Chapter 4: Chemical Reactions

Chapter Objectives:
• Learn how to distinguish strong and weak electrolytes, and nonelectrolytes.
• Learn how to recognize and predict products in precipitation, neutralization, redox, and other types of chemical reactions.

Introduction
• Much of the chemistry (both biological and non-biological) that takes place on Earth involves water in some fashion:
  – Almost 75% of the Earth’s surface is covered by water or ice.
  – About 66% of the human body consists of water.
  – A lot of important chemistry takes place in aqueous solutions, in which the solvent is water.
• In this chapter, we’ll see how some types of chemical reactions take place and how we can organize chemical reactions into different types. Most of these reactions will take place in aqueous solutions.

Strong Electrolytes, Weak Electrolytes, and Nonelectrolytes

The Role of Water as a Solvent
• Many reactions take place in aqueous solution. Water interacts with many substances, and plays an active role in many chemical processes.
• Many ionic substances dissolve in water (to at least some extent); water is very good at solvating (dissolving) cations and anions.
  – The O end of a water molecule has a slight negative charge (a partial negative charge, \( \delta^- \)) while the H ends have slight positive charges (a partial positive charge, \( \delta^+ \)).
  – Water also has an overall bent shape.
  – The combined effects of polar bonds in a bent shape make water a polar molecule, having an uneven distribution of electrons.

The Shape and Polarity of Water

Solute and Solvent Interactions
• When a solid is put into a liquid solvent such as water, there is a competition between the forces of attraction among the particles of the solute (solute-solute interactions) and the forces of attraction between the solvent molecules and the particles in the solute (solvent-solute interactions). Which interactions are stronger determines whether the solute dissolves.
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Water as a Solvent

- When sodium chloride is dissolved in water, the Na⁺ and Cl⁻ ions are attracted to each other, and both are also attracted to water molecules.
  - The Na⁺ ions are attracted to the partially negative oxygen atom.
  - The Cl⁻ ions are attracted to the partially positive hydrogen atoms.
  - The attraction between the water and the ions is greater than that of the ions for each other, and the sodium chloride dissolves.

- The ions are separated from each other, and are free to move randomly through the solution, surrounded by a crowd of water molecules.

Water as a Solvent

- Ethanol (ethyl alcohol, C₂H₅OH) dissolves in water because the partial charges on the H and O atoms in the molecule interacts strongly with the partial charges on the atoms in water.
  - The ethanol molecules themselves don’t break apart.

Electrolytes in Aqueous Solution

- Substances that dissolve in water can be classified as electrolytes or nonelectrolytes:
  - Electrolytes dissolve in water to form solutions which conduct electricity, because they dissociate to form mobile, solvated cations and anions:
    \[ \text{NaCl(s)} \xrightarrow{\text{H₂O}} \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]
  - Nonelectrolytes do not conduct electricity when dissolved in water, because they are molecules with don’t dissociate into ions (water itself is a nonelectrolyte):
    \[ \text{C₁₂H₂₂O₁₁(s)} \xrightarrow{\text{H₂O}} \text{C₁₂H₂₂O₁₁(aq)} \]

Electrolytes in Aqueous Solution

- Electrolytes are divided into two categories:
  - Strong electrolytes are dissociated to a very large extent (70-100%) — virtually all of the units of the original substance are separated into ions:
    \[ \text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]
  - Weak electrolytes are dissociated to a very small extent — only a small percentage of the substance is dissociated into ions at any one time:
    \[ \text{HC₂H₃O₂(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{C₂H₃O₂}^-\text{(aq)} \]
  - Since most particles in a weak electrolyte solution are not ionized, weak electrolytes conduct electricity, but not very well.
Weak Electrolytes and Dynamic Equilibrium

- Dissociation of weak electrolytes are often written using back-and-forth double arrows, indicating that a dynamic equilibrium is taking place, in which there is a forward and a backward direction to the process.

- Equilibria play a role in many important processes and reactions in chemistry, and is a point that we’ll return to later on (and a great deal in the second semester).

Acids as Electrolytes

- Most molecular compounds are nonelectrolytes, except for the acids.
- Acids of the general formula HA ionize into H+ ions and A- ions when they dissolve in water:

  \[ \text{HA}(g, l) \rightleftharpoons H^+ (aq) + A^- (aq) \]

  - A strong acid such as HCl ionizes completely. Every molecule of HCl splits up into H+ and Cl-:

    \[ \text{HCl}(g) \rightarrow H^+ (aq) + \text{Cl}^- (aq) \]

  - A weak acid such as HC₂H₃O₂ does not ionize completely. Only a small percentage of the molecules split up into H+ and C₂H₃O₂⁻:

    \[ \text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons H^+ (aq) + \text{C}_2\text{H}_3\text{O}_2^- (aq) \]

Classifying Electrolytes

- **Strong Electrolytes:**
  - Soluble ionic compounds.
  - Strong acids: HCl, HBr, HI, HNO₃, HClO₄, H₂SO₄

- **Weak Electrolytes:**
  - All other acids are weak acids/weak electrolytes: HF, HC₂H₃O₂, HNO₂, H₂SO₃, etc.

