Exam 1

- Gases
  - States of matter - solid, liquid, gas
  - Gas
    - material with no definite shape or volume
    - move more readily
    - N₂ is the most common gas (air)
    - Air: N₂, O₂, H₂O, Ar, He, CO₂, O₃, CH₄
  - What kind of substances are gases?
    - Mostly small molecules
    - Some free elements
      - H₂, O₂, Ar, Noble gases, N₂, F₂, Cl₂, Br₂, Hg
    - Smells are molecules in their gas state
  - Microscopic characteristics
    - Particles are randomly moving
    - Particles will collide - elastic collisions (don’t lose energy)
    - Particles exert pressure by bouncing off walls
    - Simple relationship between moles, pressure, volume, and temperature
      \( PV = nRT \)
  - Microscopic Properties
    - Gases are compressible
    - Lower density than solids of liquids
    - Completely mix - no “immiscible” gas
  - Units of Pressure
    - Pressure = \( F/A \) (Force/Area)
      - SI units of Area = m²
      - SI units of Force = N
      - N/m² = 1Pa
      - Atmospheric Pressure at sea level = 101 kPa = 1atm
      - 760 torr = 1atm = 760 mm Hg

- Relationship of physical properties of gas
  - \( V \uparrow \) P \( \downarrow \) (inverse proportion)
    - \( V \propto 1/P \)
    - \( V = k(1/P) \) where k=constant
    - VP = k
    - Boyle’s Law
      - \( V_1P_1 = V_2P_2 \)
  - V \( \downarrow \) T \( \downarrow \)
    - \( V \propto T \)
    - \( (V_1/T_1) = k = (V_2/T_2) \)
      - No change in pressure
    - Charles’ Law
      - \( (V_1/T_1) = (V_2/T_2) \)
  - V \( \uparrow \) n \( \uparrow \) (n = # of moles)
    - \( V \propto n \)
    - Avogadro’s Law
(V_1/n_1) = (V_2/n_2)
- No change in P or T
- The number of moles does not change by substance!
- \( PV = nRT \)
  - \( R = \text{ideal gas constant} = 0.082057 \text{ L atm/mol K} \)
  - See Figure 1

- **Density of a Gas**
  - Much lower than liquids or solids
  - g/L or g/cm^3
  - \( D = \frac{PM}{RT} \)
  - \( M = \text{molar mass} \)

- **Dalton’s Law of Partial Pressure (1801)**
  - Total pressure of the mixture of gases is equal to the sum of their individual pressures
  - Implies that P depends on the total number of moles, not the chemical nature
  - \( P_{tot} = P_a + P_b + P_c + ….. \)
  - \( P_{tot} = \frac{n_{tot}RT}{V} \)
  - If you have two gases, \( n_{tot} = n_a + n_b \)
  - \( P_{tot} = (n_a + n_b)RT/V \)

- **Kinetic Molecular Theory of Gases**
  - Gas molecules are separated by large spaces
  - Random motion with collisions
  - Average kinetic energy of gas particles is proportionate to the gas’s temperature
  - \( U = \sqrt{\frac{3RT}{M}} \)
    - Where \( U = \text{average of the square of speeds and } M = \text{molar mass} \)
    - Average speed depends on T and molar mass
    - RMS (root mean square)

- **Gas Diffusion**
  - Gradual mixing of 2 gases randomly
  - Graham (1832)- at a constant pressure and temperature, the rate of diffusion of gases is inversely proportional to the square of M
  - \( r_1/r_2 = \sqrt{\frac{M_1}{M_2}} \)
    - \( r = \text{rate} \)
    - \( M = \text{molar mass} \)
  - Lighter gas diffuses more quickly

- **Gas Effusion**
  - Process by which gas escapes out of a tiny opening in a container
  - Graham’s law works here too

- **Ideal Gas Assumptions**
  - no attractions between molecules (“stickiness”)
  - assume that the molecules have no volume
  - This is where the real gas law comes in

- **Intermolecular Forces**
  - Forces that hold molecules together
o Not bonds! Only forces/attractions
  ▪ Dipole-dipole
    • Attraction between $\delta^-$ and $\delta^+$ on different molecules (two polar molecules)
  ▪ Dipole-induced dipole
    • Between 2 different substances: 1 polar and 1 non-polar
    • Ex) the dipole of water repels electrons to make a dipole on C$_2$H$_6$
  ▪ London Dispersion Forces (LDF)
    • Occur between all molecules
    • Aka: induced dipole-induced dipole and Van der Waals Forces
    • Weak
    • Relatively insignificant
  ▪ Hydrogen Bonding (not a bond!)
    • The IMF between and H atom on an N, F, or O and its attraction to the lone pairs of electrons on another N, F, or O atom
      o N, F, and O are the smallest and most electronegative
    • If there is hydrogen bonding, there are dipole-dipole attractions
    • C-H: never involve hydrogen bonding because they are non-polar and there is no attraction

