

I. Atomic Structure and Properties

- Periodic table
 - Alkali metals, alkaline earth metals, transition metals, halogens, noble gases
 - Mass number = $P + N$
 - Isotopes - atoms of an element with different numbers of neutrons
 - Average atomic mass from weighted average of isotope mass and relative abundance (frequency)
- Moles
 - $PV = nRT$
 - Avogadro's number 6.022×10^{23}
 - AT STP (1 atm, 273K), 22.4 L/mol
 - Molarity $M = \text{moles/L}$
 - Percent composition - divide the mass of each element/compound by the total molar mass of the substance
 - Empirical formula is simplest ratio, molecular formula is actual formula for substance
- Energy
 - Electron potential energy increases with distance from nucleus
 - Electron energy is quantized - can only exist at specific energy levels at specific intervals, not in between
 - Coulomb's law: $F = kq_1q_2/(r^2)$ where F is electrostatic force
 - Atoms absorb energy in the form of electromagnetic radiation as electrons jump to higher energy levels; when electrons drop levels (closer), atoms give off energy
- Photoelectron spectroscopy
 - energy measured in electronvolts (eV)
 - Incoming radiation energy = binding energy + kinetic energy of the ejected electron
 - Electrons that are further away from nucleus require less energy to eject, thus will move faster
 - Photoelectron spectrum
 - Each section of peaks represents a different energy level (1, 2, 3, etc.)
 - Subshells within each energy level (shape of space electron can be found in orbiting nucleus) are represented by the peaks (1s, 2s, 2p, etc.)
 - s(2) - first subshell, p(6) - second subshell
 - Height of peaks determines number of electrons in subshell (ex. Peak of p subshell in energy level 2 will be 3x that of s subshell)
- Electron configuration

- Electron configuration - spdf - shorthand with noble gas first
- Configuration rules
 - Aufbau principle - electrons fill lowest energy subshells available first
 - Pauli exclusion principle - 2 electrons in same orbital cannot have same spin
 - Hund's rule - Electrons occupy empty subshells first
- Zn +2, Ag +1, Al +3, Cd +2, most other transition metal charges vary
- Periodic trends
 - Electrons are more attracted if they are closer to the nucleus, or if there are more protons
 - Electrons are repelled by other electrons - if there are electrons b/w the valence electrons and nucleus, the e- will be less attracted (shielding)
 - Completed shells are very stable, completed subshells are also stable; atoms will add/subtract valence electrons to complete their shell
 - INCREASING: atomic radius down left; ionization energy up right; electronegativity up right
 - Ionization energy - energy required to remove an electron from an atom
 - Electronegativity - how strongly the nucleus of an atom attracts electrons of other atoms in a bond
 - Electron affinity - energy change that occurs when an electron is added to an atom in the gas state (usually exothermic - energy is released)

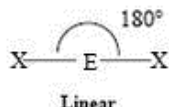
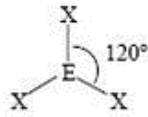
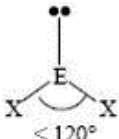
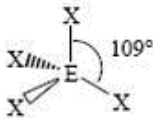
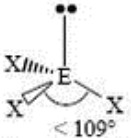

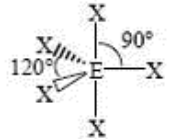
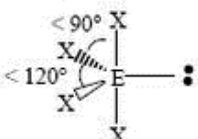
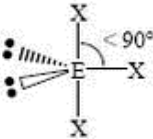
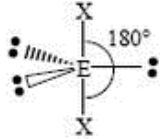
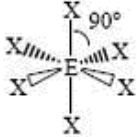
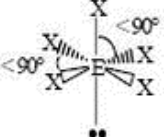
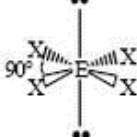
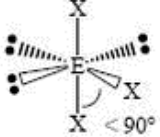
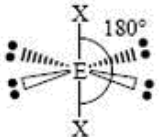
II. Molecular and Ionic Compound Structure and Properties

- Bonds
 - Atoms are more stable with full valence shells
 - Ionic bonds
 - Cation gives up electrons completely
 - Electrostatic attractions in a lattice structure
 - Metals and nonmetals (salts)
 - Coulomb's law - greater charge leads to a greater bond/lattice energy (higher melting point)
 - If both have equal charges, smaller radius will have greater coulombic attraction
 - Ionic solid - electrons do not move around lattice; ionic solids are poor conductors of electricity; ionic liquids conduct electricity because ions are free to move around, though e- are still localized around particular atoms
 - Metallic bonds

- Sea of electrons model - positively charged core is stationary while valence electrons are very mobile
 - Metals bond to form alloys - interstitial alloy w/ metals of different radii; substitutional alloy w/ metals of similar radii
- Molecular covalent bonds
 - 2 atoms share electrons - both atoms achieve complete outer shells
 - 2 nonmetals
 - Creates molecules - 2+ atoms covalently bonded together
 - Single has 1 sigma bond - order 1, longest length, least energy; double has 1 sigma and 1 pi bond - order 2, int. length, int. energy; triple has 1 sigma and 2 pi bonds - order 3, shortest length, greatest bond energy
 - Bond forms when potential energy is at minimal level
 - Too close - potential energy is too high due to repulsive forces
 - Too far - potential energy is near 0 because attractive forces are very weak
 - Minimal PE occurs when repulsive and attractive forces are balanced
 - Network covalent bonds - lattice of covalent bonds - poor conductors, high melting and boiling points
- Conductivity
 - Conductivity of different substances in different phases

	Solid	Aqueous	Liquid	Gas
Ionic	No	Yes	Yes	No
Molecular Covalent	No	No	No	No
Network Covalent	No	N/A	No	No
Metallic	Yes	N/A	Yes	No
- Lewis dot structures
 - Resonance - for bond order calculations, average together all possible orders of a specific bond
 - BORON (B) is stable with 6 electrons - only one that does not need a full octet
 - Expanded octets - any atom of an element from n=3 or greater (those with a d subshell) can have [8,12] valence electrons on center atom
 - Noble gases form bonds by filling empty d orbital with electrons
 - Formal charge - number of valence electrons minus assigned electrons (1 e- for each line "shared" bond) - 0 for neutral molecules

- Molecular geometry (VSEPR)

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal Planar	 Bent or Angular			
4	 Tetrahedral	 Trigonal Pyramid	 Bent or Angular		
5	 Trigonal Bipyramid	 Sawhorse or Seesaw	 T-shape	 Linear	
6	 Octahedral	 Square Pyramid	 Square Planar	 T-shape	 Linear

- Double and triple bonds have more repulsive strength than single bonds - occupy more space
- Lone electron pairs have more repulsive strength than bonding pairs, so molecules with lone pairs will have slightly reduced angles between terminal atoms
- Hybridization - how many atoms are attached (sp, sp², sp³, sp³d, etc.)