- **Nonelectrolytes:**
  - Molecular compounds (except for acids): water, sugar, most organic compounds, etc.

Examples: Dissociation of Ionic Compounds

1. Write the equation for the dissociation in water of Na₂S, HBr, AlCl₃, and Pb(NO₃)₂.

2. How many moles of each ion are in 1 mol of CaCl₂?
Examples: Dissociation of Ionic Compounds

3. How many moles of each ion are in 23.4 g of Na₂S?

Answer: 0.600 mol Na⁺, 0.300 mol S²⁻

Examples: Classifying Electrolytes

4. Classify the following compounds as strong electrolytes, weak electrolytes, or nonelectrolytes.
   a. HCl
   b. SCl₂
   c. AgNO₃
   d. H₂O
   e. CH₃CH₂OH
   f. Na₂SO₄
   g. HNO₂
   h. HNO₃

Precipitation Reactions

• A precipitation reaction occurs when two ionic compounds react to produce a precipitate, an insoluble substance which falls out of the solution.

• These reactions are also known as double-displacement or metathesis reactions, because the cations and anions of the reactants “change partners” in the products:

  \[ \text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB} \]

• These reactions occur when the solute-solute attractions between the ions in the precipitate are stronger than the solvent-solute attractions.

• The other ions stay in solution as spectator ions.

Soluble and Insoluble

• In some cases, the electrostatic forces in ionic compounds are too great to be overcome by water, and the substance is insoluble in water.

• This is greatly oversimplified, though; in reality, solubility is a continuum, and even “insoluble” substances dissolve in water to some slight extent.

  – Solubility of NaCl in H₂O at 25°C = 357 g/L
  – Solubility of AgNO₃ in H₂O at 25°C = 216 g/L
  – Solubility of AgCl in H₂O at 25°C = 0.0019 g/L

Precipitation Reactions

• If we mix solutions of NaCl and KI, all we get is a mixture of dissolved ions; no reaction takes place because none of the products are insoluble in water:

  \[ \text{NaCl(aq)} + \text{KI(aq)} \rightarrow \text{KCl(aq)} + \text{NaI(aq)}: \text{NR} \]
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Precipitation Reactions

• On the other hand, if we mix Pb(NO₃)₂ and KI, we get a solid product of PbI₂:

\[
Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow 2KNO_3(aq) + PbI_2(s)
\]

Predicting Precipitation Reactions

\[
AB(aq) + CD(aq) \rightarrow AD(aq) + CB(s)
\]

• In order to predict whether a precipitation reaction occurs, we use the solubility rules on the next slides to determine whether any of the potential products of the reaction are insoluble.
  – If one of the products of the reaction is insoluble, a precipitation reaction occurs, and the reaction must be balanced appropriately.
  – If no insoluble product forms, then No Reaction (NR) takes place, and all of the ions remain in solution as spectator ions.

Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds

1. All common compounds of the Group 1A ions (Li⁺, Na⁺, K⁺, etc.) and the ammonium ion (NH₄⁺) are soluble.

2. All common nitrates (NO₃⁻), acetates (C₂H₃O₂⁻), bicarbonates (HCO₃⁻), chlorates (ClO₃⁻), and most perchlorates (ClO₄⁻) are soluble.

3. All common chlorides (Cl⁻), bromides (Br⁻), and iodides (I⁻) are soluble, except those of Ag⁺, Cu²⁺, Pb²⁺, and Hg₂²⁺.

4. All common sulfates (SO₄²⁻) are soluble, except those of Ca²⁺, Sr²⁺, Ba²⁺, Pb²⁺, Hg₂²⁺, and Ag⁺.

Insoluble Ionic Compounds

5. Most metal hydroxides (OH⁻) and sulfides (S²⁻) are insoluble, except those of Group 1A, NH₄⁺, and Ca²⁺, Sr²⁺, and Ba²⁺.

6. Most carbonates (CO₃²⁻), phosphates (PO₄³⁻), chromates (CrO₄²⁻), and fluorides (F⁻) are insoluble, except those of Group 1A and NH₄⁺.

Examples: Predicting Solubility

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

   a. CaCO₃  
   b. Mg(OH)₂  
   c. Na₂S  
   d. PbSO₄  
   e. (NH₄)₃PO₄  
   f. NH₄C₂H₅O₂  
   g. HgCl₂  
   h. Hg₂Cl₂  
   i. AgC₂H₅O₂  
   j. Pb(NO₃)₂  
   k. K₂CO₃  
   l. AgCl

Representing Aqueous Reactions

• Aqueous reactions involving ionic compounds can be represented by three types of equations:
  – Molecular equation: formulas are written as if they were intact molecules (e.g., NaCl)
  – Complete (or overall) ionic equation: soluble strong electrolytes (soluble ionic compounds and strong acids) are written as ions (e.g., Na⁺, Cl⁻)
    • Insoluble precipitates, weak electrolytes, and molecules are left intact.
    • Ions that are not involved in the actual chemical change are called spectator ions.
  – Net ionic equation: shows only the ions which undergo a change, eliminating the spectator ions.
Molecular, Ionic, and Net Ionic Equations