o Molecular Level
  ▪ Solids- little movement and lots of strong IMFs
  ▪ Liquids- molecules close together, but can move
  ▪ Gases- molecules are far apart, no IMF
  ▪ Bigger molecule = more IMF’s

o Polarizability
  ▪ Ability of a molecule to react to a dipole

o Polarity
  ▪ Similar polarities mix
  ▪ Similar polarity = similar IMFs

o Transition from liquids to gas
  ▪ Liquids- lots of IMF
  ▪ Gas– No IMF
  ▪ Liquid to gas = evaporation (boiling)
  ▪ High IMF = slower evaporation = higher boiling point
  ▪ As you go down the periodic table the IMFs increase
  ▪ Vapor Pressure increases as the temperature of the liquid goes up
  ▪ Boiling point is when vapor pressure equals external pressure

o Viscosity
  ▪ Resistance to flow in a liquid
    • As IMFs go up, the viscosity also goes up
      o (IMFs and large molecules affect viscosity)
  ▪ Capillary effect pulls a liquid up into a small tube (paper and marker)
    • Non-polar molecules will move along paper
    • Polar molecules will stay attached to the paper
- Graduated Cylinder- read the the bottom of the meniscus- there is an attraction (IMF) between the water and the glass (what makes the water creep up the sides)
- Adhesive forces- attraction of water to a solid
- Cohesive forces- IMF between liquid
  - In water and glass cohesive<adhesive
  - In mercury and glass cohesive>adhesive

- Surface Tension
  - Molecules near the surface are closer together
    - Takes extra energy to pierce a liquid surface
    - This is because of hydrogen bonding between water molecules
  - Phase Diagram

![Phase Diagram](image)

- Pressure-Temperature phase diagram for CO₂
  - Triple point- all three phases exist in equilibrium
  - Critical Point- where the liquid phase of the matter ceases to exist
    - Supercritical Fluid
      - Can’t tell if it is a liquid or a gas
      - Caffeine extraction uses supercritical CO₂
      - Supercritical water
        - Flammable
        - Used for extractions (to remove contaminants)
        - Hard to reach (225atm)
  - Boiling Point- the point where vapor pressure equals atmospheric pressure
    - Stronger IMFs = higher boiling point
    - Stronger IMFs = lower melting point
      - Ionic bonds are the strongest
  - If the slope of the line between liquid and solid is positive than the solid is more dense than the liquid
  - If the slope of the line between liquid and solid is negative (like in water), than the solid is less dense than the liquid
    - Reason why ice floats in water

- Solids
  - Structural materials
    - Building
- Transportation
  - Electronic materials
  - Optical materials (fiber optics)
  - Thermoelectrics
    - Solids that get cold when conducting electricity
    - HUGE area of research
  - Kinds of Solids
    - Molecular solid (ice and CO\textsubscript{2})
      - Solid made of molecules
      - Held together by IMFs
      - Relatively weak
      - Low melting points
      - Sugar, dry ice, water
      - Non-conducting
    - Ionic solids (ions)
      - Made of ions
      - NaCl (Na\textsuperscript{+} and Cl\textsuperscript{-})
      - Very high melting points
      - Very brittle
      - Non-conducting
    - Metallic solids (metals)
      - Held together by metallic bonds
      - Positive cations in a “sea of electrons”
      - Delocalized e\textsuperscript{-} are responsible for metallic properties
        - Electrical conductivity, heat conductivity and reflectivity
      - Non-directional bonding
        - Ductile (wire), malleable
        - Bonds rearrange but don’t break
    - Covalent networks
      - Held together by covalent bonds into 2D infinite structures (graphite) or 3D infinite structures (diamonds)
      - Very high melting point
      - Very hard
      - Usually an insulator or semi-conductor
  - Two Categories of Solids
    - Amorphous
      - Lacking form or shape
      - Lacking a well-defined long range molecular level structure
      - Glass- random chains of corner sharing
    - Crystalline
      - Posses long-range well defined atomic level structure
      - Diamond, NaCl, graphite, ceramics
      - The smallest repeating unit = unit cell
      - Unit cell can be used to recreate the entire structure
Exam 2

