

# AP Chemistry Final Study Guide

May 2016

## Reactions

- Metal + Non-metal  $\longrightarrow$  Salt
- Non-metal oxide + Water  $\longrightarrow$  Acid
- Non-metal oxide + Base  $\longrightarrow$  Salt + Water
- Acid + Base  $\longrightarrow$  Salt + Water
- Metal Oxide + Water  $\longrightarrow$  Metal Hydroxide
- Metal + Oxygen  $\longrightarrow$  Metal Oxide
- Metal Oxide + Acid  $\longrightarrow$  Salt + Water
- Hydrocarbon +  $O_2 \longrightarrow CO_2 + H_2O$
- Oxidation - Lose electrons, charge increases.
- Reduction - Gain electrons, charge decreases.

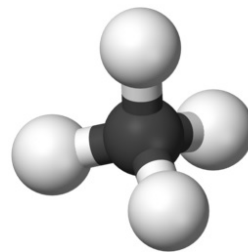


Figure 1: Methane

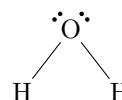


Figure 2: Water

## Gases

- $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
- $\frac{n}{V} = \frac{P}{RT} \Rightarrow \frac{nM}{V} = \frac{PM}{RT} \Rightarrow d = \frac{PM}{RT}$
- When collecting gas over water, be sure to subtract partial pressure of water from total pressure in containment vessel.
- **Kinetic Molecular Theory:** Straight line motion, no collisions with container. No loss of energy in collisions. Volume of particles is negligible. No attractive forces. Average kinetic energy directly related to temperature. Real gases behave most like ideal at high temperatures and low pressure. Real gases have lower pressure than ideal due to attractive forces and have larger volume because volume of molecules isn't negligible.
- **Effusion:** Escape of molecules into environment. Lighter gases effuse more rapidly.
- Stronger intermolecular forces raise boiling point and lower freezing point.

## Spectroscopy

- Used to find concentrations or identify patterns of light absorbed to identify unknowns. Need calibration using cuvette with solvent only. Find peak absorbance wavelength. Use known concentration standards to make calibration plot, which can be used to solve for unknown concentrations.
- **Photoelectron spectroscopy:** Electrons from each sublevel each have different amount of energy and will appear as different peaks. Electrons from same sublevel have similar energies and will add to height of absorbed peak. As nuclear charge increases, ionization energy required increases and shifts spectrum in direction of higher energy.
- **Mass spectroscopy:** Portions of molecules are broken off and we can determine parent structure from the pieces.
- **Lattice energy:** Energy required to completely separate a mole of an ionic solid into gaseous ions. Compared using  $E = \frac{kQ_1Q_2}{d}$ , where  $d$  is the row of the element in the periodic table.

## Periodic Table & Atomic Structure

- Hydrogen - High ionization energy, due to lack of nuclear shielding. Readily react with non-metals. Reacts with metals to form solid metal hydrides.
- Oxygen - Allotropes ( $O_2$ ,  $O_3$ ). Peroxides and chlorates decompose to produce  $O_2$ .
- Sulfur -  $S_8$ , Reacts with active metals, can be burned in oxygen. Phosphorous:  $P_4$ .
- Halogens - Most negative electron affinities. React to gain electrons.
- Nobel Gases - Monatomic, filled electron subshells, inert.
- Metals - Malleable, ductile, luster, conductive, form cations, metal oxides are basic, ionic solids, low electronegativity.
- Metallic character strongest for elements in leftmost of the table. Decreases as one moves to the right. Increases as one moves down a column (Exception: 1st row transition metals are generally more active than 2nd or 3rd row).
- Alkali Metals - Group I, Very reactive with water.
- Alkaline Earth Metals - Group II, increase in reactivity as one moves down group.
- **Principle Quantum No.:** Corresponds to row in periodic table.  
**Azimuthal quantum No.:** Corresponds to orbital (s-0, p-1, d-2, f-3).
- **Pauli Exclusion Principle:** No two electrons can have same set of four quantum No.s in an atom.
- **Screening effect:** Charge experienced by outer shell electrons is less than full nuclear charge because inner shell electrons offset charge.
- **Paramagnetic:** Has unpaired electrons. **Diamagnetic:** No unpaired.
- **Isoelectronic:** Identical electron configurations.
- **Semiconductors** (Group IV): **P-type:** One less valence  $e^-$  (add Group III). **N-type:** One more valence  $e^-$  (add Group V). Adds interstitial spaces, allowing  $e^-$  to move more freely.
- **Hybridization:** No. of overlapping orbitals of a bonding atom (bonding + nonbonding domains).
- **Sigma bonds:** No. of single bonds, only ones that hybridize. **Pi bonds:** No. of double/triple bonds.
- Resonance molecules:  $SO_3$ ,  $CO_3^{2-}$ ,  $O_3$ ,  $NO_3^{-1}$ .