Molecular equation:
\[ \text{Pb(NO}_3\text{)}_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{KNO}_3(\text{aq}) + \text{PbI}_2(\text{s}) \]

Ionic equation: (phase labels omitted for clarity)
\[ \text{Pb}^{2+} + 2\text{NO}_3^- + 2\text{K}^+ + 2\text{I}^- \rightarrow 2\text{K}^+ + 2\text{NO}_3^- + \text{PbI}_2(\text{s}) \]

Spectator ions: K⁺ and NO₃⁻

Net ionic equation:
\[ \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) \]

Examples: Molec., Ionic, and Net Ionic Eqns.

2. Write ionic and net ionic equations corresponding to the following molecular equations.

\[ 2\text{AgNO}_3(\text{aq}) + \text{Na}_2\text{CrO}_4(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{s}) + 2\text{NaNO}_3(\text{aq}) \]

\[ \text{H}_2\text{SO}_4(\text{aq}) + \text{MgCO}_3(\text{s}) \rightarrow \text{MgSO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g}) \]

Examples: Predicting Precipitation Reactions

3. Predict whether a precipitation reaction will occur when aqueous solutions of silver nitrate and sodium chloride are mixed. Write the ionic and net ionic equation for the reaction (if any).

Examples: Predicting Precipitation Reactions

4. Predict whether a reaction occurs when each of the following pairs of solutions are mixed. If a reaction does occur, write balanced molecular, ionic, and net ionic equations, and identify the spectator ions.

a. \( \_\_\text{CaCl}_2(\text{aq}) + \_\_\text{Na}_2\text{CO}_3(\text{aq}) \rightarrow \)

b. \( \_\_\text{Cu(NO}_3\text{)}_2(\text{aq}) + \_\_\text{NaCl(}\text{aq}) \rightarrow \)

c. \( \_\_\text{Pb(NO}_3\text{)}_2(\text{aq}) + \_\_\text{Na}_2\text{CrO}_4(\text{aq}) \rightarrow \)

d. \( \_\_\text{NiCl}_2(\text{aq}) + \_\_\text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \)

Examples: Predicting Precipitation Reactions

5. How might you use a precipitation reaction to prepare a sample of CuCO₃? Write the net ionic equation for the reaction.

Examples: Stoichiometry of Precipitation Rxns

6. Calculate the mass of solid NaCl that must be added to 1.500 L of 0.1000 M Pb(NO₃)₂ to precipitate all of the Pb²⁺ ions in the form of PbCl₂(s).

Answer: 17.53 g NaCl
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Examples: Stoichiometry of Precipitation Rxns

7. How many milliliters of 0.125 M HCl is required to completely precipitate all of the silver in 10.00 mL of a 0.150 M silver nitrate solution?

Answer: 12.0 mL

8. If 15.0 mL of 2.00 M Pb(NO₃)₂ and 45.0 mL of 1.15 M NaCl are mixed, how many grams of precipitate will be produced?

Answer: 7.20 g PbCl₂

Neutralization (Acid-Base) Reactions

Acids and Bases

• The concept of acidity and basicity has existed for a long time, and some compounds have long been designated as acids or bases:
  – Acids turn blue litmus red; their aqueous solutions have a tart taste.
  – Bases turn red litmus blue; their aqueous solutions have a bitter taste and a “soapy” feel.
• The level of acidity is measured on a logarithmic scale called the pH scale (pH = -log[H⁺]):
  – pH < 7 is acidic
  – pH > 7 is basic
  – pH = 7 is neutral

The Arrhenius Definition of Acids and Bases

• In the Arrhenius definition (Svante Arrhenius, 1887) of acids and bases:
  – An acid is a substance that produces H⁺ ions (protons) when dissolved in water.
  – A base is a substance that produces OH⁻ ions when dissolved in water.

\[
\begin{align*}
\text{HA}(aq) & \rightarrow \text{H}^+(aq) + \text{A}^-(aq) \\
\text{MOH}(aq) & \rightarrow \text{M}^+(aq) + \text{OH}^-(aq)
\end{align*}
\]

an acid

a base

Bronsted-Lowry Acids and Bases

• The Arrhenius definition of acids and bases applies only to aqueous solutions, but acid-base reactions also take place in other solvents; many species can also act as bases without containing OH⁻ ions. An extended definition was developed independently in 1923 by Johannes Brønsted and Thomas Lowry.
• The Bronsted-Lowry definition of acids and bases is based on proton (H⁺) transfer:
  – An Bronsted acid is a proton (H⁺) donor.
  – A Bronsted base is a proton (H⁺) acceptor.
  – An acid-base (neutralization) reaction is a proton transfer process.
• Any Arrhenius acid or base is also a Brønsted acid or base (but not vice versa).
**Brønsted-Lowry Acids and Bases**

\[
\begin{align*}
\text{HCl(g)} + \text{H}_2\text{O(l)} & \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq) \\
\text{NH}_3(aq) + \text{H}_2\text{O(l)} & \leftrightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq)
\end{align*}
\]

