Chapter 4. Aqueous Reactions and Solution Stoichiometry

Common Student Misconceptions

- Molarity is moles of solute per *liter of solution* not per liter of solvent.
- Students sometimes used moles instead of molarity in MinitialVinitial = MfinalVfinal.
- Students sometimes think that water is a good conductor.
- Students sometimes have a problem with the arbitrary difference between strong and weak electrolytes.
- The symbols ⇋ (equilibrium) and ↔(resonance are often confused.
- Students often do not see that the net ionic equation for the reaction between strong acids and strong bases is always $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$.
- Students try to split polyatomic ions into smaller ions when they write net ionic equations.
- Students do not appreciate the difference between equivalence point and end point.

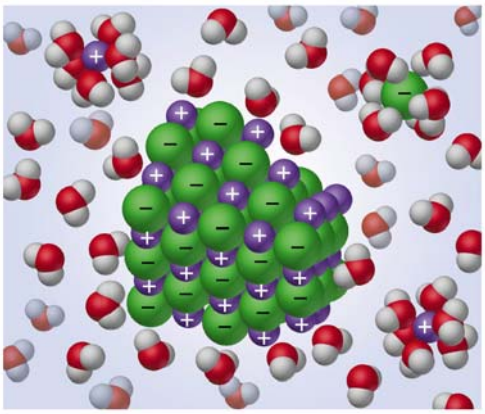
Lecture Outline

4.1 General Properties of Aqueous Solutions

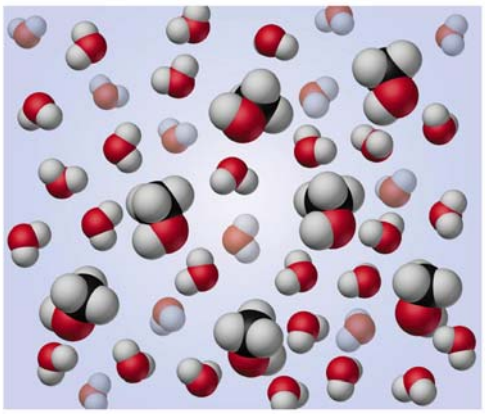
- A solution is a homogeneous mixture of two or more substances.
- A solution is made when one substance (the **solute**) is dissolved in another (the **solvent**).
- The solute is the substance that is present in smallest amount.
- Solutions in which water is the solvent are called **aqueous solutions**.

Electrolytic Properties

- All aqueous solutions can be classified in terms of whether or not they conduct electricity.
- If a substance forms ions in solution, then the substance is an **electrolyte**, and the solution conducts electricity. Example: NaCl (a)
- If a substance does not form ions in solution, then the substance is a **nonelectrolyte**, and the solution does not conduct electricity. Example: sucrose, methanol (b)



(a)



(b)

Ionic Compounds in Water

- When an ionic compound dissolves in water, the ions are said to *dissociate*.
  - This means that in solution, the solid no longer exists as a well-ordered arrangement of ions in contact with one another.
  - Instead, each ion is surrounded by a shell of water molecules.
  - This tends to stabilize the ions in solution and prevent cations and anions from recombining.
  - The positive ions have the surrounding oxygen atoms of water pointing towards the ion, negative ions have the surrounding hydrogen atoms of water pointing towards the ion.
  - The transport of ions through the solution causes electric current to flow through the solution.

Molecular Compounds in Water

- When a molecular compound (e.g. CH_3OH) dissolves in water, there are no ions formed.
- Therefore, there is nothing in the solution to transport electric charge and the solution does not conduct electricity.
- There are some important exceptions.
  - For example, $NH_3(g)$ reacts with water to form $NH_4^+(aq)$ and $OH^-(aq)$.
  - For example, $HCl(g)$ in water *ionizes* to form $H^+(aq)$ and $Cl^-(aq)$.

Strong and Weak Electrolytes

- Compounds whose aqueous solutions conduct electricity well are called **strong electrolytes**.
  - These substances exist only as ions in solution.
  - Example NaCl:

$$NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$

  - The single arrow indicates that the Na^+ and Cl^- ions have no tendency to recombine to form NaCl molecules.
  - In general, soluble ionic compounds are strong electrolytes.

- Compounds whose aqueous solutions conduct electricity poorly are called **weak electrolytes**
  - These substances exist as a mixture of ions and un-ionized molecules in solution.
    - The predominant form of the solute is the un-ionized molecule.
  - Example: acetic acid, $HC_2H_3O_2$.

$$HC_2H_3O_2(aq) \leftrightharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

  - The double arrow means that the reaction is significant in both directions.
  - It indicates that there is a balance between the forward and reverse reactions.
  - This balance produces a state of chemical equilibrium.