Molecular Geometry	Bonding Domains	Nonbonding Domains	Bonding Angles	Example
Linear	2	0	$180^\circ$	$CO_2$
Trigonal Planar	3	0	$120^\circ$	$BF_3$
Bent	2	1	$120^\circ$	$NO_2^-$
Tetrahedral	4	4	$109.5^\circ$	$CH_3$
Trigonal Pyramidal	3	1	$109^\circ$	$NH_3$
Bent	2	2	$109^\circ$	$H_2O$
Trigonal Bipryamidal	5	0	$90^\circ, 120^\circ, 180^\circ$	$PCl_5$
Seesaw	4	1	$90^\circ, 120^\circ, 180^\circ$	$SF_4$
T-shaped	3	2	$90^\circ, 180^\circ$	$ClF_3$
Linear	2	3	$180^\circ$	$XeF_2$
Octahedral	6	0	$90^\circ, 180^\circ$	$SF_6$
Square Pyramidal	5	1	$90^\circ, 180^\circ$	$BrF_5$
Square Planar	4	2	$90^\circ, 180^\circ$	$XeF_4$

# Solutions

## Solubility Rules

### Soluble

- Nitrates  $NO_3^{-1}$  - All nitrates are soluble.
- Chlorates  $ClO_3^{-1}$  - All chlorates are soluble.
- Alkali metal cations and Ammonium cation compounds ( $NH_4^{+1}$ ) are all soluble.
- Chlorides, Bromides, and Iodides - All soluble except  $Ag^{+1}$ ,  $Pb^{+2}$ , and  $Hg^{+2}$ .
- Acetates - All are soluble except  $Ag^{+1}$ .
- Sulfates - All are soluble except  $Ba^{+2}$ ,  $Pb^{+2}$ ,  $Hg^{+2}$ ,  $Ca^{+2}$ ,  $Sr^{+2}$ .

### Insoluble

- Carbonates  $CO_3^{-2}$  - all carbonates are insoluble except alkali metals and ammonium compounds.
- Chromates  $CrO_4^{-2}$  - all chromates are insoluble except alkali metals, ammonium,  $Ca^{+2}$ , and  $Sr^{+2}$ .
- Hydroxides  $OH^{-1}$  - all hydroxides are insoluble except alkali metals, ammonium,  $Ba^{+2}$ ,  $Sr^{+2}$ , and  $Ca^{+2}$ .
- Phosphates  $PO_4^{-3}$  all are insoluble except alkali metals and ammonium.
- Sulfites  $SO_3^{-2}$  all are insoluble except alkali metals and ammonium.
- Sulfides  $S^{-2}$  all are insoluble except alkali metals, alkali earth metals and ammonium.
  
- $H_2CO_3 \longrightarrow CO_2 + H_2O$ ,  $H_2SO_3 \longrightarrow SO_2 + H_2O$ ,  $NH_4OH \longrightarrow NH_3 + H_2O$
- Energy changes during solution preparation: i. Solute particle must separate (bond breaking, endothermic) ii. Solvent particles must separate (bond breaking, endothermic) iii. Solvent and solute particle interact (bond forming, exothermic).
- **Real solution:** Obeys Raoult's Law. Solutions best approx. ideal behavior when molarity is low, solute and solvent has similar molecule size and intermolecular forces.
- Saturated, unsaturated, supersaturated. Miscible vs. immiscible.
- $1 \text{ ppm} = 1 \mu\text{g/mL} = 1 \mu\text{g/g}$ .  $1\% = 10000 \text{ ppm}$ .
- **Intermolecular forces:**
  - **Ion-dipole** - Attraction between ion and partial charge on end of polar molecule.
  - **Dipole-dipole:** Positive end of polar molecule attracted to negative end of another.
  - **Hydrogen bonding** is a subset of dipole, occurs between H and N, O, or F.
  - **London Dispersion:** Attraction between non-polar molecules caused by temporary dipole when electrons are on one side of nucleus. Only significant when molecules are close. Increase with increasing number of electrons.
- **Vapor Pressure:** Equilibrium at which molecules leave the liquid surface for the gas phase equals the rate at which gas phase molecules return to the surface of the liquid.
- A nonvolatile solute added to liquid reduced the capacity of solvent to move into vapor phase. At the same time, there's no change in the rate at which solvent molecules in gas phase return to the liquid. This shift in equilibrium reduces vapor pressure over the solution. The extent to which a nonvolatile solute lowers vapor pressure is proportional to its concentration.
- A decrease in vapor pressure, slows evaporation, due to boiling point elevation and freezing point depression.