- **Acids** in their pure form (i.e., not mixed with water) are molecular compounds, but when they are dissolved in water, they **dissociate** into ions:
  - \(\text{HCl(g)} \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)\)
  - \(\text{HNO}_3(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq)\)
  - \(\text{H}_2\text{SO}_4(l) \leftrightarrow \text{H}^+(aq) + \text{SO}_4^{2-}(aq)\)

- **Polyprotic acids** contain more than one acidic proton. For instance, sulfuric acid is **diprotic**:
  - \(\text{H}_2\text{SO}_4(aq) \rightarrow \text{H}^+(aq) + \text{HSO}_4^-(aq)\)
  - \(\text{HSO}_4^-(aq) \rightarrow \text{H}^+(aq) + \text{SO}_4^{2-}(aq)\)

**The Hydronium Ion, H₃O⁺**

- An “H⁺” cation is too reactive to exist freely in an aqueous solution. An H⁺ is always attached to one or more H₂O’s as a **hydronium ion**, H₃O⁺.
- The dissociation reaction for HCl:
  - \(\text{HCl(g)} \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)\)
  - More correctly represented as:
  - \(\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(aq) + \text{Cl}^-(aq)\)

**Strong Acids and Weak Acids**

- Acids that dissociate to a large extent (~100%) are **strong electrolytes**, and are therefore called **strong acids**. There are six major strong acids:
  - Hydrochloric acid, HCl
  - Sulfuric acid, H₂SO₄
  - Hydrobromic acid, HBr
  - Nitric acid, HNO₃
  - Hydriodic acid, HI
  - Perchloric acid, HClO₄

- Acids that dissociate to only a small extent are **weak electrolytes**, and are therefore called **weak acids**. Any acid not on the above list is a weak acid:
  - Hydrofluoric acid, HF
  - Acetic acid, HC₂H₃O₂ (or CH₃CO₂H)
  - Phosphoric acid, H₃PO₄
  - Sulfurous acid, H₂SO₃
  - etc.

**Strong Bases and Weak Bases**

- Bases can also be either strong or weak.
- Most metal hydroxides are **strong bases**, which are virtually completely dissociated in water, such as:
  - Sodium hydroxide, NaOH
  - Potassium hydroxide, KOH
  - Calcium hydroxide, Ca(OH)₂
  - Barium hydroxide, Ba(OH)₂

- **Weak bases** are only partially dissociated. Weak bases do not contain OH⁻ ions, but produce them in an equilibrium reaction with water:
  - \(\text{NH}_3(aq) + \text{H}_2\text{O(l)} \leftrightarrow \text{NH}_4^+(aq) + \text{OH}^-(aq)\)
**Neutralization Reactions**

- **Acid-base reactions** or neutralization reactions occur when an acid and a base react to form water, a weak electrolyte, or a gas. (These reactions are also a form of double-displacement reaction.)

\[
\text{HA}(aq) + \text{MOH}(aq) \rightarrow \text{MA}(aq) + \text{H}_2\text{O}(l)
\]

- For a strong acid and base, this can be written as the ionic equation:

\[
\text{H}^+ + \text{A}^- + \text{M}^+ + \text{OH}^- \rightarrow \text{M}^+ + \text{A}^- + \text{H}_2\text{O}(l)
\]

  - Canceling the spectator ions gives the net ionic equation:

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)
\]

\[
\{\text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \rightarrow 2\text{H}_2\text{O}(l)\}
\]

**Examples: Neutralization Reactions**

1. Write the molecular equation, complete ionic equation, and net ionic equation for the following neutralization reactions:

\[
\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow
\]

\[
\text{HI}(aq) + \text{Ba(OH)}_2(aq) \rightarrow
\]

**Acid-Base Titrations**

- A **titration** is a procedure for determining the concentration of a solution:
  - A standard solution of known concentration is reacted with a solution of unknown concentration.
  - By measuring the volume of standard solution that reacts with a known volume of the unknown solution, the concentration can be calculated from the reaction stoichiometry.

- A common example of this process is an acid-base titration, in which an acid or base of unknown concentration reacts with a base or acid of known concentration:

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

**Acid-Base Titration**

- In the previous figure, OH⁻ from the buret is added to the acid of unknown concentration in the flask until the **equivalence point** is reached, when the number of moles of OH⁻ added equals the number of moles of H⁺ that were originally present.

\[
mol = \frac{mol \text{ NaOH}}{L} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{M}{L}
\]

sim. to Figure 10.18. The equivalence point is usually signaled by the color change of an acid-base indicator, such as phenolphthalein, which is colorless in an acidic solution but pink in a basic solution.
Examples: Acid-Base Titrations

2. A 25.0 mL sample of vinegar (dilute acetic acid, \( \text{HC}_2\text{H}_3\text{O}_2 \)) is titrated and found to react with 94.7 mL of 0.200 M \( \text{NaOH} \). What is the molarity of the acetic acid solution? 