- Solids- crystalline solids
  - Unit cell- repeating unit present in crystalline structures
  - Unit cell matches formula as a multiple
    - Simple cubic cell
      - A=B=C
      - All angles are 90°
    - Tetragonal unit cell
      - A=B≠C
      - All angles are 90°
    - Orthorhombre unit cell
      - A≠B≠C
      - All angles are 90°
  - Special locations
    - 8 corner atoms
      - Atom split by 3 planes
      - \( \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = 1/8 \)
      - 8 corner atoms at 1/8 each = 1 atom/unit cell
    - 12 edge atoms
      - Atom split by 2 planes
      - \( \frac{1}{2} \times \frac{1}{2} = \frac{1}{4} \)
      - 12 corner atoms at ¼ each = 3 atoms/unit cell
    - 6 face atoms
      - Atom split by 2 planes
      - 6 atoms at ½ each = 3 atoms/unit cell
    - Body atom
      - Atom located completely within the unit cell
      - 1 body atom
      - 1 body atom = 1 atom/unit cell
  - Only have one type of atom present (element)
    - Simple cubic structure
      - 1 atom/unit cell
      - Very rare
      - Only 2 elements that are simple cubic- Po and α Hg
      - Very inefficient
        - A lot of space
        - 52% full
    - Body centered cubic
      - 8 corner atoms at 1/8 each = 1 atom/unit cell
      - 1 body atom
      - 2 atoms/unit cell
      - 68% full
      - Fe, alkali metals
    - Face centered cubic
      - Corner atoms + face atoms
• 8 corner atoms at 1/8 each = 1 atom/unit cell
• 6 face atoms at ½ each = 3 atoms/unit cell
• 4 atoms/unit cell
• 74% full
  o Highest possible for a pure element
• Al, Ag, Au, Cu, Ni, Pt
• Hexagonal
• Closely packed
  ▪ For body centered, face centered, and hexagonal close packed
  ▪ Have planes of atoms which can slide past each other
  ▪ Ex.) steel = Carbon + Iron
    o Carbon sits in holes between iron
    o Can’t shift

• New way to look at bonding
  o Old way doesn’t work well for metals
  o O$_2 (l)$ is paramagnetic (has unpaired electrons)
  o New concept called molecular orbitals
    ▪ Modern view
  o Basic Rules of Molecular Orbital Theory
    ▪ Total number of Molecular Orbitals (MOs) = number of atomic orbitals used
    ▪ Bonding orbitals will always be lowering in energy than parents
    ▪ Antibonding orbitals will always be higher in energy than parents
    ▪ Electrons will fill orbitals from lowest to highest energy
    ▪ Orbitals combine best with orbitals of the same energy
    ▪ See Figure 2
  o Bond Order
    ▪ $\frac{1}{2}(e^- \text{ in bonding orbitals} – e^- \text{ in antibonding orbitals})$
    ▪ See Figure 3
  o How to combine p-orbitals
    ▪ $e^-$ are waves that want constructive interference in order to build on each other
  o Reactions occur in the HOMO- highest order molecular orbital
  o LUMO- lowest unoccupied molecular orbital

