nickel(II) phosphate in water is high.
4.34 The oxidation number of iodine in IF₅ is −3.

Problems and Short-Answer Questions

4.35 The following two pictures represent HX and HA. Which one is the stronger acid? Explain your reasoning.

![Diagram of HX and HA]

4.36 An aqueous solution containing the cation X⁺ (shaded spheres) is added to an aqueous solution containing the anion Y²⁻ (unshaded spheres). The following diagram represents the final solution. Given this information, write a balanced chemical equation. Explain your reasoning.

![Diagram of X⁺ and Y²⁻ reaction]

4.37 Are the following compounds ionic or molecular? Justify your answer.
(a) CaCl₂  
(b) Fe(NO₃)₃  
(c) I₂  
(d) HC₂H₃O₂

4.38 For the compounds in 4.37, describe their electrolytic behavior in water. Describe the primary species that exist in solution.

4.39 Rank the following 0.1 M solutions in order of increasing conductivity in water: C₆H₁₂O₆ (glucose), KI, HI, and HC₂H₃O₂.

4.40 (a) When does an oxidation number actually reflect the charged state of an element in a substance?  
(b) When is an oxidation number always zero?  
(c) What is the difference between an oxide ion and a peroxide ion in terms of oxidation numbers?  
(d) When assigning oxidation numbers why must you have knowledge of the charge of the substance?

4.41 Which element has the highest oxidation number in the following group of substances?
KMnO₄, H₃SO₄, NaHCO₃, Ca(ClO₃)₂

4.42 In the activity series (Table 4.5 in the textbook) copper is below hydrogen gas.
(a) What does this tell you about the reactivity of copper compared to hydrogen gas?  
(b) Will hydrogen gas react with copper metal or copper(II) ions?

4.43 Using the activity series (Table 4.5 in the textbook), write balanced chemical equations for the following reactions: (a) Mg is added to a solution of silver nitrate; (b) iron metal is added to a solution of copper (II) sulfate; (c) silver is added to a solution of zinc nitrate; (d) hydrogen gas is passed over a sample of zinc oxide; (e) hydrogen gas is passed over mercuric oxide.

4.44 10.00 mL aliquot of a base containing one hydroxide unit is titrated with 25.00 mL of a 0.30 M HCl solution. Is this sufficient information to determine the molar mass of the base? Explain without doing calculations. In your explanation identify any information that is needed and why.

4.45 A solution contains either: Ba²⁺, Fe²⁺, or Ag⁺. The metal ion reacts with a solution of sodium sulfate to form a white precipitate, but it does not react with a solution of sodium chloride. Is this sufficient information to determine the identity of the metal ion? Explain. In your explanation identify any information that is needed and why.

4.46 Critique the following statement: A 1.2 M aqueous solution of AgNO₃ contains 1.2 moles of AgNO₃ in 1.0 L of water.

4.47 A student wants to prepare 100.0 mL of a 0.100 M NaCl solution and has available the following: (1) A bottle of reagent grade solid NaCl; (2) 2.00 L of 0.0500 M NaCl; and (3) 2.00 L of 1.00 M NaCl.
Chapter 4

4.48 Determine the following for a sucrose (C₁₂H₂₂O₁₁, molar mass = 342 g/mol) solution:
(a) The number of moles of sucrose in exactly 200 mL of a 0.100 M solution.
(b) The volume of a 1.25 M solution containing 0.100 moles of sucrose.
(c) The molarity of a solution containing 10.0 g of sucrose in exactly 500 mL.

4.49 Answer the following questions about a 1.50 M HCl solution:
(a) What is the new molarity if exactly 200 mL of the solution is diluted to 1.000 L?
(b) How many milliliters of the solution must be diluted to exactly 500 mL to form a 0.100 M HCl solution?
(c) How many moles of HCl are present in a diluted solution if exactly 100 mL of the original solution are diluted to 2.000 L?