\[
\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}(aq) \rightarrow \text{NaC}_2\text{H}_3\text{O}_2(aq) + \text{H}_2\text{O}(l)
\]

Answer: 0.758 M \( \text{HC}_2\text{H}_3\text{O}_2 \)

3. Citric acid, \( \text{H}_3\text{C}_6\text{H}_5\text{O}_7 \), is a triprotic acid found in citrus juices, such as orange juice, lemon juice, grapefruit juice, etc. (a) What is the molarity of \( \text{H}_3\text{C}_6\text{H}_5\text{O}_7 \) in commercially available lemon juice if 14.26 mL of 1.751 M \( \text{NaOH} \) is required to neutralize 20.00 mL in a titration procedure? (b) How many grams of citric acid are in 100.0 mL of the juice? 

\[
\text{H}_3\text{C}_6\text{H}_5\text{O}_7(aq) + \text{NaOH}(aq) \rightarrow
\]

Answer: (a) 0.4162 M; (b) 7.996 g

Neutralizations That Don’t Produce Water

- Some acid-base reactions result in the formation of gases, either directly or in the decomposition of an unstable intermediate. This removes ions from the solution, driving the reaction to occur.
- Gases that can be produced in acid-base reactions include \( \text{CO}_2 \), \( \text{H}_2\text{S} \), \( \text{HCN} \), \( \text{SO}_2 \) and \( \text{NH}_3 \).

\[
2\text{HCl}(aq) + \text{K}_2\text{CO}_3(aq) \rightarrow 2\text{KCl}(aq) + \text{H}_2\text{CO}_3(aq)
\]

\[
\downarrow \quad \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

\[
2\text{HCl}(aq) + \text{Na}_2\text{S}(aq) \rightarrow 2\text{NaCl}(aq) + \text{H}_2\text{S}(g)
\]

\[
\text{HCl}(aq) + \text{NaCN}(aq) \rightarrow \text{NaCl}(aq) + \text{HCN}(g)
\]

Double-Displacement Reactions

- Both precipitation and acid-base reactions are examples of double-displacement or metathesis reactions. In these reactions, the cations and anions in two ionic compounds “change partners”:

\[
\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}
\]

- In order for the reaction to occur, one of four things must occur, otherwise, there is no reaction (NR).

1. In precipitation reactions, an insoluble ionic compound forms (solubility rules).

2. In acid-base (neutralization) reactions, an acid and a base form a salt and water, a gas, or a weak electrolyte.

Examples: Predicting Neutralization Rxs

4. Predict whether a reaction occurs when each of the following pairs of solutions are mixed. If a reaction does occur, write balanced molecular, ionic, and net ionic equations, and identify the spectator ions.

a. HCl and calcium carbonate [movie]

b. Hydrobromic acid and barium hydroxide

c. Nitric acid and sodium fluoride

d. Sulfuric acid and sodium cyanide

e. Sodium bicarbonate and acetic acid

f. CdS(s) + HCl
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Oxidation-Reduction (Redox) Reactions

Oxidation and Reduction
• Oxidation-Reduction (redox) reactions, are another major class of chemical reactions.
  – Historically, “oxidation” meant the combination of an element with oxygen, as in the rusting of iron:
    \[ 4\text{Fe(s)} + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s) \]
  – “Reduction” meant the removal of oxygen from an oxide, as in the heating of iron ore with charcoal in a blast furnace to form iron metal:
    \[ 2\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 4\text{Fe(s)} + 3\text{CO}_2(g) \]
  • Now, the terms “oxidation” and “reduction” have more specific meanings:

Oxidation-Reduction Reactions
• An oxidation-reduction (redox) reaction is a process in which electrons are transferred from one substance to another.
  – Oxidation is the loss of electrons.
  – Reduction is the gain of electrons.

Oxidation:
\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \]

Reduction:
\[ \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \]

Oxidizing and Reducing Agents
• The oxidizing agent is the substance that causes oxidation to occur by accepting electrons.
  – The oxidizing agent itself becomes reduced.
• The reducing agent is the substance that causes reduction to occur by losing electrons.
  – The reducing agent itself becomes oxidized.
• In general, metals tend to act as reducing agents (lose electrons), and nonmetals tend to act as oxidizing agents (gain electrons).

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

Oxidation Numbers
• In the following reaction, it is easy to see that a redox reaction is taking place, because the charges are explicitly written out:
  \[ \text{Fe(s)} + \text{Cu}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cu(s)} \]
• But what about these reactions?
  \[ 2\text{Mg(s)} + \text{O}_2(g) \rightarrow 2\text{MgO(s)} \]
  \[ \text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl(g)} \]
  \[ \text{MnO}_4^-(aq) + 5\text{Fe}^{2+}(aq) + 8\text{H}^+(aq) \rightarrow \text{Mn}^{2+}(aq) + 5\text{Fe}^{3+}(aq) + 4\text{H}_2\text{O} \]
• We can keep track of whether a reaction is a redox reaction, and what specifically is being oxidized or reduced, by using oxidation numbers (aka oxidation state). Note that oxidation number is not the same thing as charge!!!!