III. Intermolecular Forces and Properties

- Polarity
 - Covalent bond where electrons are unequally shared - polar covalent
 - Dipoles are caused by polar covalent bonds - pair of opposite electric charges separated by some distance, like partial charges on atoms in a polar covalent bond
 - If 2 identical atoms bond (ex. Cl-Cl) the electrons are equally shared, creating a nonpolar covalent bond with no dipole

- Bonds can be polar; so can molecules depending on the molecular geometry (and polarity of bonds - secondary)
- In polar molecules, more electronegative atoms will gain negative partial charge
 - Usually central atom will be positive - exception is hydrogen (terminal), which is usually positive since it has less electronegativity
- Intermolecular forces
 - Forces b/w molecules in a covalently bonded substance - need to be broken apart for covalent substances to change phases
 - Changing phase: ionic substances break bonds b/w individual ions; covalent substances keep bonds inside a molecule in place but break bonds b/w molecules
 - Dipole-dipole forces
 - Polar molecules - positive end of one molecule is attracted to negative end of another molecule
 - Greater polarity -> greater dipole dipole attraction -> larger dipole moment -> higher melting/boiling points
 - Relatively weak overall - melt and boil at low temps
 - Hydrogen bonds
 - Special type of dipole-dipole attraction where positively charged hydrogen end of a molecule is attracted to negatively charged end of another molecule containing an extremely electronegative element (F, O, N)
 - Much stronger than normal dipole-dipole forces since a hydrogen atom "sharing"/giving up its lone e- to a bond is left w/ no shielding
 - Higher melting/boiling points than substances held together only by other types of IMF
 - London dispersion forces
 - All molecules - very weak attractions due to random motion of electrons on atoms within molecules (instantaneous polarity)
 - Molecules w/ more e- experience greater LDF (more random motion)
 - Higher molar mass usually means greater LDF (as mass increases, e- increases for the molecule to remain electrically neutral)
 - IMF strength
 - Ionic substances are generally solids at room temp - melting them requires lattice bonds to be broken - necessary energy determined by Coulombic attraction

- Covalent substances (liquids at room temp) boil when IMF are broken; for molecules of similar size, from strongest to weakest: hydrogen bonds, permanent dipoles, LDF (temporary dipoles - greater for larger molecules)
 - Melting/boiling points of covalent substances are LOWER than for ionic substances
 - Bonding/Phases
 - Substances w/ weak IMF (LDF) tend to be gases at room temp (N₂); substances w/ strong IMF (hydrogen bonds) tend to be liquids at room temp (H₂O)
 - Ionic substances do not experience IMF - since ionic bonds are stronger than IMF, ionic substances are usually solids at room temp
- Vapor pressure
 - Molecules in a liquid are in constant motion - if they hit the surface of the liquid with enough kinetic energy, they can escape the IMF holding them to other molecules and transition into the gas phase
 - Vaporization (NOT boiling) - no outside energy is added
 - Temperature and vapor pressure are directly proportional
 - At the same temp, vapor pressure is dependent on strength of IMF (stronger IMF, lower vapor pressure)
- Solution separation
 - Solutes and solvents - like dissolves like
 - Paper chromatography
 - Piece of filter paper with substance on the bottom is dipped in water
 - More polar components of substance travel further up the filter paper with the polar water
 - Distance substance travels up the paper measured by retention/retardation factor $R_f = \frac{\text{distance traveled by solute - substance being separated}}{\text{distance traveled by solvent front - water}}$
 - Stronger attraction - larger R_f
 - Column chromatography
 - Column is packed with a stationary substance
 - separable solution (analyte) is injected, adhering to stationary phase
 - another solution (eluent - liquid/gas) is injected into column
 - more attracted analyte molecules will move through faster and leave column first
 - Distillation
 - Takes advantage of different boiling points of substances by boiling a mixture at an intermediate point

- Vapor is collected, cooled, and condensed back to a liquid separate of leftover liquid
- Kinetic molecular theory
 - Kinetic energy of a single gas molecule: $KE = \frac{1}{2} mv^2$
 - Average kinetic energy of a gas depends on the temperature (directly proportional), not the identity of the gas (different gases will have same KE at same temp)
 - Ideal gases have insignificant volume of molecules, no forces of attraction b/w molecules, and are in constant motion without losing KE
 - Deviations occur at low temperatures or high pressures (gas molecules are packed too tightly together)
 - Volume of gas molecules becomes significant (less free space for molecules to move around than predicted)
 - Gas molecules attract one another and stick together (real pressure is smaller than predicted pressure)
 - Maxwell-boltzman diagrams
 - Higher temp \rightarrow greater KE \rightarrow greater range of velocity
 - Smaller masses, greater velocities to have same KE
 - Effusion
 - Rate at which a gas escapes from a container through microscopic holes
 - High to low pressure
 - Greater speed, greater temp, greater rate of effusion
 - If at same temp, gas w/ lower molar mass will effuse first
- Equations
 - Ideal gas equation: $PV = nRT$
 - $R=0.0821$
 - Combined gas law: $P_1V_1/T_1 = P_2V_2/T_2$
 - Dalton's law: $P(\text{total}) = P_a + P_b + P_c + \dots$
 - Partial pressure: $P_a = P(\text{total}) * (\text{moles of gas A}) / (\text{total moles of gas})$
 - Density: $D = m/V$
 - From ideal gas law: Molar mass = DRT/P
 - Electromagnetic spectrum
 - $E=hv$
 - E = energy change; h = Planck's constant 6.626×10^{-34} ; v = frequency
 - $C = \lambda * v$
 - C = speed of light 2.998×10^8 ; v = frequency; λ = wavelength