## Thermodynamics

- **Hess' Law:** If a reaction is carried out in several steps,  $\Delta H$  for the reaction will be equal to the sum of the enthalpy changes for the individual steps.
- $\Delta H < 0$ , exothermic.  $\Delta H > 0$ , endothermic. Negative  $\Delta H$  and positive  $\Delta S$  favored.  $\Delta G < 0$ , is spontaneous.
- $q = -C\Delta T$ , where  $C = mc$ , is the heat capacity of the calorimeter.
- $\Delta H_{\text{rxn}}^o = \sum \Delta H_{(\text{Bonds Broken})} - \sum \Delta H_{(\text{Bonds Formed})}$

## Kinetics

- Factors affecting rate of reaction: Concentration of reactants, temperature, presence of a catalyst, and surface area of reactant or catalyst.
- For  $aA + bB \longrightarrow cC + dD$ ,  $\text{Rate} = \frac{-\Delta[A]}{a\Delta t} = \frac{-\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$  and Rate law  $= k[A]^m[B]^n$ .
- **Molecularity:** No. of molecules which participate as reactants in an elementary step (uni-, bi-, ter-molecular).
- **Intermediate:** Substance which is neither a reactant nor a product in overall reaction. Formed in one elementary step, consumed in the next. Not included in rate law.
- **Catalyst:** Lowers activation energy, increases rate of reaction without being used up by reaction. Only temperature can change the value of rate constant,  $k$ .
- **Heterogeneous catalyst:** Exists in a different phase than reactant molecules.  
**Homogeneous catalyst:** Exists in same phase as reactants.
- **Adsorption:** Binding of molecules to a surface. Active sites: Places where reacting molecules may become adsorbed.
- A way to distinguish between 1st and 2nd order rate laws is to plot  $\ln[A]_t$  and  $1/[A]_t$ . If the  $\ln[A]_t$  plot is linear and negatively sloped, the reaction is 1st order. If the  $1/[A]_t$  is linear and positively sloped, the reaction is second order.
- Slow step in a mechanism is called the rate-determining step and governs the rate law for the overall reaction.

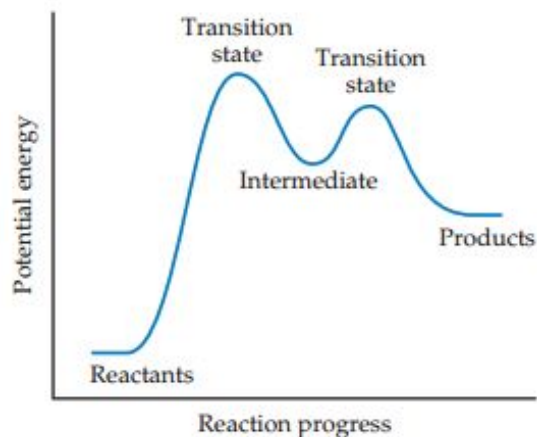


Figure 3: Potential energy diagram for a multistep reaction

# Equilibrium

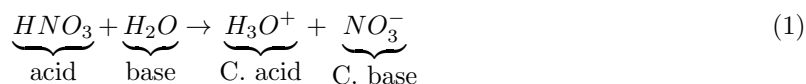
- Reaction shifts right, uses up reactants. Shift left, uses up products.