Rules for Assigning Oxidation Numbers
These rules are hierarchical. If any two rules conflict, follow the rule that is higher on the list.
1. The sum of the oxidation numbers is 0 for a neutral molecule, and is equal to the charge for an ion.
   \[ \text{H}_2\text{SO}_4, \text{ClO}_4^-, \text{ClO}_2^-, \text{NH}_4^+ \]
   \[ +1 \quad -2 \quad ? \quad -2 \quad ? \quad +1 \]
2. An atom in its elemental state has an oxidation number of zero.
   \[ \text{Na}, \text{H}_2, \text{Br}_2, \text{S}, \text{Ne} \]
   \[ +1 \quad +2 \quad +3 \quad -1 \quad -2 \quad -3 \]
3. For monatomic ions, the oxidation number is equal to the charge.
   \[ \text{Na}^+, \text{Cu}^{2+}, \text{Al}^{3+}, \text{Cl}^-, \text{O}^{2-}, \text{N}^{3-} \]
   \[ +1 \quad +2 \quad +3 \quad -1 \quad -2 \quad -3 \]
Rules for Assigning Oxidation Numbers

4. F = -1 in its compounds.
5. H = +1 in compounds
   H = -1 when bonded with a metal
6. O = -2 in its compounds
   O = -1 in the peroxide ion, O$_2^-$
7. Cl, Br, I = -1, except in compounds with O
8. Group 6A = -2, except in compounds with O
9. Group 5A = -3, except in compounds with O

Examples: Assigning Oxidation Numbers

1. Determine the oxidation number of each element in the following species.
   a. Na
   b. Na$^+$
   c. NaH
   d. sodium chloride
   e. Zinc chloride
   f. SO$_3^2$-
   g. Sulfur trioxide
   h. Sulfite ion
   i. NO$_3^-$

Examples: Identifying Redox Reactions

2. Identify the substance oxidized, the substance reduced, the oxidizing agent, and the reducing agent in each of the following reactions.
   a. $2\text{Al}(s) + 3\text{H}_2\text{SO}_4(aq) \rightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\text{H}_2(g)$
   b. PbO(s) + CO(g) → Pb(s) + CO$_2$(g)
   c. H$_2$(g) + Cl$_2$(g) → 2HCl(g)
   d. CH$_4$(g) + 2O$_2$(g) → CO$_2$(g) + 2H$_2$O(g)
   e. MnO$_4^-(aq) + 5\text{Fe}^{2+}(aq) + 8H^+(aq) \rightarrow \text{Mn}^{2+}(aq) + 5\text{Fe}^{3+}(aq) + 4H_2O$
   f. Na$_2$SO$_4$(aq) + Pb(NO$_3$)$_2$(aq) → 2NaNO$_3$(aq) + PbSO$_4$(s)

Identifying Redox Reactions

• Another way to define a redox reaction is one in which the oxidation numbers of species change:
  – oxidation is an increase in oxidation number.
  – reduction is a decrease in oxidation number.
• Any reaction in which oxidation numbers change is a redox reaction. If no oxidation numbers change, the reaction is not a redox reaction.

\[
\begin{array}{c}
\text{S} + \text{O}_2 \rightarrow \text{SO}_2 \\
0 \quad 0 \quad \uparrow \quad \uparrow \quad \downarrow \\
\text{S: } 0 \rightarrow +4 \text{ oxidized} \\
\text{O: } 0 \rightarrow -2 \text{ reduced}
\end{array}
\]

Balancing Redox Reactions

• The following reaction might look balanced:
  \(\text{Ag}^+(aq) + \text{Cu}(s) \rightarrow \text{Ag}(s) + \text{Cu}^{2+}(aq)\)
  but it isn’t, because the charges are not balanced.
• This reaction is essentially a net ionic equation, because the spectator ions have been eliminated. If the spectator ions are included, simple redox reactions can be balanced by inspection:
  \(_{\text{AgNO}_3}(aq) + _{\text{Cu}}(s) \rightarrow _{\text{Ag}}(s) + _{\text{Cu(NO}_3)_2}(aq)\)
• To balance the skeleton form of a redox reaction, the reaction must be divided into its half-reactions:
Chapter 4: Chemical Reactions

Balancing Redox Reactions

1. Separate the components of the reaction into the oxidation and reduction half-reactions.
2. Balance the atoms in each half-reaction except O and H.
3. Balance O atoms by adding H₂O molecules.
4. Balance H atoms by adding H⁺ ions.
5. Balance the charge by adding electrons (e⁻).
6. Multiply the coefficients in each half-reaction by a number which makes the number of electrons in each half-reaction equal.
7. Add the two half-reactions, and cancel out any species that are the same on both side. (The electrons must cancel out.)