Sample Exercise 4.1 (p. 116)

The diagram on the left (p. 116) represents an aqueous solution of one of the following compounds: $MgCl_2$, KCl, or K_2SO_4. Which solution does it best represent?

Practice Exercise 4.1

If you were to draw diagrams (such as that shown on the left of p. 116) representing aqueous solutions of each of the following ionic compounds, how many anions would you show if the diagram contained six cations?

a) $NiSO_4$
b) $Ca(NO_3)_2$
c) Na_3PO_4
d) $Al_2(SO_4)_3$

4.2 Precipitation Reactions

- Reactions that result in the formation of an insoluble product are known as **precipitation reactions**.
- A precipitate is an insoluble solid formed by a reaction in solution.
  - Example: $Pb(NO_3)_2(aq) + 2KI(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$

Solubility Guidelines for Ionic Compounds

- The solubility of a substance is the amount of that substance that can be dissolved in a given quantity of solvent.
- A substance with a solubility of less than 0.01 mol/L is regarded as being *insoluble*.
- Experimental observations have led to empirical guidelines for predicting the solubility.

- Solubility guidelines for common ionic compounds in water:
  - Compounds containing alkali metal ions or ammonium ion are soluble.
  - Compounds containing NO_3^- or $C_2H_3O_2^-$ are soluble.
  - Compounds containing Cl^-, Br^- or I^- are soluble.
    - Exceptions: Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}.
    - Compounds containing SO_4^{2-} are soluble.
      - Exceptions: Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
    - Compounds containing S^{2-} are insoluble.
      - Exceptions: Compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}.
    - Compounds of CO_3^{2-} or PO_4^{3-} are insoluble.
      - Exceptions: Compounds of NH_4^+ and the alkali metal cations.
    - Compounds of OH^- are insoluble.
      - Exceptions: Compounds of the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}.

TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	$C_2H_3O_2^-$	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}

Sample Exercise 4.2 (p. 118)

Classify the following ionic compounds as soluble or insoluble in water:

a) sodium carbonate (Na_2SO_4)

b) lead sulfate ($PbSO_4$)

Practice Exercise 4.2

Classify the following compounds as soluble or insoluble in water:

a) cobalt (II) hydroxide

b) barium nitrate

c) ammonium phosphate

Exchange (Metathesis) Reactions

- **Exchange reactions** or **metathesis reactions** involve swapping ions in solution:

$$\mathbf{A}X + B\mathbf{Y} \rightarrow \mathbf{AY} + BX.$$

- Many precipitation and acid-base reactions exhibit this pattern.

Sample Exercise 4.3 (p. 119)

a) Predict the identity of the precipitate that forms when solutions of $BaCl_2$ and K_2SO_4 are mixed.

b) Write the balanced chemical equation for the reaction.

Practice Exercise 4.3

a) What compound precipitates when solutions of $Fe_2(SO_4)_3$ and LiOH are mixed?

b) Write a balanced equation for the reaction.

c) Will a precipitate form when solutions of $Ba(NO_3)_2$ and KOH are mixed?

Ionic Equations

- Consider $2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$.
- Both $KI(aq) + Pb(NO_3)_2(aq)$ are colorless solutions. When mixed, they form a bright yellow precipitate of PbI_2 and a solution of KNO_3.
- The final product of the reaction contains solid PbI_2, aqueous K^+ and aqueous NO_3^- ions.
- Sometimes we want to highlight the reaction between ions.

- The **molecular equation** lists all species in their molecular forms:

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

- The **complete ionic equation** lists all strong soluble electrolytes in the reaction as ions:

$$Pb^{2+}(aq) + 2NO_3^-(aq) + 2K^+(aq) + 2I^-(aq) \rightarrow PbI_2(s) + 2K^+(aq) + 2NO_3^-(aq)$$

  - Only strong electrolytes dissolved in aqueous solution are written in ionic form.
  - Weak electrolytes and nonelectrolytes are written in their molecular form.

- The **net ionic equation** lists only those ions which are not common on both sides of the reaction:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

  - Note that **spectator ions**, ions that are present in the solution but play no direct role in the reaction, are omitted in the net ionic equation.

Sample Exercise 4.4 (p. 121)

Write the net ionic equation for the precipitation reaction that occurs when solutions of calcium chloride and sodium carbonate are mixed.

Practice Exercise 4.4

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of silver nitrate and potassium phosphate are mixed.

4.3 Acid-Base Reactions

Acids

- **Acids** are substances that are able to ionize in aqueous solution to form H^+.
  - Ionization occurs when a neutral substance forms ions in solution.
    Example: $HC_2H_3O_2$ (acetic acid).
- Since H^+ is a naked proton, we refer to acids as proton donors and bases as proton acceptors.
- Common acids are HCl, HNO_3, vinegar and vitamin C.
- Acids that ionize to form *one* H^+ ion are called *monoprotic* acids.
- Acids that ionize to form *two* H^+ ions are called *diprotic acids*.