- Beer's law: $A = abc$
 - A = absorbance; a = molar absorptivity (constant depending on solution); b = path length of light through solution (constant); c = concentration of solution
 - Colorimetry - direct relationship b/w concentration and absorbance

IV. Chemical Reactions

- Types of reactions
 - Synthesis: everything combines to form one compound
 - Decomposition: one compound + heat is split into multiple elements/compounds
 - Acid-base rxn: Acid + base \rightarrow water + salt
 - Oxidation-reduction (redox) rxn: changes the oxidation state of some species
 - Combustion: substance w/ H and C + $O_2 \rightarrow CO_2 + H_2O$
 - Precipitation: aqueous solutions \rightarrow insoluble salt (+ more aq sometimes)
 - Can be written as net ionic - Those free ions not in net ionic are spectator ions
- Solubility rules
 - Alkali metal cations or ammonium (NH_4^+) cations are ALWAYS soluble
 - Compounds with a nitrate (NO_3^-) anion are ALWAYS soluble
- Common polyatomic ions

Common Polyatomic Ions			
$C_2H_3O_2^-$	acetate	OH^-	hydroxide
NH_4^+	ammonium	ClO^-	hypochlorite
CO_3^{2-}	carbonate	NO_3^-	nitrate
ClO_3^-	chlorate	NO_2^-	nitrite
ClO_2^-	chlorite	$C_2O_4^{2-}$	oxalate
CrO_4^{2-}	chromate	ClO_4^-	perchlorate
CN^-	cyanide	MnO_4^-	permanganate
$Cr_2O_7^{2-}$	dichromate	PO_4^{3-}	phosphate
HCO_3^-	bicarbonate	SO_4^{2-}	sulfate
HSO_4^-	bisulfate	SO_3^{2-}	sulfite
HSO_3^-	bisulfite		

- Calculations
 - Percent error: $100 * \frac{\text{abs}(\text{experimental} - \text{expected})}{\text{expected}}$

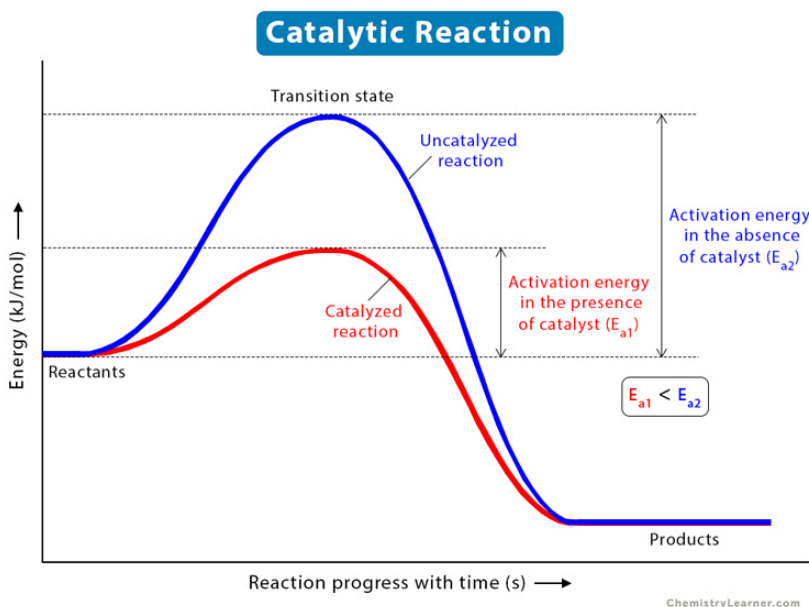
- Combustion analysis - use law of conservation of mass (if x g of CO₂ is produced, find g of C which will be starting amt)
- Gravimetric analysis - when asked to determine the identity of a certain compound, find g of component produced, then use mass percent (g found / total sample mass) and compare to mass percent of options (molar mass of component / molar mass of entire compound)
- Oxidation states
 - Neutral atoms not bonded to other atoms have an oxidation state of 0
 - Monoatomic ions have an oxidation state equal to the charge on that ion (ex. Zn²⁺ will be +2)
 - Oxygen is -2 (EXCEPTION: in hydrogen peroxide, H₂O₂, O is -1)
 - Hydrogen is +1 w/ nonmetals, -1 with metals
 - In absence of oxygen, most electronegative element in a compound will take an oxidation state equal to its usual charge (ex. F is -1 in CF₄)
 - IF none of the above rules apply, determine the oxidation state by adding up all elements' oxidation states to 0/charge on ion
 - C, N, S, P frequently vary oxidation states (low electronegativity)
- Redox reactions
 - Write full rxn as 2 half reactions (oxidation and reduction; OIL RIG)
 - Add H₂O to compensate for oxygen on one side
 - Add H⁺ to compensate for H from H₂O on other side
 - Balance 2 half rxns to have the same number of electrons and add them together to produce one complete reaction
 - ACIDIC: stop here
 - BASIC: Add OH⁻ to both sides - enough for all H⁺ on one side to be converted to H₂O; then cancel out H₂O so it only remains on one side
- Acids and bases (briefly)
 - Color change signals the end of a titration (can be redox or acid/base)
 - Acids are capable of donating protons (H⁺); bases are capable of donating electrons
 - Species with the H⁺ ion are acids, same species but without H⁺ is a base - conjugate acid/base pairs
 - Water can act as an acid or base - amphoteric