8. If the reaction occurs in basic solution (i.e., there are excess OH⁻ ions):
   a. Add OH⁻ ions to both sides of the equation in numbers equal to the number of H⁺ ions.
   b. Combine H⁺ and OH⁻ ions to make H₂O molecules.
   c. If there are H₂O’s on both sides, simplify the equation.
9. Double-check that the number of atoms and total charges are the same on both sides.

Examples: Balancing Redox Reactions

3. Balance the following redox reactions using the half-reaction method.
   a. Ag⁺(aq) + Cu(s) → Ag(s) + Cu²⁺(aq)
   b. Cr₂O₇²⁻(aq) + Fe²⁺(aq) → Cr³⁺(aq) + Fe³⁺(aq)

Single-Displacement Reactions; Activity Series

• A particular kind of redox reaction, called a single-displacement reaction occurs when an uncharged metal (A⁰) “displaces” a charged metal (B⁺) in an ionic compound (B⁺C⁻):
  \[ A⁰ + B⁺C⁻ \rightarrow A⁺C⁻ + B⁰ \]
  – The reacting metal (A⁰) becomes charged (A⁺), forming a new ionic compound (A⁺C⁻), and the displaced metal (B⁺) becomes uncharged (B⁰):
  • This reaction only occurs when the metal A⁰ is a more active (i.e., higher on the activity series) metal than the metal cation B⁺. The products of the reaction are written using ionic charge rules.

The Activity Series of the Metals

<table>
<thead>
<tr>
<th>Behavior toward H⁺</th>
<th>Most active</th>
<th>Least active</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>K</td>
<td>Au</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Zr</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>Hg</td>
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</tr>
<tr>
<td>Fe</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>Ag</td>
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</tr>
<tr>
<td>Ni</td>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Pb</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>Bi</td>
<td></td>
</tr>
</tbody>
</table>

Fe(s) + Cu³⁺(aq) → Fe²⁺(aq) + Cu(s)
Cu(s) + 2Ag⁺(aq) → Cu²⁺(aq) + 2Ag(s)
Examples: Single-Displacement Reactions

4. Predict whether the following reactions will occur.
   a. \( \text{Hg}^2+(aq) + \text{Zn}(s) \rightarrow \text{Hg}(l) + \text{Zn}^2+(aq) \)
   b. \( 2\text{H}^+(aq) + 2\text{Ag}(s) \rightarrow \text{H}_2(g) + 2\text{Ag}^+(aq) \)
   c. \( \text{CaCl}_2(aq) + \text{Mg}(s) \rightarrow \text{Ca}(s) + \text{MgCl}_2(aq) \)
   d. \( \text{Ca}(s) + \text{MgCl}_2(aq) \rightarrow \text{CaCl}_2(aq) + \text{Mg}(s) \)
   e. \( \text{Zn}(s) + \text{SnCl}_2(aq) \rightarrow \text{ZnCl}_2(aq) + \text{Sn}(s) \)

Examples: Single-Displacement Reactions

5. Predict the products (if any) of the following reactions.
   a. \( \text{Al}(s) + \text{CuCl}_2(aq) \rightarrow \)
   b. \( \text{AlCl}_3(aq) + \text{Cu}(s) \rightarrow \)
   c. \( \text{K}(s) + \text{H}_2\text{O}(l) \rightarrow \)
   d. \( \text{Au}(s) + \text{H}_2\text{O}(l) \rightarrow \)

Combustion Reactions

• Combustion reactions are a type of redox reaction in which a substance reacts with molecular oxygen \((\text{O}_2)\) to form one or more oxygen-containing products. These reactions are usually accompanied by the release of large amounts of heat and light (burning).

\[
2\text{Mg}(s) + \text{O}_2(g) \rightarrow 2\text{MgO}(s) \quad \text{(movie)}
\]

\[
4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)
\]

\[
\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(s) \quad \text{[or SO}_3(g)]
\]

\[
2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \quad \text{(movie)}
\]

\[
\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \text{[burning of coal]}
\]

Combustion Reactions

• In a limited oxygen supply, carbon monoxide or elemental carbon may form instead; hot elemental carbon glows with an orange color, producing the colors associated with burning wood or candles.

• The metabolism of glucose \((\text{C}_6\text{H}_{12}\text{O}_6)\) in the body is similar to combustion reactions:

\[
\text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{energy}
\]

In living cells the process occurs slowly, in a complex series of steps that release energy in a controlled way.

Combustion Reactions

• The primary type of combustion reaction is the combustion of hydrocarbons to produce carbon dioxide and water (as well as heat energy, which can be converted to other forms of energy):

\[
\text{Hydrocarbon} + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g)
\]

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \text{(methane)}
\]

\[
\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)
\]

\[
\text{2C}_8\text{H}_{18}(l) + 25\text{O}_2(g) \rightarrow 16\text{CO}_2(g) + 18\text{H}_2\text{O}(g) \quad \text{(gasoline)}
\]

\[
\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(g) \quad \text{(ethanol)}
\]

Other Applications of Redox Reactions

• Bleaching uses redox reactions to decolorize or lighten colored materials (hair, clothes, paper, etc.).