• Solid Materials
  o Metals, covalent networks
  o Each atom brings orbitals to make molecular orbital
  o Metals
    ▪ Promote electrons to higher energy, you need very, very little energy (conductors)
    ▪ Electrons once excited can easily move through the entire metal, due to MOs
    ▪ Therefore metals conduct electricity
    ▪ See Figure 4
  o Insulator
    ▪ Takes a lot of energy to promote electrons to higher energy
- Insulators do no conduct electricity
  - See Figure 5
- Semi-conductors
  - Requires energy, but is possible
  - Can switch between conducting and not conducting by applied voltage
  - See Figure 6
- Conductivity as a Function of Temperature
  - For metals
    - As T increases conductivity decreases
    - Higher T = more Energy (move nuclei)
      - Impedes flow of electrons
  - For Semi-conductors
    - As T increases conductivity increases
    - Additional energy naturally excites more electrons into conducting band
- For Special Metals- Super Conductors
  - Below a certain T, conduct electrons without any resistnce
- Solutions
  - What makes up a solution?
    - Solvent- liquid (component in greater amount)
    - Solute- what is dissolved (component in lesser amount)
    - Solution will have the same phase as the solvent
  - Consider solubility with liquids as a solvent
    - Solubility- how much solute dissolves
    - Effect of pressure doesn’t really effect solubility on liquid and solid solutions
      - However, gases do see an effect
        - As pressure increases solubility increases (in a liquid)
      - Henry’s Law (gas)
        - $S_g = K_H P_g$
        - Solubility = constant (pressure)
        - Ex.) scuba diver goes down pressure goes up
          - $O_2$ and $N_2$ become more soluble in the blood
          - When diver comes up, pressure decreases, solubility decreases and therefore the gases come out of solution
            - Break capillaries
          - The solution is to use a mix of $O_2$ and He
            - He is non-soluble at high pressure
  - Effect of temperature on solubility
    - As temperature increases $S_g$ decreases
    - Boiling $H_2O$
      - First get bubbles because the gas is coming out of solution
  - Solubility of liquids
    - Depend on IMFs
    - Liquids that mix are miscible
• Liquids that don’t mix are immiscible
• As the temperature increases the solubility of a liquid increases
  o Overcome differences in IMFs
• Solubility of solids
  • When solids dissolve
    o If heat is released $\Delta H<0$
      ▪ Exothermic reaction
      ▪ Liquid IMFs are greater than solid IMFs (lower energy)
    o If energy is absorbed $\Delta H>0$
      ▪ Endothermic reaction
      ▪ Solid IMFs are greater than liquid IMFs
  o As temperature increases, solubility increases
• Colligative Properties
  o Properties of solutions depend only on the concentration of solute particles, not on the chemical nature
    ▪ Vapor Pressure
    ▪ Boiling Point Elevation
    ▪ Freezing Point Depression
    ▪ Osmotic Pressure
  o Vapor Pressure
    ▪ Fewer molecules can escape because some surface sites are taken by solute
    ▪ See Figure 7
    ▪ $P_{\text{solvent}} = (X_{\text{solvent}})(P^0_{\text{solvent}})$
      ▪ $P = \text{Vapor Pressure}$
      ▪ $X = \text{mole fraction}$
      ▪ $P^0 = \text{pressure of pure solvent}$
      ▪ $X_{\text{solvent}} = n_{\text{solvent}}/([n_{\text{solvent}} + n_{\text{solute}}](i)]$
        ▪ $i$ is the dissociation constant
        ▪ See Figure 8
  o Boiling Point Elevation
    ▪ The boiling point of the solution is always higher than the boiling point of the solvent
    ▪ $\Delta T = K_{bp}mi$ (where $m = \text{molality}$)
    ▪ As $V$ increases, $T$ increases and Molarity decreases
      ▪ Concentration is dependent of $T$
    ▪ See Figure 9
  o Freezing Point Depression
    ▪ Solid of pure substance
      ▪ Maximize IMF
    ▪ As solution
      ▪ Not quite as “pretty” of an arrangement
      ▪ Don’t “fit” right
      ▪ Lower IMFs than pure solvent
      ▪ Freezing point goes down
• Expect lower IMFs to result in a lower freezing point
• Example: salt on the roads lowers the freezing point
• $\Delta T = K_f p(m)(i)$ where $m =$ molality
• See Figure 10
  o Osmotic Pressure
    ▪ See Figure 11
    ▪ Osmosis-water moves to try to equilibrate concentrations
    ▪ Difference in pressure = osmotic pressure
    ▪ $\Pi = MRTi$
      ▪ $M =$ molarity
      ▪ $R =$ constant
      ▪ $T =$ temperature
      ▪ $i =$ dissociation constant
• Chemical Kinetics
  o Chemical kinetics- the study of rates of reactions
    ▪ Going into the arrow of the reaction
  o Rate of chemical reaction- rate of change of concentration of reactants
    ▪ See Figure
    ▪ Depends on which time period
      ▪ Reaction rate changes over time
      ▪ Average rate of reaction
        ▪ Over time, rate of reaction slows, so average goes down
      ▪ Instantaneous Rate- rate of reaction at any moment
        ▪ Derivation of concentration vs. time gives instantaneous rate
  o What effects rate of reaction?
    ▪ Temperature
    ▪ Solubility
    ▪ Pressure
    ▪ Concentration of product and reactants
    ▪ Quantity
    ▪ IMFs
  o Collision Theory of Reactions
    ▪ Reactants must collide for reaction to occur
    ▪ Reactants must collide with “sufficient energy”
    ▪ Reactants must collide in the proper orientation to react
    ▪ Examples
      ▪ As concentration increases more collisions occur and therefore the rate of the reaction increases
      ▪ As temperature increases, speed increases, kinetic energy increases and therefore the rate of the reaction increases
  o Catalyst- increases the rate of reaction but isn’t used up
  o In general…
    ▪ $aA + bB \rightarrow cC + dD$
    ▪ Rate of reaction $= k[A]^x[B]^y$
      ▪ $x$ and $y$ (exponents) must be determined experimentally
• ex: $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$
  o rate of the reaction = $k [\text{NO}_2]^2$

• Determining Rate Laws
  o Integrated rate laws
    ▪ First Order Rate Law
      • $\ln[R]/[R]_o = -kt$
      • linear
    ▪ Second Order Rate Law
      • $1/[R] = kt + 1/[R]_o$
      • Slope = $k$
    ▪ Zero Order
      • $[R] = -kt + [R]_o$
      • The change in concentration has no effect on the rate of reaction for zero order reactions
    ▪ In order to determine the correct order, graph all of them and look for the best $R^2$ value
  o Pseudo Rate Laws- when one reactant is in vast excess

• Half Life (Radioactive Decay)
  o 1st order: $t_{1/2} = \ln2/k$
  o 2nd order: $t_{1/2} = [R]_o/2k$
  o 3rd order: $t_{1/2} = 1/k[R]_o$