V. Kinetics

- Rate law
 - $\text{Rate} = k [\text{A}]^x [\text{B}]^y [\text{C}]^z$

- Can calculate x, y, z via a table from $(\text{concentration factor})^x = (\text{rate factor})$
 - K is only dependent on temperature (always increases w/ T)
 - $K_{eq} = K_1 (\text{rate constant of forward rxn}) / K_2 (\text{rate constant of reverse rxn})$
 - K calculated by dividing any rate in table by the concentrations to their respective powers
 - Units for rate are M/s, units for conc are M \rightarrow calculate units for k from there
 - If $A + 2B + C \rightarrow D$; rate of formation of D = rate of disappearance of A and $C = 0.5 \times$ rate of disappearance of B
- Orders
 - Zero-order
 - Rate = k
 - Concentration vs time has slope -k
 - First-order
 - Rate = $k[A]$
 - $\ln[A]$ vs time has slope -k
 - $\ln[A]_t = -kt + \ln[A]_0$
 - Second-order
 - Rate = $k[A]^2$
 - $1/[A]$ vs time has slope k
 - $1/[A]_t = kt + 1/[A]_0$
 - Half-life
 - First order reactions only have a constant half life
 - $t_{1/2} = \ln(2)/k = 0.693/k$
- Collision theory
 - Chemical reactions occur because reactants are constantly moving and colliding with one another
 - When reactants collide with sufficient energy (activation energy E_a), a reaction occurs
 - Gaseous/aqueous: increased concentration increases rate of reaction (more likely to collide)
 - Stirring increases reaction rate for heterogeneous mixtures (causing heterogeneous mixture to move around increases collisions; insignificant once the mixture becomes homogeneous due to the number of collisions happening due to inherent motion of aq molecules)

- Greater temp increases reaction rate (greater fraction of reactant molecules has sufficient energy to exceed activation energy barrier - vertical line on Maxwell-Boltzmann w/ multiple temps)
- Reactions only occur if reactants collide with correct orientation to break the right bonds
- Reaction energy profile

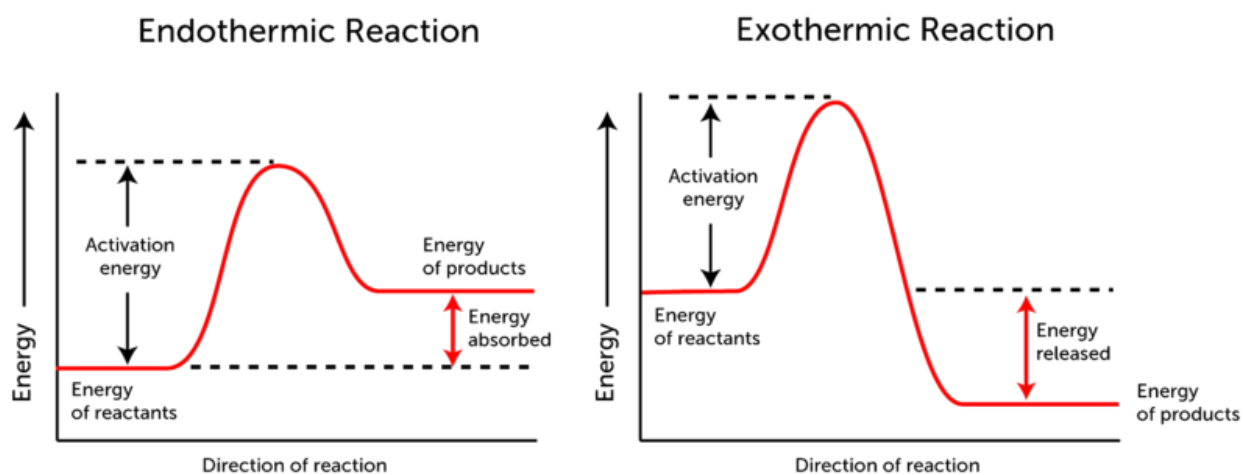


- Reaction mechanisms
 - Species that are produced in a mechanism but are also fully consumed and do not appear in the balanced equation are intermediates
 - Adding up all mechanism steps and canceling out different species leads to the balanced rxn
 - Elementary steps w/ 2 reactants (even if they are the same) are bimolecular; elementary steps w/ 1 reactant are unimolecular
 - Speed is determined by slow step (rate determining step)
 - consistency is determined by slow step and those leading up to it
 - Make rate for slow step (ex. If $X + B \rightarrow Y$, rate = $k[X][B]$)
 - Substitute in rate for X from above equilibrium reaction
 - Compare to actual reaction's rate equation
 - Slow step has highest activation energy
- Catalysts
 - Catalysts increase rate of chemical reaction without being consumed in the process
 - Catalysts do not appear in balanced equation
 - In a reaction mechanism, catalysts enter first, then exit

- Catalysis (reaction with a catalyst)
 - Surface catalysis - reaction intermediate is formed
 - Enzyme catalysis - catalyst binds to reactants to reduce activation energy
 - Acid-base catalysis - reactants lose/gain protons to change reaction rate