## LeChatelier's Principle

- Increase in temp. shifts exothermic reaction to the left. Can change  $K_{eq}$ .
- Increase in pressure, shifts reaction to side with more moles of gas.
- Catalysts and addition of inert gases won't affect equilibrium, but can change rate at which a reaction approaches equilibrium.
- **Homogeneous equilibria:** Equilibrium in which all substances are in the same phase.
- **Heterogeneous equilibria:** Equilibrium in which all substances are in different phases.
- $Q$  is the reactant quotient. If  $Q > K$  reaction shifts left, if  $Q < K$  reaction shifts right, if  $Q = K$  reaction is at equilibrium.
- Pressure constant is related to concentration constant by  $K_p = K_c(RT)^{\Delta n}$ .

## Acid/Base Equilibria

- Strong Acids -  $HCl$  (Hydrochloric),  $H_2SO_4$  (Sulfuric),  $HNO_3$  (Nitric),  $HBr$  (Hydrobromic),  $HI$  (Hydroiodic),  $HClO_3$  (Chloric),  $HClO_4$  (Perchloric).
- Weak Acids -  $HF$  (Hydrofluoric - hydrogen bonding),  $H_3PO_4$  (Phosphoric),  $-COOH$  acids.
- Strong Bases - Group I and heavy group II metal hydroxides.
- Weak Bases -  $NH_3$ , amines.
- **Arrhenius:** Acids  $\rightarrow H^+$  and Bases  $\rightarrow OH^-$ .
- **Brønsted-Lowry:** Acids donate protons, pairs with conjugate base, bases accept protons, pairs with conjugate acid.



- **Lewis acid:** Acid is an  $e^-$  pair acceptor while a base is an  $e^-$  pair donator.
- **Amphoprotic/Amphoteric:** Acts as either an acid or a base (e.g.  $H_2O$ ).
- Based on LeChatelier's, adding water to the reactants, i.e. diluting an acid, will shift equilibrium to the right, i.e. more acid dissociates.
- **Polyprotic acids:** Acids that have more than  $H^+$  that can ionize.  $K_{a1} > K_{a2}$  because it's easier to remove the first proton from a polyprotic acid than the second. In general, since successive  $K_a$  values differ by a factor of  $10^3$  or more, one can estimate the pH of a polyprotic acid solely considering  $K_{a1}$ .
- **Hydrolysis:** Reaction of ions with water to produce  $H^+$  or  $OH^-$ .
- Hydrides: In a periodic table row, the most basic hydrides are on the left and most acidic on the right.
- Non-metals: In a column, acidity increases with increasing atomic number.
- Oxy/carboxylic acids: Strength of acid increases as the number of electronegative atoms bound to the central atom increases. (e.g.  $HClO < HClO_2 < HClO_3 < HClO_4$  or  $CH_3COOH < CF_3COOH$ ).
- Hydrolysis of metal ions: Positively charged metal ions are attracted by electron pairs on oxygen in water (hydration).

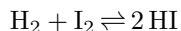
## ICEbox

Given initial values for a system at equilibrium and one of the equilibrium values, you should find:

- A - The other equilibrium values
- B - The equilibrium constant

### Example:

A closed system initially containing  $1.0 \times 10^{-3} \text{ M H}_2$  and  $2.0 \times 10^{-3} \text{ M I}_2$  at  $448^\circ\text{C}$  is allowed to reach equilibrium. Analysis of the equilibrium mixture shows the  $K_c = 50.5$ . Find the equilibrium concentrations for  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$ .



Initial	$1.0 \times 10^{-3} \text{ M}$	$2.0 \times 10^{-3} \text{ M}$	$0.0 \text{ M}$
Change	$-x$	$-x$	$+2x$
Equilibrium	$1.0 \times 10^{-3} - x$	$2.0 \times 10^{-3} - x$	$2x$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{4x^2}{(1.0 \times 10^{-3} - x)(2.0 \times 10^{-3} - x)} = 50.5 \Rightarrow x = 0.935 \times 10^{-3}$$
$$[\text{H}_2] = 0.065 \times 10^{-3}, [\text{I}_2] = 1.065 \times 10^{-3}, [\text{HI}] = 1.879 \times 10^{-3}$$

**Common Ion Effect:** The effect of ionization of a weak electrolyte is decreased by adding a strong electrolyte that has an ion in common with the weak electrolyte.

**Equivalence Point:** Point at which all acid has been neutralized, not necessarily at  $\text{pH} = 7.0$ . Choose an indicator whose  $\text{p}K_a$  is near the  $\text{pH}$  at the equivalence point.