• Reaction Mechanisms
  o Step by step process of breaking and making bonds
  o Sum of steps of mechanism must equal reaction
    ▪ NO + O₃ $\rightarrow$ NO₂ + O₂
      • Single step mechanism
        o All bonds occur at once
        ▪ Elementary steps- individual steps of mechanisms
        ▪ Intermediate steps- species that are formed and then subsequently used in a mechanism
        ▪ Unimolecular steps- involves 1 molecule
        ▪ Bimolecular steps- involves 2 molecules
        ▪ Termolecular steps- involves 3 molecules
        ▪ Catalyst- a species that is used then subsequently reformed
  o How do we distinguish between mechanisms?
    ▪ Individual steps have their own rate laws
      • in these rate laws, exponents are determined by coefficients
      • rate of any reaction is defined by the slowest step of the mechanism
        ▪ if first step is slow than mechanism #1 is the rate law
      ▪ However, you do not want any intermediates in the rate law (if slow step is not the first step)
      ▪ All steps before the slow step are assumed to be in equilibrium (reaction occurring at equal rates in both directions)
        • Rate of forward reaction = rate of reverse reaction
      ▪ Intermediates after the slow step always have a very low concentration (will be used up as soon as it’s formed)
- Intermediates before the slow step can build up in concentration

Exam 3

- Kinetics (con’t)
  - See Figure 11

- Equilibrium
  - Rates of forward and reverse reactions are equal
  - No macroscopic change
    - Example:
      - \( \text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4 \)
      - Rate = \( k[\text{H}_2\text{O}][\text{SO}_3] \)
      - In equilibrium…
        - \( k_1[\text{H}_2\text{O}][\text{SO}_3] = k_{-1}[\text{H}_2\text{SO}_4] \)
  - So far we’ve only looked at \( k_c \) (indicates concentration)
    - \( k_p \) = equilibrium using pressure
      - Used only for gases
      - See figure 12

- All \( k \)'s are unitless
- Relationship between \( k_c \) and \( k_p \)
  - \( k_p = k_c (RT)^\Delta n \)
- Reaction Quotient- not in equilibrium
  - \( Q = [C]^a[D]^b/[A]^c[B]^d \)
  - Compare \( Q \) to \( k_{eq} (k_c \) or \( k_p \))
    - If \( Q < k \) then there needs to more products so the reaction shifts to the right
    - If \( Q > k \) then there needs to be more reactants so the reaction shifts to the left
    - If \( Q = k \) then the reaction is at equilibrium

- Le Chatelier’s Principle
  - A system at equilibrium will try to counter any stress
    - For gases, if volume decreases then pressure increases
    - It is important to know whether the reaction is endothermic or exothermic

- Steps to Solve Equilibrium Problems
  - Write out equilibrium
  - Use \( Q \) to determine the direction of shift, if not in equilibrium (if one of the products or reactants is missing, reaction will shift to from it)
  - Set up ICE table (use balanced equation in order to find relative change)
  - Plug “E” values into our \( k \) expression
  - Solve algebraically for “x” (change)
  - Use \( x \) to find equilibrium values
    - See Figure 12

- Acid/Base
  - Proton transfer chemistry
  - Bronstead Definition
    - Acid: donates \( \text{H}^+ \) in aqueous solutions
    - Base: accepts \( \text{H}^+ \) in aqueous solutions
  - Acid
    - Strong acids
- HCl, H$_2$SO$_4$, HBr, HI, HNO$_3$, HClO$_4$
- Which means they completely dissociate in water
  - Conjugate acid- species formed when the base gains H$^+$
  - Conjugate base- species formed when the acid loses H$^+$$\$

- **Base**
  - Strong bases
    - OH$^-$ (soluble OH$^-$ salts), H$, RO^-$, R$^-$, NH$_2^-$
    - They will completely dissociate in water
  - All other bases are “weak” and will be mostly organic compounds with an N atom or O containing anions

- H$_2$O is amphiprotic meaning that it can donate or accept H$^+$ (it can be an acid or a base)
- $k_w$ is the equilibrium of water with itself
  - It is often called the autoionization constant with water
    - At $25^\circ$C $k_w = 1.0 \times 10^{-14}$
    - This equilibrium will be true for all aqueous solutions

- [H$_3$O$^+$] > [OH$^-$], then the solution is acidic
- [H$_3$O$^+$] < [OH$^-$], then the solution is basic
- Equations:
  - $\text{pH} = -\log[H_3O^+]$ therefore $[H_3O^+] = 10^{-\text{pH}}$
  - $\text{pOH} = -\log[OH^-]$ therefore $[OH^-] = 10^{-\text{pOH}}$
  - $k_w = [H_3O^+][OH^-]$
  - 14 = pH + pOH
- pH is a logarithmic scale
  - [H$_3$O$^+$] = 0.1 then pH = 1
  - [H$_3$O$^+$] = 0.01 then pH = 2
  - [H$_3$O$^+$] = 0.001 then pH = 3
- See figure 14

- **Weak Acids**
  - HA + H$_2$O $\leftrightarrow$ A$^-$ (aq) + H$_3$O$^+$ (aq)
  - $k_a = [A^-][H_3O^+]/[HA]$
    - $k_a$ represents an acid reaction with H$_2$O
  - $-\log(k_a) = p_{k_a}$
    - As $k_a$ increases the stronger the acid is
    - As $k_a$ increases, $p_{k_a}$ decreases
    - As $p_{k_a}$ decreases, the stronger the acid is