VI. Thermodynamics

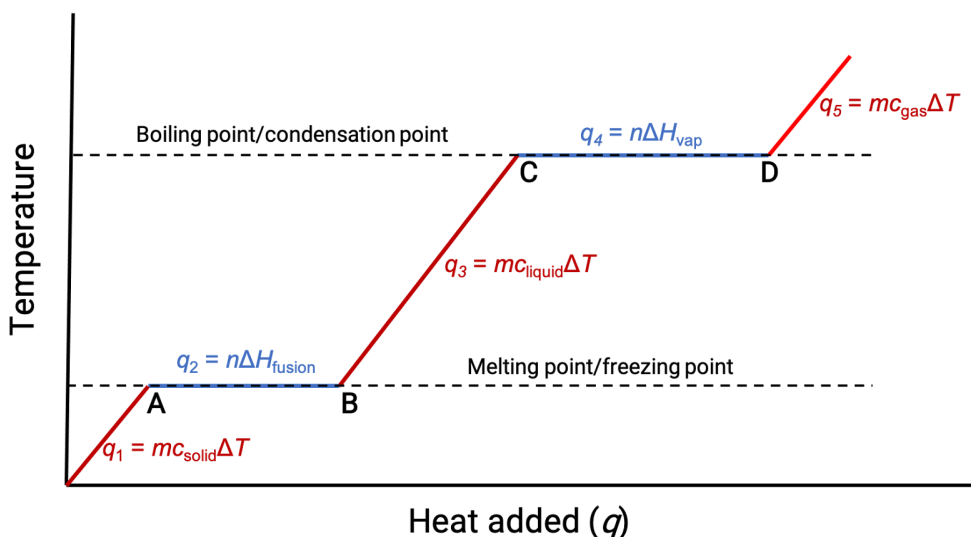
- Temperature/heat
 - Temperature is the average amount of kinetic energy due to molecular motion in a given substance
 - Heat is the energy flow between 2 different substances at different temperatures
 - First law of thermodynamics: energy can be neither created nor destroyed
 - When bonds are formed, energy is released; when bonds are broken, energy is absorbed
 - Exothermic - energy transferred from system to surroundings (ΔH is negative)
 - More energy is released when the product bonds form than is necessary to break reactant bonds
 - Endothermic - energy transferred from surroundings into system (ΔH is positive)
 - More energy is required to break reactant bonds than is released when bonds in products form
- Energy diagrams



- Enthalpy
 - Enthalpy of formation
 - Change in energy when one mole of a compound is formed from its component pure elements under standard conditions (25C/298K)
 - $\Delta H_f = \Delta H_f \text{ for products} - \Delta H_f \text{ for reactants}$
 - Multiply ΔH_f for each product/reactant by the coefficient

- If ΔH_f is negative, energy is released when the compound is formed, so the product is more stable (exothermic)
 - If ΔH_f is positive, energy is absorbed when the compound is formed, so the product is less stable than its constituent elements (endothermic)
 - Heat of formation is 0 when the pure element is in its standard state (ex. $H_2(g)$ or $F_2(g)$)
- Bond energy
 - $\Delta H (J) = \text{bond energies of reactants} - \text{bond energies of products}$
 - Multiply bond energies for each bond by the coefficient
- Hess's law
 - Finding ΔH for the overall reaction from knowing ΔH for the steps of the reaction
 - Flipping the equation flips the sign of ΔH
 - Multiplying/dividing the equation by a coefficient multiplies/divides ΔH by that coefficient
 - Adding/subtracting equations adds/subtracts their ΔH values
- Enthalpy of solution
 - Ionic substances dissolving in water
 - 1: Breaking of solute bonds - energy required is equal to the lattice energy (positive ΔH since bonds are being broken)
 - 2: Separation of solvent molecules - water molecules must spread out to make room for the solute ions (requires energy to weaken the IMF between water molecules - positive ΔH)
 - 3: Creation new attractions - free floating ions are attracted to the dipoles of water molecules (energy is released - negative ΔH)
 - Hydration energy = step 2 + step 3 energies
 - Coulombic energy - increases with charge magnitude, decreases as size increases
 - Enthalpy of solution = step 1 + 2 + 3 energies
- Phase changes
 - Solid to gas is sublimation, gas to solid is deposition
 - When vapor pressure equals the surrounding atmospheric pressure, the liquid boils - lower atmospheric pressure (high elevation) means a lower boiling point
 - Enthalpy of fusion - energy to melt a solid; heat of fusion - heat given off by a substance when it freezes
 - Enthalpy of vaporization - energy to turn a liquid into a gas; heat of vaporization - heat given off by a substance condensing

- IMF is stronger for a liquid than a gas, and for a solid than a liquid, and the stronger IMF is more stable, therefore going from a gas to a liquid or a liquid to a solid releases energy (exothermic)
- As heat is added to a substance, the temperature of the substance can increase OR it can change phases, but not both at once
 - When a substance is changing phases, the temperature of the substance remains constant
- Calorimetry
 - Specific heat - amount of heat required to raise the temperature of one gram of a substance by one degree C/K
 - Large specific heat - can absorb much heat without a significant temperature change
 - Low specific heat - quickly changes temperature
 - Heat added (J or cal) $q = mc\Delta T$
 - $q_1 = q_2$ for mixtures
 - Calorimetry - measurement of heat changes during chemical reactions
 - Find J from q, find mol from stoich, divide the two to find delta H
 - Delta H measured in J/mol
- Heating curves



- For problems where a solid completely melts or the like, add q from mc at to (moles) * (heat of fusion) for the total heat required for process to occur

VII. Equilibrium

- Keq
 - Reaction is at equilibrium when all concentrations stop changing

- Reaction does not stop - rate of forward and reverse reactions become equal
- All concentrations do NOT sum to initial concentration of reactants
 - In reaction $2A \rightarrow B$, concentration of A will decrease 2x as much as concentration of B increases
- Equilibrium expression/law of mass action
 - For the reaction $aA + bB \rightarrow cC + dD$: $K_{eq} = \frac{[C]^c * [D]^d}{[A]^a + [B]^b}$
 - [A], etc. are molar concentrations/partial pressures at equilibrium
 - Products in numerator, reactants in denominator
 - Coefficients in balanced equation become exponents in equilibrium expression
 - Only gaseous and aqueous species are included in the expression
 - K_{eq} has no units
 - $K > 1$ favors forward rxn; $K < 1$ favors reverse rxn
- Different equilibrium constants
 - K_c for molar concentrations
 - K_p for partial pressures
 - K_{sp} is solubility product (no denominator because reactants are solids)
 - K_a is acid dissociation constant for weak acids
 - K_b is base dissociation constant for weak bases
 - K_w describes the ionization of water ($K_w = 1 * 10^{-14}$)
- Manipulating K_{eq}
 - K_{eq} for a flipped reaction is the reciprocal of K_{eq} for initial rxn
 - K_{eq} for a reaction multiplied by a coefficient is the initial K_{eq} to the power of the coefficient
 - K_{eq} for two reactions added together is their respective initial K_{eq} values multiplied together
- Le Chatelier's principle
 - Increasing concentration of reactants shifts rxn to favor products (forward) and vice versa
 - Increasing pressure increases partial pressure of all gases in container and shifts rxn to side with fewer gas molecules (moles of gas)
 - Increasing volume decreases pressure and vice versa
 - Adding a non-reacting gas (noble gas) to a non-rigid container causes the volume to increase while not changing total pressure
 - Adding a non-reacting gas to a rigid container would increase the total pressure of the container and not affect the partial pressures of other species - no reaction shift occurs