• Batteries use spontaneous redox reactions which occur in separated compartments; the electrons that move between the oxidation compartment (anode) and the reduction compartment (cathode) can be used to deliver electrical energy.

• Metallurgy is the processes involved in extracting and purifying metals from their ores. Roasting ores with carbon (coke) carries away oxygen in the form of CO or CO}_2\) yielding the pure metal:

\[
\text{ZnO}(s) + \text{C}(s) \rightarrow \text{Zn}(s) + \text{CO}(g)
\]

• Corrosion is the deterioration of a metal by oxidation, as in the rusting of iron in moist air.

\[
4\text{Fe}(s) + 3\text{O}_2(g) + \text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(s)
\]
Synthesis Reactions

Combination Reactions that Are Redox Reactions
1. Metal + nonmetal → ionic compound
   \[ \text{Zn(s)} + \text{S(s)} \rightarrow \text{ZnS(s)} \]
   \[ 2\text{Al(s)} + 3\text{Cl}_2(g) \rightarrow 2\text{AlCl}_3(s) \]

2. Nonmetal + nonmetal → molecular compound
   \[ \text{S(s)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \]
   \[ 2\text{S(s)} + 3\text{O}_2(g) \rightarrow 2\text{SO}_3(g) \]

3. Compound + element → molecular compound
   \[ 2\text{NO(g)} + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \]
   \[ \text{PCl}_3(l) + \text{Cl}_2(g) \rightarrow \text{PCl}_5(s) \]

Combination Reactions that Are Not Redox Rxns
1. Metal oxide + nonmetal oxide → ionic compound w/polyatomic ion
   \[ \text{Li}_2\text{O(s)} + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) \]

2. Metal oxide + water → metal hydroxides (bases)
   Metal oxides are also known as basic anhydrides.
   \[ \text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(s) \]
   \[ \text{Na}_2\text{O(s)} + \text{H}_2\text{O} \rightarrow 2\text{NaOH(aq)} \]
   \[ \text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3(aq) \]

3. Nonmetal oxide + water → acid
   Add the elements of water into the nonmetal oxide formula and reduce the subscripts to lowest terms.
   For phosphorus oxides, add three molecules of water.
   Nonmetal oxides are also known as acidic anhydrides.
   \[ \text{CO}_2(g) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3(aq) \]
   \[ \text{N}_2\text{O}_3(g) + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3(aq) \]
   \[ \text{P}_2\text{O}_5(s) + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4(aq) \]

Decomposition Reactions

• In a decomposition reaction, one reactant breaks down to form two or more products.
   \[ \text{C} \rightarrow \text{A} + \text{B} \]

Thermal Decomposition
1. Ionic compound with oxoanion →
   \[ \text{CaCO}_3(s) \xrightarrow{\Delta} \text{CaO(s)} + \text{CO}_2(g) \]

2. Many metal oxides, chlorates, and perchlorates release \( \text{O}_2 \) when heated.
   \[ 2\text{KClO}_3(s) \xrightarrow{\Delta} 2\text{KCl(s)} + 3\text{O}_2(g) \]
   \[ 2\text{NaNO}_3(s) \xrightarrow{\Delta} 2\text{NaNO}_3(s) + \text{O}_2(g) \]
Decomposition Reactions

**Electrolytic Decomposition** — occurs when compounds absorb electrical energy and undergo electrolysis.

1. Decomposition of water.
   \[
   2\text{H}_2\text{O}(l) \xrightarrow{\text{electricity}} 2\text{H}_2(g) + \text{O}_2(g)
   \]

2. Molten ionic compounds decompose into their elements.
   \[
   \text{MgCl}_2(l) \xrightarrow{\text{electricity}} \text{Mg}(l) + \text{Cl}_2(g)
   \]
   \[
   2\text{NaCl}(l) \xrightarrow{\text{electricity}} 2\text{Na}(l) + \text{Cl}_2(g)
   \]

Decomposition Reactions

**Decomposition of Binary Compounds** — may occur by thermal decomposition, electrolysis, or other conditions.

1. Binary compound → element + element
   \[
   2\text{I}_2(s) \xrightarrow{\text{tickle}} \text{N}_2(g) + 3\text{I}_2(g) \quad (+ \text{bang!})
   \]

   • The decomposition of binary compounds are the only decomposition reactions for which you’ll be asked to predict the products. Be able to recognize and balance the other types of decompositions.

Examples: Predicting Chemical Reactions

1. Complete the following reactions and classify them as synthesis, decomposition, single-displacement, acid-base, precipitation, or combustion reactions.
   a. Magnesium + nitrogen →
   b. \(\text{H}_2\text{SO}_4(\text{aq}) + \text{NaF}(\text{aq})\) →
   c. \(\text{Na}_2\text{S}(\text{aq}) + \text{HCl}(\text{aq})\) →
   d. Hydrogen peroxide(\(l\)) →
   e. \((\text{NH}_4)_2\text{SO}_4(\text{aq}) + \text{K}_2\text{PO}_4(\text{aq})\) →
   f. Cadmium + lead(II) nitrate →

The End