4.50 Identify the acid and base in each of the following reactions:
(a) NH₄⁺(aq) + H₂O(l) → NH₃(aq) + H₃O⁺(aq)
(b) HClO₂(aq) + H₂O(l) → H⁺(aq) + ClO₂⁻(aq)
(c) HF(aq) + NaOH(aq) → NaF(aq) + H₂O(l)

4.51 Complete and balance the following neutralization reactions. Underline the acid reactant with one line and the base reactant with two lines.
(a) Be₂(OH)₂(aq) + HBr(aq) →
(b) NH₃(aq) + H₂SO₄(aq) →

4.52 Write balanced net ionic equations for each of the following reactions:
(a) Na₂H₂O₂(aq) + HCl(aq) →
(b) KCl(aq) + H₂S(aq) →
(c) Ni(NO₃)₂(aq) + CuSO₄(aq) →
(d) HC₃H₂O₃(aq) + NaOH(aq) →

4.53 Using solubility rules or reasonable extensions of them, predict whether each of the following compounds is soluble in water:
(a) PbBr₂
(b) CsCl
(c) Cu₂(OH)₃Cl
(d) Mn(OH)₂
(e) Cu₃(PO₄)₂
(f) ZnS
(g) Hg₂Cl₂
(h) Ag₂SO₄
(i) K₃PO₄

4.54 Identify the following substances as strong or weak acids or bases in water:
(a) HCl
(b) H₂S
(c) NH₃
(d) KOH
(e) HClO₄
(f) HF

4.55 What is the molarity of a nitric acid solution if 36.00 mL of it reacts completely with 2.00 g of NaOH?

4.56 What is the molarity of a solution of H₃PO₄ if 80.00 mL of it is titrated with 25.86 mL of 0.1201 M NaOH? Assume that all three hydrogens in H₃PO₄ react with NaOH.

Integrative Exercises

4.57 10.30 mL of 0.1500 M HCl is reacted with 11.25 mL of 0.1355 M NaOH.
(a) What is the limiting reactant?
(b) How many grams of NaCl are formed?

4.58 A 20.05 mL sample of vinegar (an aqueous solution of acetic acid, H₃C₂H₃O₂) has a density of 1.061 g/mL. The vinegar is titrated completely with 40.10 mL of 0.4100 M KOH. What is the percentage by mass of acetic acid in the vinegar?

4.59 An excess of silver (I) nitrate reacts with 100.0 mL of a barium bromide solution to give 0.300 g of a solid compound.
(a) Write the net ionic equation for the chemical reaction.
(b) What is the molarity of the barium bromide solution?

4.60 How many K⁺ ions are there in 200.0 mL of a 0.20 M K₂SO₄ solution?

Multiple-Choice Questions

4.61 Which of the following represents the net ionic equation for NH₄⁺(aq) + HBr(aq) → ?
(a) NH₄⁺(aq) + HBr(aq) → NH₄⁺(aq) + Br⁻(aq)
(b) NH₄⁺(aq) + H₂O(l) → NH₃(aq) + H₃O⁺(aq)
(c) NH₃(aq) + H⁺(aq) + Br⁻(aq) → NH₄Br(aq)

4.62 Which is a spectator ion in the following reaction in water? ZnCl₂ + NaOH →
(a) Zn²⁺(aq)
(b) Cl⁻(aq)
(c) OH⁻(aq)
(d) There is no spectator ion.