- Increasing temperature in an endothermic reaction shifts the rxn to favor products (forward); increasing temperature in an exothermic reaction shifts the rxn to favor reactants (reverse)
 - Treat “heat” as a reactant (endothermic) or product (exothermic) to see shifts like with concentration change
- Diluting aqueous equilibria shifts the rxn to favor the side with more aqueous species; removing water (evaporation) shifts the rxn to favor the side with less aqueous species
- Shifts caused by concentration/pressure are temporary shifts and do not change K_{eq} ; shifts caused by temperature permanently affects K_{eq} and ratio of products to reactants since it adds/removes energy from the system
- Reaction quotient Q
 - Q can be calculated at any point with current concentrations/pressures; K_{eq} can only be calculated with equilibrium values
 - For the reaction $aA + bB \rightarrow cC + dD$: $Q = \frac{[C]^c * [D]^d}{[A]^a + [B]^b}$
 - $[A]$, etc. are initial molar concentrations or partial pressures
 - If $Q < K$, rxn shifts right; if $Q > K$, rxn shifts left; if $Q = K$, rxn is at equilibrium
- Solubility
 - A salt is considered soluble if more than 1g can be dissolved in 100mL of water
 - Soluble salts are assumed to dissociate completely in aqueous solutions
 - Most solids become more soluble in a liquid as temp increases
 - Solubility product K_{sp}
 - For the reaction $A_aB_b(s) \rightleftharpoons aA^{b+}(aq) + bB^{a-}(aq)$: $K_{sp} = [A^{b+}]^a * [B^{a-}]^b$
 - Molar solubility is determined by subbing x , $2x$, $3x$, etc. in for concentrations in K_{sp} expression (x if coefficient is 1 in balanced reaction, $2x$ if coefficient is 2, etc.)
 - Molar solubility of a salt is equal to the concentration of any ion that occurs in a 1:1 ratio with the salt
 - Molar solubility typically increases with temperature since there is more energy available to force water molecules apart to make room for solute ions
 - Common ion effect
 - Newly added ions from a separate solution affect equilibrium of initial solution if some elements are present in both, even though newly added ions did not come from the initial compound
 - ex. Adding $NaCl$ to $AgCl$ affects Cl which affects $AgCl$ equilibrium)

VIII. Acids and Bases

- pH
 - Formulas
 - $\text{pH} = -\log([\text{H}^+])$
 - $\text{pOH} = -\log([\text{OH}^-])$
 - $\text{pK}_a = -\log(K_a)$
 - $\text{pK}_b = -\log(K_b)$
 - $\text{pK}_w = -\log(K_w)$
 - $[\text{H}^+] = [\text{OH}^-] \Rightarrow$ neutral, $\text{pH} = 7$
 - $[\text{H}^+] > [\text{OH}^-] \Rightarrow$ acidic, $\text{pH} < 7$
 - $[\text{H}^+] < [\text{OH}^-] \Rightarrow$ basic, $\text{pH} > 7$
 - Increasing pH means decreasing $[\text{H}^+]$ (less acidic solution) and vice versa

- Strong acids
 - Strong acids dissociate completely in water (rxn goes to completion); no equilibrium, eq constant, or dissociation constant
 - Important strong acids/bases

6 Strong Acids		6 Strong Bases	
HClO_4	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\text{Ca}(\text{OH})_2$	calcium hydroxide
HNO_3	nitric acid	$\text{Sr}(\text{OH})_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$\text{Ba}(\text{OH})_2$	barium hydroxide

- No tendency for reverse rxn to occur (\rightarrow not \rightleftharpoons) so conjugate base of a strong acid is very weak
 - pH of strong acid solution can be found directly from $[\text{H}^+]$ since it dissociates completely
 - Best conductors of electricity
- Weak acids
 - Weak acid + water causes a small fraction of its molecules to dissociate into H^+ and A^- (conjugate base) ions

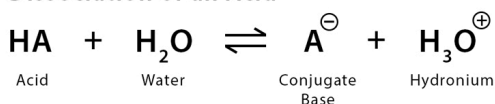
- Ka and Kb are measures of the strengths of strong/weak acids - equilibrium constants specific to acids/bases
 - Acid dissociation constant $K_a = \frac{[H^+][A^-]}{[HA]}$
 - Base dissociation constant $K_b = \frac{[HB^+][OH^-]}{[B]}$
- Greater K_a means a greater extent of dissociation and a stronger acid
- Greater K_b means a stronger base; base is not dissociating but rather accepting a proton (hydrogen ion) from an acid (protonates/ionizes, not dissociates)
- Set up RICE table w/ values of x for gained/lost concentration to solve for $[H^+]$ and pH from K_a or vice versa
- Acid Strength
 - Percent dissociation
 - The more H^+ ions an acid can donate (the easier it is for H^+ ions to break free), the stronger the acid is
 - Lower concentration \rightarrow higher percent dissociation; a greater concentration will lead to more of the conjugate base, making it easier for the reverse rxn to take place \rightarrow more HA present in solution and less H_3O^+ ions (lower percent dissociation)
 - Percent ionization: $\frac{[H_3O^+]}{[HA]} \times 100$
 - Acid/base structure
 - H is written in front of acids even if H is contained in the conjugate base because that H is attached to a (usually O) atom at the end of the molecule, making it easier for it to detach
 - H in a hydroxyl group ($-OH$) are dissociable due to O being much more electronegative than H
 - H bonded to C is almost never dissociable since H and C have similar electronegativity values and share their electrons equally
 - Solubility
 - Hydroxides dissolve well in solutions with low pH (more H^+ ions to react with OH^- and speed rxn along)
 - Polyprotic acids
 - Acids that can give up more than one hydrogen ion (ex. H_3PO_4)
 - More willing to give up first proton than others (after 1st, resulting negative charge attracts remaining protons more strongly)
 - H_3PO_4 is a stronger acid than $H_2PO_4^-$, HPO_4^{2-} , etc.
 - Amount of each succeeding acid decreases: $[H_3PO_4] > [H_2PO_4^-] > [HPO_4^{2-}] > [PO_4^{3-}]$
- K_w