- **Weak Bases**
  - B$^{(aq)}$ + H$_2$O $\leftrightarrow$ BH$^+$ (aq) + OH$^-$ (aq)
  - $k_b = [BH^+][OH^-]/[B]$  
    - $k_b = \text{equilibrium constant for base reacting with water}$
  - $-\log(k_b) = p_{k_b}$
    - As $k_b$ increases, the base strength increases
    - As $p_{k_b}$ decreases, the base strength increases

- Few things about $k_b$ and $k_a$
  - If $k_a$ increases, the acid is stronger
    - If $k_b$ decreases, for CB, weaker base
- If $k_a$ decreases, the acid is weaker
  - If $k_b$ increases, CB is stronger
- Conjugate bases of strong acids have basically no base strength and vice versa
  - Largest $k_a$ value = strongest acid
  - Strongest CB = smallest $k_a$ value
- Predicting acidity/basicity of salts
  - $\text{NaNO}_3$
    - $\text{Na}^+$
      - No effect on pH
      - All alkali metals have no effect
    - $\text{NO}_3^-$
      - $\text{HNO}_3$ is a strong acid and therefore $\text{NO}_3^-$ has no base strength
      - Therefore $\text{NaNO}_3$ is neutral
  - $\text{KNO}_2$
    - $\text{K}^+$
      - No effect
    - $\text{NO}_2^-$
      - $\text{HNO}_2$ is a weak acid
      - Therefore $\text{KNO}_2$ is a weak base
- Predicting the Direction of an Acid/Base reaction
  - Strongest acid reacts with strongest base
- Polyprotic Acids: acids with more than one acidic hydrogen
  - Release 1 $\text{H}^-$ at a time
  - $\text{pH}$ usually defined only by the 1st equilibrium (if pure)
- Buffers
  - Buffer is a solution that resists changes in pH (when acid/base is added)
  - A buffer must be able to react with $\text{H}_3\text{O}^+$ and $\text{OH}^-$
  - Must contain an acid and base
  - Acid and base must not react with each other
    - Conjugate acid/base pair
    - See Figure 15
  - How do you make a buffer?
    - Add a weak acid and conjugate base to the same solution
    - Ass a weak acid and less strong base
    - Add a weak base and less strong acid
  - How do you find the $\text{pH}$ of a buffer?
    - Do equilibrium problem (will ALWAYS work)
    - Henderson-Hasselbach Equation (H-H equation)
      - $\text{pH} = pk_a + \log([\text{A}^-]/[\text{HA}])$
        - gives $\text{pH}$ of a Buffer ONLY
      - $\text{pH}$ remains constant even when volume changes
        - Assumption: assume that there is a significant concentration of each the weak acid and weak base
    - $\text{pOH} = pk_b + \log([\text{HB}^+]/[\text{B}])$
      - not used often due to not caring about $\text{pOH}$
- Titrations- acid/base
Quantitative reaction between an acid and base
Neutralization reaction
Slowly adding 1 reagent to the other
Go to http://www.shodor.org/UNChem/basic/ab/#titra for more information on acid/base chemistry and extra problems and how to do them

- Salt Solubility
  - What happens when you put salt in water?
    - It dissolves
      - Ex. NaCl $\leftrightarrow$ Na$^+$ (aq) + Cl$^-$ (aq)
    - $k_{sp}$ = solubility product
      - $k_{sp}$ = [Na$^+$][Cl$^-$]
    - small $k_{sp}$ values = not very soluble (favor reactants)
    - high $k_{sp}$ values = very soluble
    - Insoluble- doesn’t dissolve in water, much
  - See Figure 16

Information for Final

- What you need to know about electrochemistry
  - How to balance a redox equation
  - How to determine voltage ($E^o$) of an electrochemical cell
  - How to draw an electrochemical cell
  - Batteries
  - Redo Chemistry- requires the transfer of electrons from one atom to another
    - Identifiable by change in oxidation state
    - Oxidation numbers change
      - One will gain an electron
      - One will lose an electron
    - Look at hand-out “Balancing Redox Reactions” for steps
  - In principle, we can separate oxidation and reduction processes
    - Electrons move through a wire (electricity)
    - Need to separate two different half reactions
      - Voltaic cell
        - Named after Count Alessandra Volta (1745-1827)
        - See Figure 17
  - Batteries
    - AA battery (alkaline- basic)
    - See figure 18 for picture of battery
      - Cathode- reduction
      - Anode- oxidation
      - The battery dies because you run out of MnO$_2$
    - Rechargeable batteries
      - Lead storage battery (car battery)
        - 12-V battery
        - Alternate anode/cathode
          - Pb(s)- Anode
            - Oxidation
            - $\text{Pb}(s) + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2e^-$
- **PbO₂- Cathode**
  - **Reduction**
    - \( \text{PbO}_2(s) + 4H^+ + 2e^- + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(s) + 2H_2O(l) \)
- 6 units (cathode/anode, cathode/anode, cathode/anode...) and 2V each = 12-V total
- In order to make reaction go backward, you need to apply electrical voltage greater than the voltage of the cell \( (E^0) \)