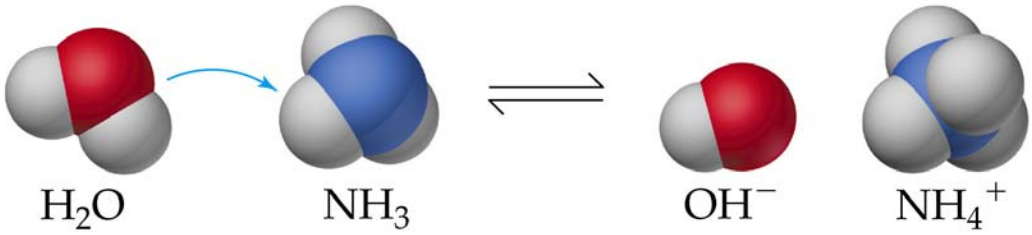
Bases

- **Bases** are substances that accept or react with the H^+ ions formed by acids.
- Hydroxide ions, OH^-, react with the H^+ ions to form water:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

- Common bases are NH_3 (ammonia), Draino, milk of magnesia.
- Compounds that do not contain OH^- ions can also be bases.
  - Proton transfer between NH_3 (a weak base) and water (a weak acid) is an example of an acid-base reaction.
  - Since there is a mixture of NH_3, H_2O, NH_4^+, and OH^- in solution, we write

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$



Strong and Weak Acids and Bases

- **Strong acids** and **strong bases** are strong electrolytes.
  - They are completely ionized in solution.
  - Strong bases include: Group 1A metal hydroxides, $Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$.
  - Strong acids include: HCl, HBr, HI, $HClO_3$, $HClO_4$, H_2SO_4, and HNO_3.
  - We write the ionization of HCl as:

$$HCl \rightarrow H^+ + Cl^-$$

- **Weak acids** and **weak bases** are weak electrolytes.
  - Therefore, they are partially ionized in solution.
  - HF(*aq*) is a weak acid; most acids are weak acids.
  - We write the ionization of HF as: $HF \rightleftharpoons H^+ + F^-$

Table 4.2 Common Strong Acids and Bases **MEMORIZE THESE!**

Strong Acids	Strong Bases
Hydrochloric, HCl Hydrobromic, HBr Hydroiodic, HI Chloric, $HClO_3$ Perchloric, $HClO_4$ Nitric, HNO_3 Sulfuric, H_2SO_4	Group 1A metal hydroxides (LiOH, NaOH, KOH, RbOH, CsOH) Heavy Group 2A metal hydroxide ($Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$)

Sample Exercise 4.5 (p. 123)

The diagrams on p. 123 represent aqueous solutions of three acids (HX, HY, and HZ) with water molecules omitted for clarity. Rank them from strongest to weakest.

Practice Exercise 4.5

Imagine a diagram showing 10 Na^+ ions and 10 OH^- ions. If this solution were mixed with the one pictured above for HY, what would the diagram look like that represents the solution after any possible reaction?

Identifying Strong and Weak Electrolytes

- Compounds can be classified as strong electrolytes, weak electrolytes or nonelectrolytes by looking at their solubility.
- Strong electrolytes:
  - If a compound is water soluble and ionic, then it is probably a strong electrolyte.
  - If a compound is water soluble and not ionic, and is a strong acid, then it is a strong electrolyte.
  - Similarly, if a compound is water soluble and not ionic, but is a strong base, then it is a strong electrolyte.
- Weak electrolytes:
  - If a compound is water soluble and not ionic, and is a weak acid or weak base, then it is a weak electrolyte.
- Nonelectrolytes:
  - Otherwise, the compound is probably a nonelectrolyte.

TABLE 4.3 Summary of the Electrolytic Behavior of Common Soluble Ionic and Molecular Compounds

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids (H . . .) Weak bases (NH_3)	All other compounds

Sample Exercise 4.6 (p. 124)

Classify each of the following dissolved substances as a strong electrolyte, weak electrolyte, or nonelectrolyte:

$CaCl_2$

HNO_3

C_2H_5OH (ethanol)

$HCHO_2$ (formic acid)

KOH

Practice Exercise 4.6

Consider solutions in which 0.1 mol of each of the following compounds is dissolved in 1 L of water: $Ca(NO_3)_2$ (calcium nitrate), $C_6H_{12}O_6$ (glucose), $NaC_2H_3O_2$ (sodium acetate), and $HC_2H_3O_2$ (acetic acid). Rank the solutions in order of **increasing electrical conductivity**, based on the fact that the greater the number of ions in solution, the greater the conductivity.