- The equilibrium constant of water due to the following reaction: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 25 C for any aqueous solution
 - $\text{pH} + \text{pOH} = 14$
 - $K_w = 1 \times 10^{-14} = K_a \cdot K_b$
 - $\text{p}K_a + \text{p}K_b = 14$
- Knowing K_a for a weak acid, K_b can be found for its conjugate base
- pH is not limited to a 0-14 scale - very rarely is $\text{pH} > 14$ or < 0 , but it does occur at high concentrations
- Increase in temperature increases K_w (dissociation of water is endothermic) so $\text{p}K_w$ and pH decrease
- Neutralization reactions
 - When an acid and base mix, the acid donates protons to the base in a neutralization rxn
 - Strong acid + strong base
 - Both substances dissociate completely
 - Net ionic is always the creation of water: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$
 - All other ions are spectator ions
 - Strong acid + weak base
 - Strong acid (which dissociates completely) will donate a proton to the weak base
 - Product is conjugate acid of weak base
 - Ex. $\text{HCl} + \text{NH}_3$: Net ionic is $\text{H}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq})$
 - Weak acid + strong base
 - Strong base will accept protons from weak acid
 - Products are conjugate base of weak acid and water
 - Ex. $\text{HC}_2\text{H}_3\text{O}_2 + \text{NaOH}$: Net ionic is $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - Weak acid + weak base
 - Simple proton transfer reaction - acid gives protons to base
 - Ex. $\text{HC}_2\text{H}_3\text{O}_2 + \text{NH}_3$: Net ionic is $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{NH}_4^+(\text{aq})$
- Buffers
 - Solution with a very stable pH; acid/base can be added to a buffer solution without greatly affecting pH; gain/loss of water also does not change pH
 - Buffers are created by placing large amounts of a weak acid/base into a solution with its conjugate (salt)
 - Weak acid and conjugate base remain in solution together without neutralizing each other

- Presence of the conjugate pair makes the buffer effective
- If enough strong acid/base is added that all of the acid or conjugate base is reacted, the buffer breaks
- Higher concentrations of the conjugate pair resist pH change (better buffers) better than lower concentrations
- Henderson-Hasselbalch

Henderson Hasselbalch Equation

Dissociation of an Acid



Equation

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{A}^{\ominus}]}{[\text{HA}]}$$

pH : pH value of the solution

K_a : Dissociation constant of the acid

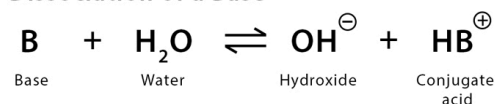
$[\text{A}^{\ominus}]$: Concentration of the conjugate base (A^{\ominus})

$[\text{HA}]$: Concentration of the acid (HA)

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Henderson Hasselbalch Equation for Base

Dissociation of a Base



Equation

$$\text{pOH} = \text{pK}_b + \log_{10} \frac{[\text{HB}^{\oplus}]}{[\text{B}]}$$

pH : pH value of the solution

K_b : Dissociation constant of the base

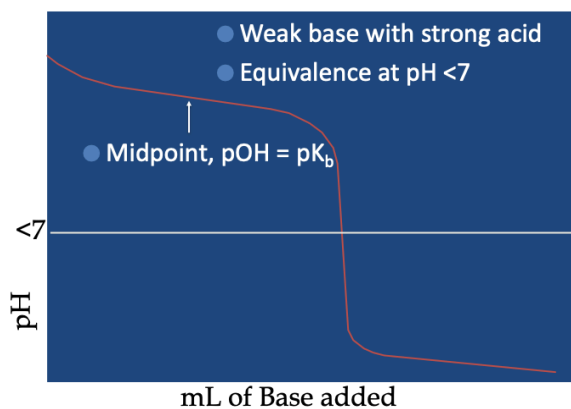
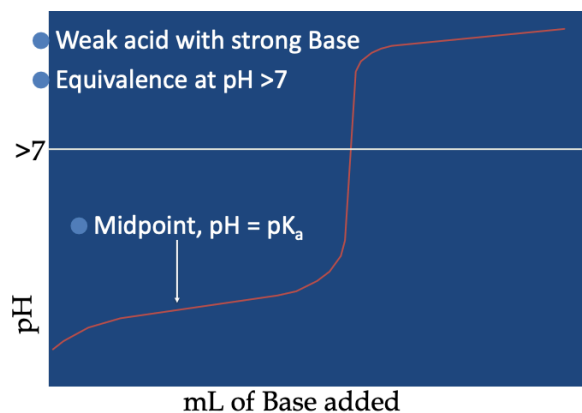
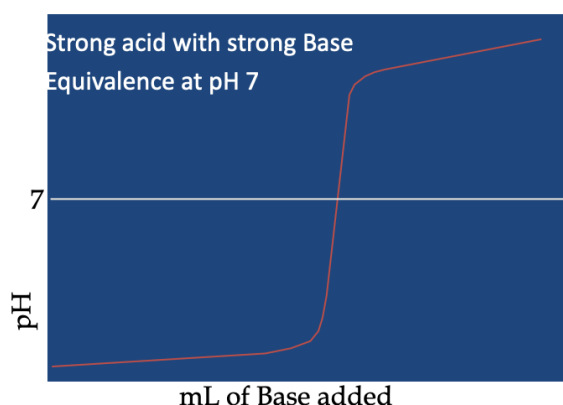
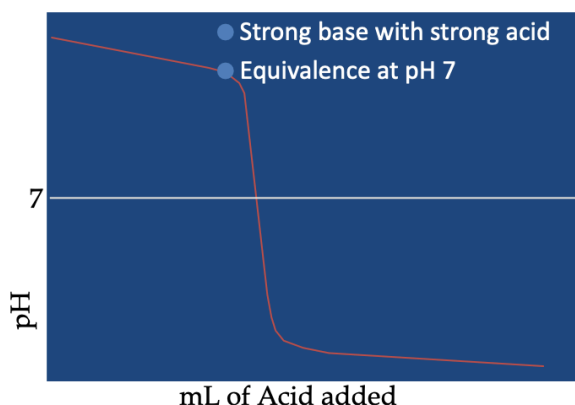
$[\text{HB}^{\oplus}]$: Concentration of the conjugate acid (HB^{\oplus})