## Buffers

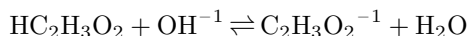
Resist change in  $\text{pH}$  in either direction. Best buffers have equimolar amounts of their components:

1. Weak acid or base.
2. Conjugate acid/base.

**Buffer Capacity:** Amount of acid/base the buffer can neutralize before  $\text{pH}$  changes significantly.

### Example:

A buffer is made by adding  $0.300 \text{ mol HC}_2\text{H}_3\text{O}_2$  ( $K_a = 1.8 \times 10^{-5}$ ) and  $0.300 \text{ mol NaC}_2\text{H}_3\text{O}_2$  to make a  $1.00 \text{ L}$  solution. The  $\text{pH}$  of the buffer is  $4.74$ . Calculate the  $\text{pH}$  after  $0.020 \text{ mol}$  of  $\text{NaOH}$  is added.



Initial	0.300	0.020	0.300	—
Change	$-0.020$	$-0.020$	$+0.020$	—
Equilibrium	0.280	0.000	0.320	—

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^{-}]}{[\text{HA}]}\right) \Rightarrow \text{pH} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.320}{0.280}\right)$$
$$\text{pH} = 4.80.$$

## Titration

Strong Base - Weak Acid: Conjugate base of the weak acid undergoes hydrolysis, which affects pH. Two step procedure for calculating pH:

1. Stoichiometry: Allow strong acid to react completely, to form a solution of the weak acid and its conjugate base.
2. Equilibrium: Set up ICEbox or use Henderson-Hasselbalch equation.

Strong Acid - Weak Base: Same as strong base-weak acid.

Differences in titration curves:

1. Solution of weak acid has a higher initial pH than a strong acid of same concentration.
2. pH rises more rapidly initially, but more slowly near equivalence.
3. pH at equivalence point isn't 7.0, it's equal to the pH of the resultant salt solution.

## Equilibrium of Salts

The solubility product constant,  $K_{sp}$ , equals the product of the concentration of the ions involved in equilibrium, each raised to the power of its coefficient in the equilibrium equation.

**Solubility:** Quantity of a substance that dissolves to form a saturated solution.

**Molar Solubility:** No. of moles of a solute that dissolves to form a liter of saturated solution.

## Complex Ions

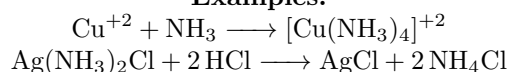
Common ion metals: Fe, Co, Ni, Cr, Cu, Zn, Ag, Al, Pt

Common ligands:  $\text{NH}_3$ ,  $\text{CN}^{-1}$ ,  $\text{OH}^{-1}$ ,  $\text{SCN}^{-1}$

General Rule: The number of ligands will be twice the charge of the metal ion.

Exceptions:  $[\text{Al}(\text{OH})_4]^{-}$ ,  $[\text{FeSCN}]^{+2}$

### Examples:



## Naming

### Organic

• $C_1$ : meth	• Alcohol	→	-ol	(R-OH)
• $C_2$ : eth	• Carboxylic acid	→	-oic	(R-COOH)
• $C_3$ : prop	• Ester	→	-yl or -oate	(R-COO-R)
• $C_4$ : but	• Ether	→	-yl -yl ether	(R-O-R)
• $C_5$ : pent	• Ketone	→	-one	(R-CO-R)
• $C_6$ : hex	• Amine	→	-amine	(R-NH <sub>2</sub> )
• $C_7$ : hept	• Amide	→	-amide	(R-CONH <sub>2</sub> )
• $C_8$ : oct	• Aldehyde	→	-al	(R-CHO)

### Acids

- ---ate → ---ic acid. e.g.  $\text{H} + \text{NO}_3 \rightarrow \text{HNO}_3$  (Nitric acid).
- ---ite → ---ous acid. e.g.  $\text{H} + \text{NO}_2 \rightarrow \text{HNO}_2$  (Nitrous acid).
- Hydro + (stem)ic. e.g.  $\text{H} + \text{Br} \rightarrow \text{HBr}$  (Hydrobromic acid).