4.63 Which of the following aqueous solutions has the greatest total concentration of ions present?
(a) 0.01 M HCl
(b) 0.05 M CaBr₂
(c) 0.02 M Ca(NO₃)₂
(d) 0.02 M Al(NO₃)₃

4.64 Which of the following metal ions form sulfate compounds that are insoluble in water: (1) K⁺, (2) Ba²⁺, (3) Ag⁺, (4) Mg²⁺, and (5) Pb²⁺?
(a) (1) and (2)
(b) (3) and (4)
(c) (1) and (3)
(d) (2), (3), and (5)
4.65 Which of the following metal ions form carbonate salts that are insoluble in water: (1) Na⁺, (2) Ca²⁺, (3) NH₄⁺, (4) Pb²⁺, and (5) K⁺?
(a) (1) and (2)  (b) (3) and (4)  (c) (2) and (4)  (d) (3) and (5)

4.66 Which atom undergoes reduction in the following reaction? 2 Fe₃O₄(s) + 3 CO(g) → 2 Fe(s) + 3 CO₂(g)
(a) Fe  (b) O  (c) C  (d) It is not an oxidation-reduction reaction.

4.67 What are the products of the neutralization reaction between hydrogen iodide and calcium hydroxide in water?
(a) calcium and water  (b) CaI₂  (c) Ca₂ and water  (d) water

4.68 What is the molarity of an aqueous HBr solution if 35.00 mL is neutralized with 70.00 mL of a 0.500 M NaOH solution?
(a) 0.250 M  (b) 0.500 M  (c) 0.750 M  (d) 1.00 M

4.69 How many grams of KCl (molar mass = 74.6 g/mol) are contained in 500 mL of a 0.250 M KCl aqueous solution?
(a) 0.125  (b) 9.33  (c) 125  (d) 9330

4.70 What is the molarity of a solution consisting of 1.25 g of NaOH in enough water to form exactly 250 mL of a solution?
(a) 1.25 M  (b) 0.800 M  (c) 8.00 M  (d) 0.125 M

4.71 A 300-mL solution of 3.0 M HCl is diluted to 2.0 L. What is the final molarity?
(a) 0.45 M  (b) 450 M  (c) 20 M  (d) 0.05 M

4.72 A 3.000-g sample of a soluble chloride is titrated with 52.60 mL of 0.2000 M AgNO₃. What is the percentage of chloride in the sample?
(a) 37.29%  (b) 24.86%  (c) 12.43%  (d) 37.29%

4.73 Which substance contains Mn in a +7 oxidation state? (1) MnO₃, (2) KMnO₄, (3) MnO₂, (4) Mn₂O₇
(a) (1)  (b) (2)  (c) (3) and (4)  (d) (2) and (4)

Self-Test Solutions

4.1 (b) 4.2 (k) 4.3 (l) 4.4 (c) 4.5 (a) 4.6 (d) 4.7 (q) 4.8 (o) 4.9 (e) 4.10 (f)
4.11 (m) 4.12 (p) 4.13 (g) 4.14 (m) 4.15 (i) 4.16 (h) 4.17 (j) 4.18 True. 4.19 True.
4.20 False. All nitrate salts are soluble in water; silver iodide is the insoluble substance. 4.21 True.
4.22 False. Ammonia is the solvent because it is in greatest quantity and has the phase of the solution.
4.23 False. One or more solutes.
4.24 False. The number of moles of solute increases upon dilution, but the number of moles of solute does not change.
4.25 True. 4.26 True. 4.27 True. 4.28 True. 4.29 False. It is a strong acid.
4.30 False. It is a strong base. Metallic hydroxides generally are strong bases. 4.31 True. 4.32 True.
4.33 False. According to solubility rules, most metallic phosphates are insoluble, and nickel is not one of the exceptions.
4.34 False. Fluorine is always assigned a −1 oxidation number; thus, the oxidation number of iodine is +3.
4.35 HX is the stronger acid, although it is a weak acid. In the HX solution, we see undissociated HX particles and separate ions; however, it is only partial dissociation. In the HA solution, we see that all the particles are undissociated, thus HA is not acting as an acid.
4.36 We see in the first solution eight X⁻ ions and in the second solution seven Y²⁻ ions. In the final solution, we see most of the ions have come together as particles in a precipitate and excess Y²⁻ ions remain. Eight X⁻ ions have combined with four Y²⁻ ions to form a precipitate. The balanced chemical equation is:
8 X⁻(aq) + 4 Y²⁻(aq) → 4 X₂Y(s)
4.37 An ionic compound will consist of a metal cation and a nonmetal anion. If a substance contains a metal, it is very likely ionic. Molecular compounds generally contain all nonmetals:
(a) Ionic.  (b) Ionic. The nitrate ion is a polyatomic ion containing nonmetals.
(c) Molecular.  (d) Molecular.
4.38 a. A strong electrolyte; it dissociates completely to form hydrated Ca²⁻ and Cl⁻ ions. Ionic substances are strong electrolytes in water except for a few cases.
(b) A strong electrolyte; it dissociates completely into hydrated Fe³⁺ and NO₃⁻ ions.
Chapter 4