$[\text{B}]$: Concentration of the base (B)

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- When concentrations of acid and conjugate base in a solution are the same, $\text{pH}=\text{pK}_a$ and $\text{pOH}=\text{pK}_b$
- Choosing an acid for a buffer solution requires choosing an acid with a pK_a close to the desired pH (almost equal amounts of acid and conjugate base; makes buffer flexible in neutralizing both added H^+ and OH^-)
- Buffers cannot be created from a very strong acid and its conjugate base because the conjugate base will be very weak and will not readily accept protons
- Indicators
 - Weak acids which change colors in certain pH ranges due to LeChatelier's principle
 - $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$
 - $K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$
 - Protonated HIn state must be a different color from deprotonated In^- state
 - Acidic environment causes excess H^+ to drive equilibrium to the left (color of HIn); basic environment causes excess OH^- to react with H^+ from indicator and drive reaction right (color of In^-)
 - Color change occurs when $[\text{HIn}] = [\text{In}^-]$; or $\text{pH} = \text{pK}_a$
 - Choose an indicator whose pK_a matches the pH at the titration's equivalence point
- Titration

- Neutralization reactions are performed by titration, where a base of known concentration is slowly added to an acid or vice versa
- Titration curves



- Midpoint also called half equivalence point occurs when $[HA] = [A^-]$ ($pH = pK_a$)
- Equivalence point occurs when just enough base has been added to neutralize all the acid initially present (equimolar)
- HA , A^- present before midpoint; A^- at midpoint, OH^- after midpoint

IX. Applications of Thermodynamics

- Entropy
 - Measure of randomness or dispersion of the system
 - 0 entropy is a solid crystal at 0K (has never been reached experimentally)
 - Standard entropies are calculated at 25 C
 - Standard entropy change $\Delta S = S \text{ for products} - S \text{ for reactants}$
 - If left side of a reaction has more motion, ΔS is negative; if right side has more motion ΔS is positive
- Gibbs free energy

- $\Delta G = G_f \text{ of products} - G_f \text{ of reactants}$
- Negative ΔG is spontaneous (thermodynamically favored); positive ΔG is nonspontaneous (thermodynamically unfavored); $\Delta G = 0$ means rxn is at equilibrium
- $\Delta G = \Delta H - T\Delta S$ (T in K)
- Favorability

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	Spontaneous at all T ($\Delta G < 0$)	Spontaneous at high T (when $T\Delta S$ is large)
$\Delta S < 0$	Spontaneous at low T (when $T\Delta S$ is small)	Non-spontaneous at all T ($\Delta G > 0$)

- ΔG in phase changes is 0 since at a normal phase transition temp, the substance is equally stable in either phase
 - Boiling/melting point can be solved for knowing ΔH and S since $\Delta G = 0$
- $\Delta G = -RT \ln K$ ($R = 8.314$, T in K, K_{eq})
- The larger the reduction potential on a half reaction, the more likely it is to occur
- Galvanic/voltaic cells
 - Favored redox rxn generates a flow of current
 - Oxidation at - anode (left); reduction at + cathode (right)
 - Electrons flow from anode to cathode (L to R)
 - Electrons released from oxidation pass to chamber to be consumed in reduction
 - Flow of electrons creates current
 - Salt bridge between two cells maintains electrical neutrality
 - positive cations from salt bridge solution flow to cathode which is losing positive charge (needs + to balance); negative anions from salt bridge solution flow to anode which is gaining positive charge (needs - to balance)

- Under standard conditions (1M solutions, 1 atm, 25 C), cell voltage is the same as total redox voltage
 - $K_{eq} \gg 1$, $Q = 1$
- Non standard conditions
 - If $Q=K_{eq}$, cell voltage drops to 0; increasing Q decreases cell potential and vice versa
 - Overall potential decreases as a reaction progresses (product conc increases, reactant conc decreases)
 - Nernst equation: $E_{cell} = E^0_{cell} - (RT/nF) \cdot \ln(Q)$ where n is # of electrons transferred (always positive)
- Electrolytic cells
 - Outside source of voltage is used to force an unfavored redox reaction to occur
 - Occur primarily in aqueous solutions (chemical dissolved in water; ion/water molecule is oxidized/reduced)
 - Compare reduction potential of cation with that of water (reduction) to determine which is reduced; compare oxidation potential of anion with that of water (oxidation) to determine which is oxidized
 - Then balance the 2 oxidation/reduction half reactions to form one net ionic equation
 - value for cell potential from the half reactions should always be negative
 - Oxidation at + anode (left); reduction at - cathode (right)
 - Signs change from galvanic cell setup
 - Electrons flow from anode to cathode (L to R)
 - + to - (instead of - to + like in galvanic cells)
 - Used for electroplating
 - $I = q/t$
 - Moles of electrons = coulombs/ 96500 C/mol
 - Moles of metal from moles of electrons (from metal half reaction)
 - Moles of metal -> grams
- Voltage and favorability
 - Redox reaction is favored if potential is positive
 - $\Delta G = -n \cdot F \cdot E^0$ (n is positive # of electrons transferred, F is 96500, E^0 is standard cell potential in V = J/C)

X. Laboratory Overview

- Weighing hot objects on a scale creates convection currents, making object appear lighter than it truly is
- Not rinsing a buret in a titration leads to it being diluted