- **Voltage**
  - Voltage shows difference in potential energy
    - Always measure potential difference
    - Remember: electrons want to go down (from high to low energy levels)
    - Can’t find absolute potentials so we define a “zero point”
      - \( \text{H}_2(g) + 2\text{H}_2\text{O} \leftrightarrow 2\text{H}_3\text{O}^+ + 2e^- \)
      - \( E = 0.00V \)
  - **Voltage**
    - \( E^0 = E_{\text{ox}} + E_{\text{red}} \)
    - \( E_{\text{ox}} = -E_{\text{red}} \)
    - **Standard Reduction Potential Table (p.967)**
      - As voltage increases, reduction is more likely
      - As voltage decreases, oxidation is more likely
    - If \( E^0<0 \) reaction is NOT spontaneous
    - If \( E^0>0 \) reaction IS spontaneous

- **Electrochemistry**
  - Thermodynamics
    - \( \Delta H \)- enthalpy (heat)
    - When \( \Delta H<0 \) the reaction is favorable (giving off E)
      - Endothermic- gets cold
      - Exothermic- gets hot
    - **1st Law of Thermodynamics**
      - \( \Delta E=0 \)
      - Energy is neither created nor destroyed
    - **2nd Law of Thermodynamics**
      - In a spontaneous process, the entropy of the universe increases
      - Spontaneous- process that proceeds on its own (does not necessarily mean fast)
      - **Entropy**- molecular order or randomness (denoted as \( S \))
        - Favor more random
        - \( \Delta S = S_{\text{final}} - S_{\text{initial}} \) (change in entropy)
          - \( \Delta S_{\text{system}} \)
          - \( \Delta S > 0 \) increased randomness...good!
          - \( \Delta S < 0 \) decreased randomness...not good
- No matter what we do, it's going to be an inefficient process
  - See Figure 19
- **Probability- drives entropy**
  - Unlike H (enthalpy), entropy can be absolutely known
  - S for any material at 0K = 0
  - T > 0K, entropy is positive
- **Calculating S°**
  - \( \Delta S^o = \Sigma S^o \text{ products} - \Sigma S^o \text{ reactants} \)
  - Use table to determine S
- \( \Delta S_{\text{univ}} > 0 \), reaction is spontaneous
- \( \Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \)
- \( \Delta G = \text{Gibb’s free energy} \)
  - Potential energy available to do work
  - \( \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \)
  - \( \Delta S_{\text{univ}} > 0 \), reaction is spontaneous
  - \( \Delta G_{\text{system}} < 0 \), reaction to be spontaneous
  - \( \Delta G_{\text{system}} = 0 \), reaction not spontaneous
  - \( \Delta G = 0 \), the reaction is in equilibrium
  - At equilibrium:
    - \( \Delta G^o = -RT\ln(K) \)
  - See Figure 20
- **What you need to know about Nuclear Chemistry... for the Exam**
  - Types of Radiation
  - Why gamma and x-rays are emitted
  - Balancing nuclear reactions
  - Fission v. Fusion
  - Half life calculations (like in 1st order kinetics)
- **Nuclear Chemistry**
  - Reaction of the nucleus
    - All other reactions we have done have been with electrons
  - Relevant to medicine, energy, warfare, present in environment, and food safety
  - Discovered in 1896 by Henri Becquerel
    - Uranium compounds could expose photographic paper
    - 1898 Marie Curie isolated Po and Ra from U ore
    - 1899 she proposed the concepts of radioactivity
    - Isotopes emit nuclear particles
      - 1907 Rutherford showed that during radioactive decay atoms are converted from 1 element to another
  - See Figure 21
  - All elements and isotopes are radioactive if z > 83 (bismuth)
  - Even stable elements have radioactive isotopes
    - Like Carbon 14
- **Types of Radiation**
  - \( \gamma \) (gamma) ray
    - extremely dangerous
    - discovered by Villard
More energy than x-rays
Often occur after other forms of radiation
After nuclear decay form an unstable nucleus
When nuclei drop in energy they release γ rays
In order to stop a γ ray you need a very thin lead sheet

- α (alpha) particles
  - Positively charged
  - Large and slow
  - Relatively low energy
  - Discovered by Rutherford
  - Stopped by a piece of paper

- β (beta) particles
  - Fast and Light
  - Moderate energy
  - Ejected from nucleus
  - Discovered by Rutherford
  - Neutron decays into a proton and an e⁻
    - Neutron → proton + beta particle
  - Can be stopped by a thin piece of lead

- Positron decay (anti-beta particle)
  - Positron is an electron (anti-matter)
    - Proton → neutron + beta particle
  - Used medically in positron emission topography (PET scan)