(c) Molecular iodine is not very soluble in water unless iodide ion is also present. The form that exists in water is I\(_2\)\((aq)\).

(d) Acetic acid is a weak acid and only slightly ionizes. The primary species in water is \(\text{HC}_2\text{H}_3\text{O}_2\)\((aq)\).

4.39 glucose [non-electrolyte] \(\text{< HCl}_2\text{H}_3\text{O}_2\) [weak acid] \(\text{< KI} [\text{ionic}] \approx \text{HI [strong acid]}

4.40 (a) When an element is an ion in an ionic substance the oxidation number equals the charge of the ion.
(b) When an element is in its natural elemental state (e.g., \(\text{O}_2\)), it is assigned an oxidation number of zero. The oxide ion is \(\text{O}^{2-}\) and the superoxide ion is \(\text{O}_2^{2-}\). The oxidation number for the oxygen in the oxide ion is \(-2\) and in the superoxide ion it is \(-1\).
(d) When assigning oxidation numbers in a substance, you must account for the requirement that the sum of oxidation numbers must equal the charge of the substance.

4.41 Manganese in \(\text{KMnO}_4\) has the highest oxidation number; \(+7\) \([+1, +7, 4(-2)]\). Sulfur in sulfuric acid has a +6 oxidation number, carbon has a +4 oxidation number in \(\text{NaHCO}_3\) and chlorine has a +5 oxidation number in \(\text{ClO}_3^-\) in \(\text{Ca(ClO}_3\)\(]_2\).

4.42 (a) Elements above hydrogen gas are more reactive than hydrogen, and elements below it are less reactive with respect to oxidation. Thus, copper is less reactive as an element compared to hydrogen gas.
(b) Hydrogen gas will react with copper(II) ions to form hydrogen ions and metallic copper.

4.43 (a) \(\text{Mg(s)} \rightarrow 2 \text{AgNO}_3(aq) \rightarrow \text{Mg(NO}_3\text{)}_2(aq) + 2 \text{Ag(s)}\);
(b) \(\text{Fe(s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{FeSO}_4(aq) + \text{H}_2(g)\);
(c) No reaction. Ag lies below zinc in the activity series.
(d) No reaction. \(\text{H}_2\) gas lies below \(\text{Zn}\) in the activity series.
(e) \(\text{H}_2\text{O}_2(g) \rightarrow \text{H}_2\text{O}_2(l) + \text{H}_2\text{O}(l)\).

4.44 No. The reaction between the base and acid is 1:1 because the base has only one hydroxide unit and HCl is a monoprotic acid. Thus, you can determine the molarity of the base at the equivalence point using the relationship: moles of acid = moles of base. The molarity of the base equals \(\frac{\text{moles of base}}{\text{volume of base in liters}}\). This permits you to calculate the number of moles of base.

The definition of moles is \(\frac{\text{grams}}{\text{molar mass}}\); you cannot calculate the molar mass because you are not given the grams or chemical formula of the base.

4.45 Yes, the metal ion is barium. Only barium ion reacts with sulfate ion to form a precipitate. Silver ion reacts with chloride ion to form a precipitate, but no precipitate is observed. Iron (II) ion is soluble with both reagents added.