Neutralization Reactions and Salts

- A **neutralization reaction** occurs when an acid and a base react:
  - $HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$
  - (acid) + (base) → (water) + (salt)

- In general an acid and base react to form a **salt**.

- A salt is any ionic compound whose cation comes from a base and anion from an acid.

- The other product, H_2O, is a common weak electrolyte.

- Typical examples of neutralization reactions:

  - Reaction between an acid and a metal hydroxide:
    - $Mg(OH)_2$ (milk of magnesia) is a suspension.
    - As HCl is added, the magnesium hydroxide dissolves, and a clear solution containing Mg^{2+} and Cl^- ions is formed.

    - Molecular equation:

      $$Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$$

    - Net ionic equation:

      $$Mg(OH)_2(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + 2H_2O(l)$$

      - Note that the magnesium hydroxide is an insoluble solid; it appears in the net ionic equation.

Sample Exercise 4.7 (p. 125)

a) Write a balanced complete chemical equation for the reaction between aqueous solutions of acetic acid ($HC_2H_3O_2$) and barium hydroxide ($Ba(OH)_2$)

b) Write the net ionic equation for this reaction.

Practice Exercise 4.7

a) Write a balanced equation for the reaction of carbonic acid (H_2CO_3) and potassium hydroxide (KOH).

b) Write the net ionic equation for this reaction.

Acid-Base Reactions with Gas Formation

- There are many bases besides OH^- that react with H^+ to form molecular compounds.
  - Reaction of sulfides with acid gives rise to $H_2S(g)$.
    - Sodium sulfide (Na_2S) reacts with HCl to form $H_2S(g)$:
    - Molecular equation:

$$Na_2S(aq) + 2HCl(aq) \rightarrow H_2S(g) + 2NaCl(aq)$$

    - Net ionic equation:

$$2H^+(aq) + S^{2-}(aq) \rightarrow H_2S(g)$$

  - Carbonates and hydrogen carbonates (or bicarbonates) will form $CO_2(g)$ when treated with an acid.
    - Sodium hydrogen carbonate ($NaHCO_3$; baking soda) reacts with HCl to form bubbles of $CO_2(g)$:
    - Molecular equation:

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g) + NaCl(aq)$$

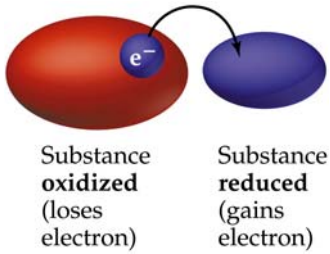
    - Net ionic equation:

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

4.4 Oxidation-Reduction Reactions

Oxidation and Reduction

- **Oxidation-reduction** or *redox* reactions involve transfer of electrons between reactants.



Terms come from chemical history.

Note that when one substance is oxidized, another compound must be reduced, and vice-versa.

Oxidation = + **oxygen** to a compound;

Reduction = - oxygen in a compound.

e.g. $2Ca_{(s)} + \mathbf{O_{2(g)}} \rightarrow 2Ca\mathbf{O}_{(s)}$

Oxidation = - **hydrogen** from a compound ("dehydrogenate");

Reduction = + **hydrogen** to a compound.

e.g. $CH_3C\mathbf{H_2}O\mathbf{H} \rightarrow CH_3CHO + \mathbf{H_2}$

alcohol dehydrogenase

Modern usage:

Oxidation = - **electrons** from a substance;

Reduction = + **electrons** to a substance.

$\mathbf{Mg}_{(s)} + 2\,\mathbf{H}Cl_{(aq)} \rightarrow \mathbf{Mg}Cl_{2(aq)} + \mathbf{H_{2(g)}}$

0 **+1** -1 **+2** -1 **0**

Note: The transfer of electrons during oxidation-reduction reactions often produce energy (when spontaneous), which can be in the form of electricity.

And electrical energy can be used to make nonspontaneous chemical reactions occur.

→ "Electrochemistry" (Chapter 20), later this semester

Examples of Redox Reactions

1. **Combustion**: "rapid **oxidation** reaction in which a large amount of heat and usually light are released"

   $C + O_2 \rightarrow CO_2, CO$

   $S + O_2 \rightarrow SO_2$

   What was oxidized? What was reduced?

2. **Metal + acid** (SR)

   $Zn_{(s)} + HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

   Total ionic equation:

   What was oxidized? What was reduced?

3. **Metal + salt** (SR)

   $Mg_{(s)} + CoSO_{4(aq)} \rightarrow MgSO_{4(aq)} + Co_{(s)}$

   Total ionic equation:

   What was oxidized? What was reduced?

Oxidation Numbers

- Electrons are not explicitly shown in chemical equations.
- **Oxidation numbers** (or *oxidation states*) help up keep track of electrons during chemical reactions.