- e⁻ capture
  - e⁻ is pulled into the nucleus from a core shell
    - proton + electron → neutron
  - When electron drops from 3d to 1s, it gives of LOTS of energy
  - Always emits an x-ray as an outer electron drops down to fill in the “hole”

- See Figure 22

Balancing Nuclear Reaction
- Must balance A and Z
- See Figure 23

Two Other Nuclear Reactions
- Fission
  - A heavy nuclei will break down into lighter nuclei
    - Usually requires bombardment with something
  - Basis for nuclear energy and nuclear weapons (A-bomb)
  - Where does all of this energy come from?
    - A chain reaction
    - Mass of the products < the mass of the reactants
    - A small mass change = lots of energy
      - E=mc² (because c is very large- 3.0x10⁸)
  - For nuclear weapons we need ²³⁵U>20%
    - Very, very hard to obtain

- Fusion
  - Lighter nuclei come together to form heavier ones
- O.7% mass of H are converted to energy
  - 100 billion tons react per second
  - Requires a temp of greater than $10^8$ K
- High temperature is required to bring protons together
  - In light mass stars
    - $\text{H} \rightarrow \text{He} \rightarrow \text{C}$
  - In high mass stars
    - $\text{H} \rightarrow \text{He} \rightarrow \text{C} \rightarrow \text{O} \rightarrow \text{Ne} \rightarrow \text{Na} \rightarrow \text{Mg} \rightarrow \text{Si} \rightarrow \text{S} \rightarrow \text{Ar} \rightarrow \text{Ca} \rightarrow \text{Fe}$
  - All other elements are synthesized during a supernova
- Uncontrolled Fusion
  - H-bomb
- Nuclear Kinetics
  - Radioactive decay
    - 1$^{\text{st}}$ order kinetics
    - The rate depends only on nuclear stability
    - $T$ has no effect
    - $\ln(N_i/N_f) = kt$
      - $N_i$=amount of radioactive nuclei
    - Half life
      - $t_{1/2} = \ln2/k$

Practice Exam Questions (from 3$^{\text{rd}}$ exam to present)

1. Describe how to set up a voltaic cell to generate an electric current using the reaction: $\text{Fe(s)} + \text{Cu}^{2+}(aq) \rightarrow \text{Cu(s)} + \text{Fe}^{2+}(aq)$. Which electrode is the anode and which electrode is the cathode? In which direction do electrons flow? In which direction do the positive and negative ions flow in the salt bridge? Write half-reactions that occur at each electrode.
2. Tritium (X=H, A=3, Z=1) is a radioactive isotopes that has a half-life of 12.3 years
   - a. Starting with 1.5mg of the isotope, how many milligrams remain after 49.2 years?
   - b. How long will it take for a sample of it to decay to one eighth of its activity?
   - c. Estimate the length of time necessary for the sample to decay to 1% of its original activity?
3. Calculate if the following reaction is spontaneous at 30°C?
   $\text{CO (g)} + 1/2 \text{O}_2 (g) \leftrightarrow \text{CO}_2 (g)$
   - a. Calculate the $\Delta H$ for the above reaction
   - b. Calculate the $\Delta S$ for the reaction.
   - c. Plug values into formula and determine if $\Delta G$ is positive or negative.
4. Go to this website for additional info and questions on Gibb’s Free Energy and Spontaneity…http://www.scs.sk.ca/cyber/elem/learningcommunity/sciences/chemistry30/curr_content/chem30/modules/module3/lesson6/entropychange.htm
5. Balance the following redox reaction:
   - a. In a sulfuric acid solution potassium permanganate will titrate with oxalic acid to produce manganese II sulfate, carbon dioxide, water, and potassium sulfate in solution.
6. What is the molar Solubility of AgCl in 0.02M AlCl$_3$ Solution
7. The net reaction that occurs in a voltaic cell is $\text{Zn(s)} + 2\text{Ag}^+(aq) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}$
a. Identify the half-reactions that occur at the anode and the cathode, and calculate a potential for the cell (standard conditions)

8. Balance the following reaction (in acid solution)
   a. Ag(s) + NO₃⁻(aq) → NO₂(g) + Ag⁺(aq)
   b. MnO₄⁻(aq) + HSO₃⁻(aq) → Mn²⁺(aq) + SO₄²⁻(aq)

9. Name two insoluble salts for each of the following ions
   a. Cl⁻
   b. Zn²⁺
   c. Fe²⁺

10. Balance these nuclear reactions: number 12
    a. \( \frac{54}{26} Fe + \frac{4}{2} He \longrightarrow \frac{2}{0} n + ? \)
    b. \( \frac{27}{13} Al + \frac{4}{2} He \longrightarrow \frac{30}{15} P + ? \)
    c. \( \frac{32}{16} S + \frac{1}{0} n \longrightarrow \frac{1}{1} H + ? \)