4.46 The definition of molarity is the number of moles of solute divided by the volume of the solution in liters. In the statement, the reference is to the volume of water, which is the solvent not the solution.

4.47 (a) Samples (1) and (3) can be used to prepare the desired solution. Sample (1), a solid, can be weighed and added to a volumetric flask and water added to the mark. Sample (3) has a more concentrated solution from which a measured sample can be diluted to obtain the desired volume and molarity. Sample (2) has a concentration less than that desired and thus it cannot be diluted to form a higher concentration.

(b) For sample (1), the amount of NaCl needed to prepare 100.0 mL of a 0.100 M NaCl solution is calculated using the definition of molarity. The required amount of solid is carefully weighed and added to a 100.0 mL volumetric flask. Water is carefully added, and the solution is swirled carefully. Water continues to be added until the 100.0 mL mark is reached. Sample (3) is used to prepare the desired solution by taking an aliquot of it and diluting the aliquot in a 100.0 mL volumetric flask to the mark. The volume of the aliquot is determined by the relationship: \(\text{Molarity of concentrated solution} = \left(\frac{\text{Molarity of dilute solution}}{\text{Volume of dilution}}\right)\) - the volume of the concentrated solution, the aliquot, is calculated from the molarity of the concentrated solution (1.00 M NaCl), the required molarity of the diluted NaCl (0.100 M), and the volume of the diluted solution (100.0 mL).

4.48 (a) \(\text{mol sucrose} = M \times V = \frac{\text{grams}}{\text{molar mass}} = \frac{100 \text{ g}}{342 \text{ g/mol}} = 0.292 \text{ mol}\).
(b) \(V = \text{mol} / M = 0.100 \text{ mol} / 1.25 \text{ M} = 0.0800 \text{ L}\).
(c) \(M = \frac{\text{grams}}{\text{molar mass}} \times \frac{1}{V} = 10.0 \text{ g} / 342 \text{ g/mol} = 0.0292 \text{ M}\).
(d) \(M = \frac{M}{M_o} = \frac{1.50 \text{ M}}{0.100 \text{ M}} = 15.0 \text{ M}\).

4.49 (a) \(V = \frac{M}{M_o} = 1.50 \text{ M} / 0.100 \text{ M} = 15.0 \text{ M}\).
(b) \(V = \frac{M}{M_o} = 0.100 \text{ M} / 1.50 \text{ M} = 0.0667 \text{ M}\).
(c) The number of moles does not change on dilution, only the concentration.

4.50 (a) acid: \(\text{NH}_4^+\); base: \(\text{H}_2\text{O}\).
(b) acid: \(\text{HC}_2\text{H}_3\text{O}_2^-\); base: \(\text{H}_2\text{O}\).
(c) acid: \(\text{HF}\); base: \(\text{NaOH}\).

4.51 (a) \(\text{Ba(OH)}_2(aq) + 2 \text{HCl}(aq) \rightarrow \text{BaCl}_2(aq) + 2 \text{H}_2\text{O}(l)\);
(b) \(2\text{NH}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow (\text{NH}_4)_2\text{SO}_4(aq)\).

4.52 (a) \(\text{H}_2\text{O}(aq) + \text{C}_2\text{H}_5\text{O}_2^-\rightarrow \text{HC}_2\text{H}_3\text{O}_2(aq)\);
(b) \(\text{Hg}_2^{2+}(aq) + 2 \text{Cl}^-\rightarrow \text{Hg}_2\text{Cl}_2(s)\).
(c) No reaction—predicted products NiSO₄ and Cu(NO₃)₂ are both soluble and strong electrolytes in water; 
(d) HCl₂H₂O₂(aq) + OH⁻(aq) → H₂O(l) + C₂H₃O₂⁻(aq).

4.53 Table 4.1 of the textbook is used to reach the following conclusions:
(a) insoluble, an 
(b) soluble; 
exception to rule 
(c) soluble; 
that all bromide 
(salts are soluble; 
(d) insoluble; 
(e) insoluble; 
(f) insoluble; 
(g) insoluble; 
(h) insoluble; 
(i) soluble. 