Rules:

1. Elemental form – oxidation number = 0
2. Monatomic ion – oxidation number = charge on the ion
3. nonmetals – usually have negative oxidation numbers
   a) Oxygen – usually -2 (exception is peroxide ion, oxygen has oxidation number of -1)
   b) Hydrogen - +1 when bonded to nonmetals, -1 when bonded to metals
   c) Fluorine - -1 in all compounds (*why?*)
   Other halogens - -1 in most situations,
   positive when combined with oxygen (e.g. oxyanions)
   d) sum of oxidation numbers of all atoms in a neutral compound = 0
   c) sum of oxidation numbers in a polyatomic ion = charge on the ion

- The oxidation of an element is evidenced by its increase in oxidation number; reduction is accompanied by a decrease in oxidation number.

Sample Exercise 4.8 (p. 129)

Determine the oxidation state of sulfur in each of the following:

a) H_2S

b) S_8

c) SCl_2

d) Na_2SO_3

e) SO_4^{2-}

Practice Exercise 4.8

What is the oxidation state of the boldfaced element in each of the following:

a) $\mathbf{P}_2O_5$

b) Na**H**

c) $\mathbf{Cr}_2O_7^{2-}$

d) **Sn**Br_4

e) Ba$\mathbf{O}_2$

Oxidation of Metals by Acids and Salts

- reaction of a metal with either an acid or a metal salt
  = a **displacement reaction.**

- General pattern: A + B**X** → A**X** + B

  - Metals often produce $H_{2(g)}$ when they react with acids.
    e.g. $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

    The metal is oxidized and the H^+ is reduced.

  - Metals may be oxidized in the presence of a salt:
    e.g. $Fe(s) + Ni(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Ni(s)$

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

    Fe has been oxidized to Fe^{2+} while Ni^{2+} has been reduced to Ni.

Sample Exercise 4.9 (p. 130)

Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.

Practice Exercise 4.9

a) Write the balanced molecular and net ionic equations for the reaction between magnesium and cobalt (II) sulfate.

b) What is oxidized and what is reduced in the reaction?

The Activity Series

activity series = list of metals in **decreasing** ease of oxidation.

- Metals at the top of the activity series = *active metals*.
- Metals at the bottom of the activity series = *noble metals*.
- A metal in the activity series can only be oxidized by a metal ion **below** it.
- e.g. If we place Cu into a solution of Ag^+ ions, then Cu^{2+} ions can be formed because Cu is above Ag in the activity series:

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

or

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

TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^-$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$

Sample Exercise 4.10 (p. 133)

Will an aqueous solution of iron (II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.

Practice Exercise 4.10

Which of the following metals will be oxidized by $Pb(NO_3)_2$:
Zn, Cu, Fe?

4.5 Concentrations of Solutions

- The term **concentration** is used to indicate the amount of solute dissolved in a given quantity of solvent or solution.

Molarity: the concentration of solution in $\frac{\text{moles solute}}{\text{L solution}}$ ***not*** L **solvent**

e.g. What is the molarity of a solution of potassium chloride with a volume of 400. mL that contains 85.0 g of KCl?

Known: $\frac{85.0\text{ g KCl}}{400.\text{ mL solution}}$ Unknown: $\frac{?\text{ mol KCl}}{\text{L solution}}$

Setup: $\frac{85.0\text{ g KCl}}{400.\text{ mL}} \times \frac{10^3\text{ mL}}{1\text{ L}} \times \frac{1\text{ mol KCl}}{74.55\text{ g KCl}}$ = 2.85 mol KCl/L solution or 2.85 M KCl

Note: the concentration of electrolytes (ions) must take the chemical formula into account.

Practice:
What is the molarity of a solution 125.0 g K_2CO_3 in 746 mL of water?

What is the molarity of K^+ in this solution?

What is the molarity of CO_3^{2-} in this solution?

Sample Exercise 4.11 (p. 134)

Calculate the molarity of a solution made by dissolving 23.4 g of sodium sulfate (Na_2SO_4) in enough water to form 125 mL of solution.

(1.32 M)

Practice Exercise 4.11

Calculate the molarity of a solution made by dissolving 5.00 g of glucose ($C_6H_{12}O_6$) in sufficient water to form exactly 100 mL of solution.

(0.278 M)

Expressing the Concentration of an Electrolyte

- When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound.
  - e.g.: 1.0 *M* solution of NaCl: 1.0 *M* in Na^+ ions and 1.0 *M* in Cl^- ions.
  - e.g.: 1.0 *M* solution of Na_2SO_4: 2.0 *M* in Na^+ ions and 1.0 *M* in SO_4^{2-} ions.

Sample Exercise 4.12 (p. 136)

What are the molar concentrations of each of the ions present in a 0.025 M aqueous solution of calcium nitrate?