**Alkane:** Only single bonds between carbons.

**Alkene:** At least one double bond between carbons.

**Alkyne:** At least one triple bond between carbons.

Table 1: Common Polyatomic Ions

Name	Formula
Sulfite/Sulfate	$\text{SO}_3^{-2}/\text{SO}_4^{-2}$
Chlorate/Perchlorate	$\text{ClO}_3^-/\text{ClO}_4^-$
Hypochlorite/Chlorite	$\text{ClO}^-/\text{ClO}_2^-$
Nitrite/Nitrate	$\text{NO}_2^-/\text{NO}_3^-$
Phosphate	$\text{PO}_4^{-3}$

## Electro Chemistry

- The chemical that has been **oxidized** is the **reducing agent**. The chemical that has been **reduced** is the **oxidizing agent**.
- Disproportionation Reaction:** Redox reaction in which same species is oxidized and reduced.
- Galvanic/Voltaic Cells:** There are two beakers (cells) with salt and  $e^-$ s in each solution. A salt bridge between the two solutions allows passage of ions. One side is identified as the cathode (reduction) and the other the anode (oxidation). The cations go to the cathode and the anions go to the anode. The  $e^-$ s go to the cathode.

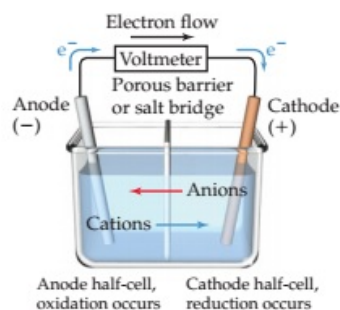
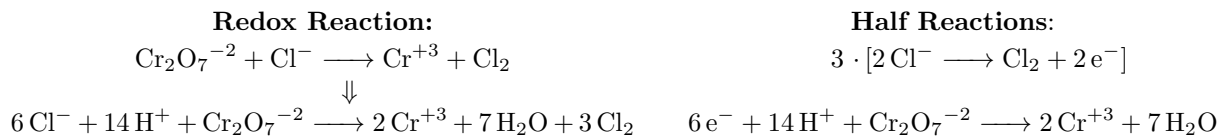


Figure 4: Voltaic Cell ( $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ )

## Balancing Redox Reactions

- Add  $\text{H}_2\text{O}$  to side deficient in oxygen.
- Add  $\text{H}^+$  to side now deficient in hydrogen.
- If the reaction is basic, add  $\text{OH}^-$ , equal to number of  $\text{H}^+$  added, to both sides.



**Electrolysis:** Electrical energy is used to drive a non-spontaneous redox reaction. Anode and cathode are in one cell.

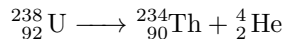


## Nuclear Chemistry

All nuclear decay reactions are first order.

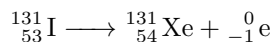
### Alpha Decay ( $\alpha$ )

An alpha particle ( ${}^4_2\text{He}$ ) is emitted.



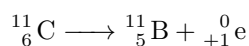
### Beta Decay ( $\beta$ )

A beta particle ( ${}^0_{-1}\text{e}$ ) is emitted. A neutron decomposes into a proton and an electron.



### Positron Emission

A positron ( ${}^0_{+1}\text{e}$ ) is emitted. The emission of a positron converts a proton into a neutron.



## Lab Techniques

- When diluting concentrated acid, always add the acid to water.
- When collecting gas over water, take into account the pressure/volume of the water vapor.
- When titrating, rinse the buret with the solution that will be used in the titration after rinsing with water, so as to not dilute the titrant.

## Separation Methods

- **Filtration:** Separates solids from liquids.
- **Distillation:** Separates liquids based on boiling point.
- **Chromatography:** Separates liquids based on charge or polarity.

**Titration:** Process in which a standardized solution is used to determine the concentration of another solution.

Conduction: Non-ionic and solid ionic compounds don't conduct electricity. However, solid metals and ionic solutes, will conduct.

Flame Tests:  $\text{Sr}^{2+}$  (red),  $\text{Na}^+$  (yellow),  $\text{Cu}^{2+}$  (blue),  $\text{Cu}^+$  (green),  $\text{Mn}^{7+}$  (purple),  $\text{Cr}^{6+}$  (orange),  $\text{I}_2$  (purple),  $\text{PbI}_2$  (yellow),  $[\text{Cu}(\text{NH}_3)_4]^{3+}$  (dark blue).

Some diagrams from *Chemistry: The Central Science* by Brown, LeMay, et al.