4.54 (a) strong acid; 
(b) weak acid; 
(c) weak base; 
(d) strong base; 
(e) weak acid; 
(f) strong acid; 
(g) weak acid.

4.55 Reaction: HNO₃ + NaOH → NaNO₃ + H₂O.
Conversions required: grams NaOH → moles NaOH → moles HNO₃ → molarity HNO₃.
Equivalences: 40.00 g NaOH = 1 mol NaOH; 1 mol NaOH = 1 mol HNO₃ (from neutralization reaction).

\[ M \text{HNO}_3 = \frac{\text{moles HNO}_3}{\text{volume in liters}} = \frac{(2.00 \text{ g NaOH})(1 \text{ mol NaOH})}{(40.00 \text{ g NaOH})(1 \text{ mol HNO}_3)(36.00 \text{ mL})(1000 \text{ mL})} = \frac{1.39 \text{ mol HNO}_3}{1 \text{ L}} = 1.39 \text{ molar} \]

4.56 Reaction equation: H₃PO₄ + 3 NaOH → Na₃PO₄ + 3 H₂O.
Conversions required: milliliters NaOH → moles NaOH → moles H₃PO₄.
Equivalences: 0.2101 mol NaOH = 1 L of NaOH solution; 1 mol H₃PO₄ = 3 mol NaOH.

\[ \text{Moles H₃PO}_4 = \frac{25.86 \text{ mL NaOH}}{1000 \text{ mL}} \times \frac{0.1201 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol H₃PO}_4}{3 \text{ mol NaOH}} = 1.035 \times 10^{-3} \text{ mol} \]

\[ M \text{H₃PO}_4 = \frac{\text{moles H₃PO}_4}{\text{volume in liters}} = \frac{1.035 \times 10^{-3} \text{ mol}}{0.0500 \text{ L}} = 0.02070 M \]

4.57 (a) The neutralization reaction is HCl(aq) + NaOH(aq) → H₂O(aq) + NaCl(aq). The number of moles of each reactant is:

\[ \text{mol HCl} = M \times V = (0.01030 \text{ L})(0.1500 \text{ M}) = 0.001545 \text{ mol HCl} \]

\[ \text{mol NaOH} = M \times V = (0.01125 \text{ L})(0.1355 \text{ M}) = 0.001524 \text{ mol NaOH} \]

The limiting reactant is NaOH because HCl and NaOH react in a 1:1 mole ratio. Since the number of moles of NaOH is smaller, only 0.001524 mol HCl are needed; HCl is in excess.

(b) The number of moles of NaCl formed is the same number as that for NaOH, the limiting reactant, since there is a 1:1 mole ratio between NaOH and NaCl. Therefore, the number of grams of NaCl is (0.001524 mol NaCl)(58.44 g/1 mol) = 0.08906 g NaCl.

4.58 To determine the percentage by mass of acetic acid, H₂C₂H₃O₂, in the vinegar sample, we need to calculate the mass of acetic acid. The reaction between acetic acid and KOH is:

\[ \text{H₂C₂H₃O}_2(aq) + \text{KOH}(aq) → \text{H}_2\text{O}(aq) + \text{K₂C₂H₃O}_2(aq) \]

The number of moles of KOH can be calculated from the relation: \( M \times V = \text{moles} \)

\[ \text{mol KOH} = (0.04010 \text{ L})(0.4100 \text{ M}) = 0.01644 \text{ mol KOH} \]

The number of moles of acetic acid is the same as for KOH because they react in a 1:1 mole ratio. Therefore, the number of grams of acetic acid is:

\[ (0.01644 \text{ mol H₂C₂H₃O₂})(60.04 \text{ g/1 mol}) = 0.9871 \text{ g H₂C₂H₃O₂} \]