(0.025 M Ca^{2+}; 0.050 M NO_3^-)

Practice Exercise 4.12

What is the molar concentration of K^+ ions in a 0.015 M solution of potassium carbonate?

(0.030 M K^+)

Interconverting Molarity, Moles, and Volume

- The definition of molarity contains three quantities: molarity, moles of solute, and liters of solution.
  - If we know any two of these, we can calculate the third.
  - Dimensional analysis is very helpful in these calculations.

Sample Exercise 4.13 (p. 137)

How many grams of Na_2SO_4 are required to make 0.350 L of 0.500 M Na_2SO_4?
(24.9 g)

Practice Exercise 4.13

a) How many grams of Na_2SO_4 are there in 15 mL of 0.50 M Na_2SO_4?
(1.1g)

b) How many milliliters of 0.50 M Na_2SO_4 solution are needed to provide 0.038 mol of this salt?
(76 mL)

Dilution

- A solution in concentrated form (*stock solution*) is mixed with solvent to obtain a solution of lower solute concentration.
  - This process is called **dilution**.

- An alternate way of making a solution is to take a solution of known molarity and dilute it with more solvent.

- Since the number of moles of solute remains the same in the concentrated and dilute forms of the solution, we can show:

$$M_{initial}V_{initial} = M_{final}V_{final}.$$

- An alternate form of this equation is:

$$M_{concentrated}V_{concentrated} = M_{dilute}V_{dilute}$$

Remember: Moles are central!

Example

How much 6.0 M HCl do you need to prepare 1.0 L of 2.0 M HCl?

$M_1 = 6.0$ $M_2 = 2.0$ M

$V_1 = ?$ $V_2 = 1.0$ L

$$V_1 = \frac{M_2V_2}{M_1} = \frac{(2.0\text{ M})(1.0\text{ L})}{(6.0\text{ M})} = 0.33\text{ L of 6.0 M HCl}$$

Subtract the amount of concentrated HCl (stock solution, = 330. mL) from the total desired volume (1.0 L) to find out how much distilled water to add

How do you prepare it?

Add about 500 mL distilled water to a volumetric flask.

Add 330. mL of 6.0 M HCl to a volumetric flask.

Add distilled water until total volume is 1000 mL or 1.0 L.

(i.e. add 670. mL dH_2O total)

Sample Exercise 4.14 (p. 138)

How many milliliters of 3.0 M H_2SO_4 are needed to make 450 mL of 0.010 M H_2SO_4?

(15 mL)

Practice Exercise 4.14

a) What volume of 2.50 M lead nitrate solution contains 0.0500 mol of Pb^{2+}?
(20.0 mL)

b) How many milliliters of 5.0 M $K_2Cr_2O_7$ solution must be diluted to prepare 250 mL of 0.10 M solution?
(5.0 mL)

c) If 10.0 mL of a 10.0 M stock solution of NaOH is diluted to 250 mL, what is the concentration of the resulting solution?
(0.40 M)

4.6 Solution Stoichiometry and Chemical Analysis

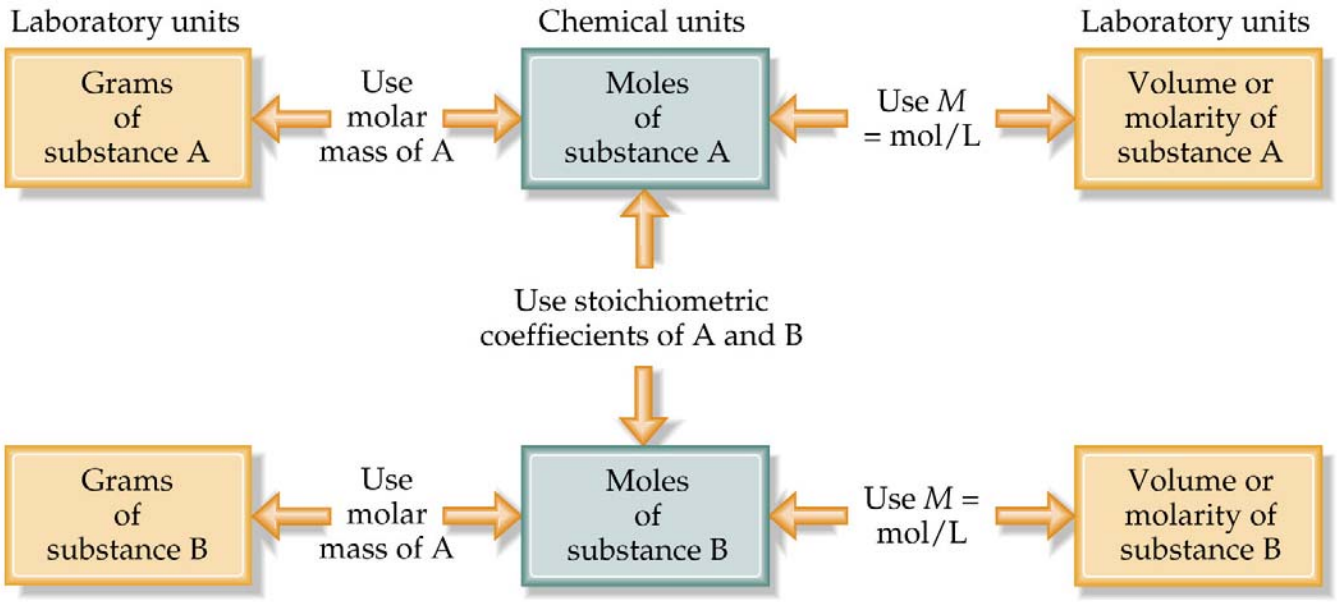
- In approaching stoichiometry problems:

  - Recognize that there are two different types of units:
    - Laboratory units (the macroscopic units that we measure in lab) and
    - Chemical units (the microscopic units that relate to moles).

  - Always convert the laboratory units into chemical units first.
    - Convert grams to moles using molar mass.
    - Convert volume or molarity into moles using M = mol/L.

  - Use the stoichiometric coefficients to move between reactants and products.
    - ***This step requires the balanced chemical equation.***

  - Convert the laboratory units back into the required units.
    - Convert moles to grams using molar mass.
    - Convert moles to molarity or volume using M = mol/L.



Sample Exercise 4.15 (p. 140)

How many grams of calcium hydroxide are needed to neutralize 25.0 mL of 0.100 M HNO_3?

(0.0926 g)

Practice Exercise 4.15

a) How many grams of NaOH are needed to neutralize 20.0 mL of 0.150 M H_2SO_4 solution?
(0.240 g)

b) How many liters of 0.500 M HCl(aq) are needed to react completely with 0.100 mol of $Pb(NO_3)_{2(aq)}$, forming a precipitate of $PbCl_{2(s)}$?
(0.400 L)

Titrations

- A common way to determine the concentration of a solution is via **titration**.
- We determine the concentration of one substance by allowing it to undergo a specific chemical reaction, of known stoichiometry, with another substance whose concentration is known (**standard solution**).

= A method of volumetric analysis in which a volume of one reagent is added to a known volume of another reagent slowly from a buret until an end point is reached. If one of the solutions has a known concentration, the concentration of the other can be calculated.

Standard solution = reagent solution of **known** concentration

Titrant = reagent solution of **unknown** concentration

Equivalence point = the point at which stoichiometrically equivalent quantities are brought together

End point = color change (v. close to equivalence point)

- Example: Suppose we know the molarity of an NaOH solution and we want to find the molarity of an HCl solution.

  - What do we know?
    - Molarity of NaOH, volume of HCl.

  - What do we want?
    - Molarity of HCl.

  - What do we do?

  - Take a known volume of the HCl solution (i.e., 20.00 mL) and measure the number of milliliters of NaOH required to react completely with the HCl solution.

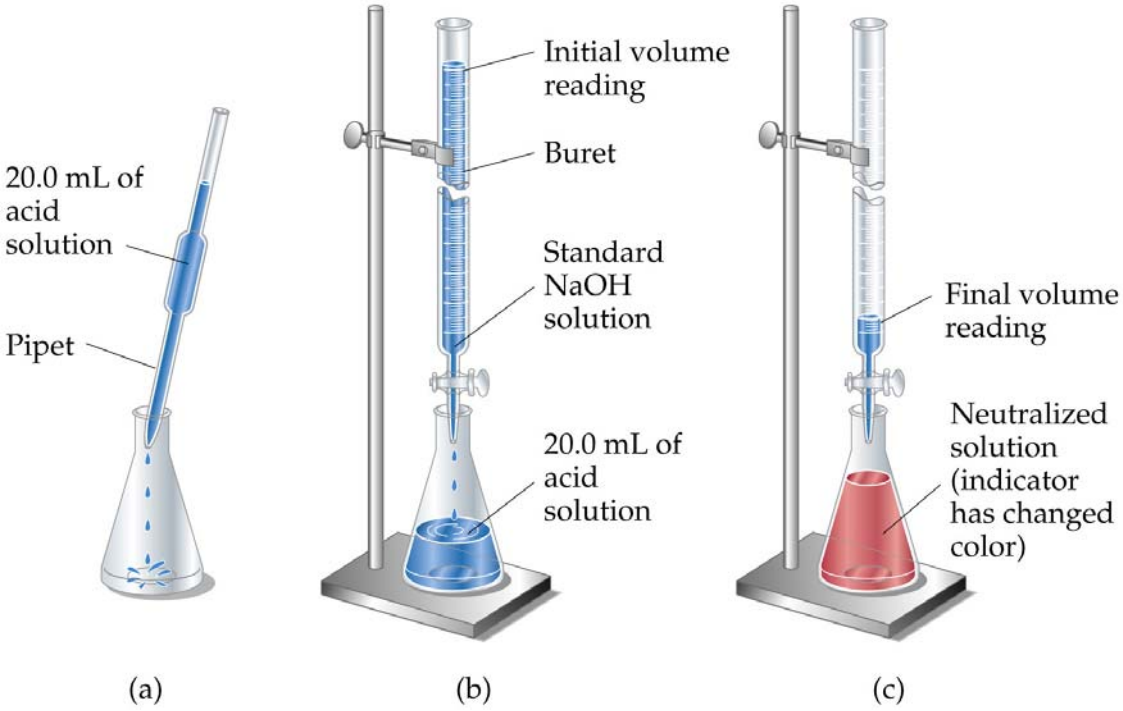
  - The point at which stoichiometrically equivalent quantities of NaOH and HCl are brought together is known as the **equivalence point** of the titration.