The percentage by mass of acetic acid is: \([\text{mass H₂C₂H₃O₂/mass vinegar solution}] \times 100\). The mass of vinegar solution is calculated using density: (20.05 mL)(1.061 g/1 mL) = 21.27 g vinegar. Thus, the percentage by mass of acetic acid is:

\[ \frac{0.9871 \text{ g H₂C₂H₃O₂}}{21.27 \text{ g vinegar}} \times 100 = 4.641\% \]

4.59 (a) BaBr₂(aq) + 2 AgNO₃(aq) → Ba(NO₃)₂(aq) + 2 AgBr(s)
Net ionic equation: Ag⁺(aq) + Br⁻(aq) → AgBr(s)
(b) moles BaBr₂ = (0.300 g AgBr) \left( \frac{1 \text{ mol AgBr}}{187.77 \text{ g AgBr}} \right) \left( \frac{1 \text{ mol BaBr₂}}{2 \text{ mol AgBr}} \right) = 7.99 \times 10^{-4} \text{ mol BaBr₂}

Molarity = \frac{7.99 \times 10^{-4} \text{ mol BaBr₂}}{0.1000 \text{ L}} = 7.99 \times 10^{-3} \text{ molar}

4.60 Potassium sulfate is a strong electrolyte:

\[ \text{K}_2\text{SO}_4(aq) \rightarrow 2 \text{ K}^+(aq) + \text{SO}_4^{2-}(aq). \]

number of K⁺ ions = \left( \frac{0.200 \text{ mol}}{1 \text{ L}} \right) \left( \frac{2 \text{ mol K}^+ \text{ ions}}{1 \text{ mol K}_2\text{SO}_4} \right) = 4.8 \times 10^{22} \text{ K}^+ \text{ ions.}

4.61 (d) HBr and NH₄Br are both strong electrolytes.
4.62 (b)
4.63 (b) 3 \times 0.05 \text{ M} = 0.15 \text{ M} \text{ in total ions. Note that although (d) has four ions per formula, the total ion concentration is 0.08 M.}
4.64 (d) 4.65 (c) 4.66 (a) 4.67 (c) 4.68 (d) 4.69 (b)
4.70 (d)

\[ \frac{\text{mol NaOH}}{\text{volume in liters}} = \frac{(1.25 \text{ g NaOH})(1 \text{ mol NaOH})}{40.01 \text{ g NaOH}} \frac{1 \text{ L}}{250. \text{ mL}} \frac{1000 \text{ mL}}{1 \text{ L}} = 0.125 \text{ M} \]

4.71 (a)

\[ M_i V_i = M_j V_j \]

\[ M_j = M_i \frac{V_i}{V_j} = (3.0 \text{ M}) \left[ \frac{300 \text{ mL}}{2.0 \text{ L}} \frac{1000 \text{ mL}}{1 \text{ L}} \right] = 0.45 \text{ M} \]

4.72 (c) The reaction of interest is Cl⁻(aq) + AgNO₃(aq) → AgCl(s) + NO₃⁻(aq). We need to make the following conversions: Milliliters AgNO₃ → moles AgNO₃ → moles Cl⁻ → grams Cl⁻. Hence,

\[ \text{Grams Cl}^- = (52.60 \text{ mL AgNO₃}) \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.2000 \text{ mol AgNO₃}}{1 \text{ L AgNO₃}} \right) \left( \frac{1 \text{ mol Cl}^-}{1 \text{ mol AgNO₃}} \right) \]

\[ \times \left( \frac{35.45 \text{ g Cl}^-}{1 \text{ mol Cl}^-} \right) = 0.3729 \text{ g Cl}^- \]

\% Cl⁻ in sample = \left( \frac{\text{mass of Cl}^- \text{ in sample}}{\text{sample mass}} \right) \times 100

\% Cl⁻ in sample = \left( \frac{0.3729 \text{ g Cl}^-}{3.000 \text{ g sample}} \right) \times 100 = 12.43% 

4.73 (d)