  - In a titration we often use an acid-base **indicator** to allow us to determine when the equivalence point of the titration has been reached.
    - Acid-base indicators change color at the *end point* of the titration.
    - The indicator is chosen so that the end point corresponds to the equivalence point of the titration.

  - What do we get?
    - Volume of NaOH. Since we already have the molarity of the NaOH, we can calculate moles of NaOH.

  - Next step?
    - We also know HCl + NaOH → NaCl + H_2O.
    - Therefore, we know moles of HCl.

  - Can we finish?
    - Knowing mol (HCl) and volume of HCl, we can calculate the molarity.



Titration Practice Problems

Remember: Moles are central!

1. In the titration of 35 mL of liquid drain cleaner containing NaOH, 50. mL of 0.40 M HCl must be added to reach the equivalence point. What is the molarity of the base in the cleaner? (0.57 M)

2. A 20.0 mL sample of an HCl solution is titrated with 27.4 mL of a standard solution of $Ba(OH)_2$. The concentration of the standard is 0.0154 M. What is the molarity of the HCl? (0.0422 M)

3. How many mL of 0.25 M $Ca(OH)_2$ must be added to titrate 46 mL of 0.40 M $HClO_4$? (37 mL)

4. What is the molar hydrogen ion concentration in a 3.00 L solution of HNO_3 in which 1.90 g of HNO_3 is present? Assume the acid is a strong acid. (0.10 M)

Sample Exercise 4.16 (p. 142)

The quantity of Cl^- in a water supply is determined by titrating the sample with Ag^+:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

a) How many grams of chloride ion are in a sample of the water if 20.2 mL of 0.100 M Ag^+ is needed to react with all the chloride in the sample?
(7.17×10^{-2} g Cl^-)

b) If the sample has a mass of 10.0 g, what percent Cl^- does it contain?
(0.717% Cl^-)

Practice Exercise 4.16

A sample of an iron ore is dissolved in acid,k and the iron is converted to Fe^{2+}. The sample is then titrated with 47.20 mL of 0.02240 M MnO_4^-. The oxidations-reduction reaction that occurs during titration is as follows:

$$MnO_4^-{}_{(aq)} + 5\ Fe^{2+}_{(aq)} + 8\ H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 5\ Fe^{3+}_{(aq)} + 4\ H_2O_{(l)}$$

a) How many moles of MnO_4^- were added to the solution?
(1.057×10^{-3} mol MnO_4^-)

b) How many moles of Fe^{2+} were in the sample?
(5.286×10^{-3} mol Fe^{2+})

c) How many grams of iron were in the sample? (0.2952 g)

d) If the sample had a mass of 0.8890 g, what is the percentage of iron in the sample? (33.21%)

Sample Exercise 4.17 (p. 142)

One commercial method used to peel potatoes is to soak them in a solution of NaOH for a short time, remove them from the NaOH, and spry off the peel. The concentration of NaOH is normally in the range of 3 to 6 M. The NaOH is analyzed periodically. In one such analysis, 45.7 mL of 0.500 M H_2SO_4 is required to neutralize a 20.0 mL sample of NaOH solution. What is the concentration of the NaOH solution?

(2.28 M)

Practice Exercise 4.17

What is the molarity of an NaOH solution if 48.0 mL is needed to neutralize 35.0 mL of 0.144 M H_2SO_4?

(0.210 M)

Sample Integrative Exercise 4

A sample of 70.5 potassium phosphate is added to 15.0 mL of 0.050 M silver nitrate, resulting in the formation of a precipitate.

a) Write the molecular equation for the reaction.

b) What is the limiting reactant in the reaction?

c) Calculate the theoretical yield, in grams, of the precipitate that forms.
(0.10 g Ag_3PO_4)