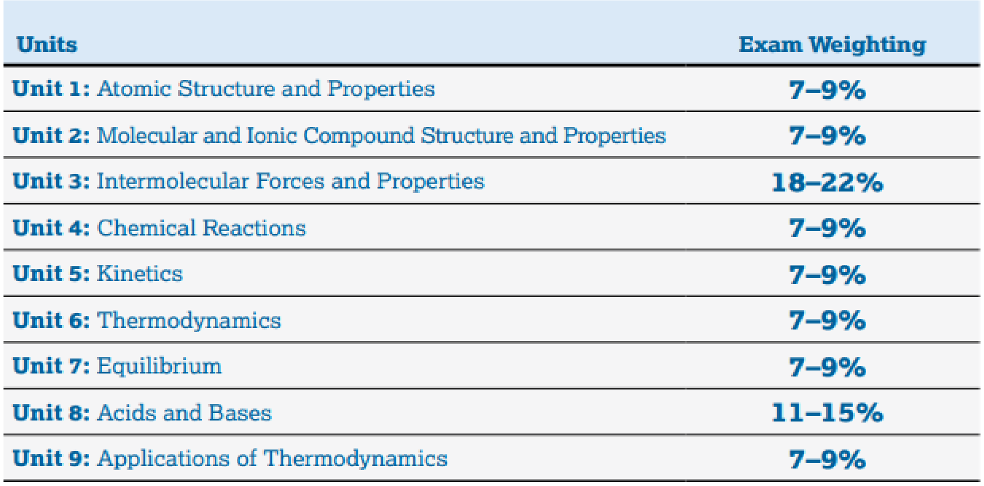
AP CHEMISTRY REVIEW



Units	Exam Weighting
Unit 1: Atomic Structure and Properties	7–9%
Unit 2: Molecular and Ionic Compound Structure and Properties	7–9%
Unit 3: Intermolecular Forces and Properties	18–22%
Unit 4: Chemical Reactions	7–9%
Unit 5: Kinetics	7–9%
Unit 6: Thermodynamics	7–9%
Unit 7: Equilibrium	7–9%
Unit 8: Acids and Bases	11–15%
Unit 9: Applications of Thermodynamics	7–9%

DO NOT WASTE TIME ON QUESTIONS YOU DO NOT KNOW.

TEST TIPS- MC:

- Aim to answer 37/60 MC questions correctly. Then relax and go back to the questions you skipped
- Cross out ridiculous answers; answers that do not make sense (ex: pH of acid/base)
- Know how to do stoichiometry/dimensional analysis
- Pay close attention to units!

HELPFUL EQUATIONS NOT ON EQUATION SHEET

For dilutions: $M_1V_1 = M_2V_2$

Similarly, for acid base titrations at equivalence point (only if 1:1 ratio): $M_AV_A = M_BV_B$

For gases: $(P_1V_1)/(n_1T_1) = (P_2V_2)/(n_2T_2)$

$P_{atm} = P_g + P_{water}$

$MW = dRT/P$

TEST TIPS- FRQ

- If you get stuck on a part of a question and there are subsequent parts that rely on that answer, assume a number (or explanation) and then use that number on the subsequent parts. You will lose the point(s) on the original part but can still earn credit on the other parts.
- If question says "Include units" then the correct units are worth 1 pt.
- Use. Your. Equation. Sheet!
- All explanation questions can be answered in 2-3 sentences max. Get to the point.
- ALL parts on the FRQ section are worth 1-2 points. No more. Use your time wisely.

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Unit 1: ATOMIC STRUCTURE AND PROPERTIES

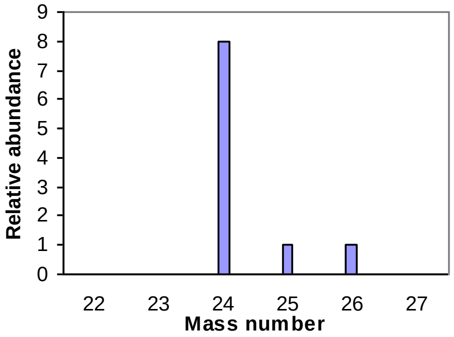
1.1 Mass and molar mass **1.2** Mass spectroscopy **1.3** elemental composition of pure substances **1.4** Composition of mixtures **1.5** Atomic Structure and electron configuration **1.6** photoelectron spectroscopy **1.7** period trends **1.8** Valence Electrons and ionic compounds

PERIODIC TRENDS: Electronegativity, Ionization energy, atomic radius
Two main explanations:

- Nuclear charge: Going across the periodic table, nuclear charge (number of protons) increases. This:
  - Causes radius to decrease because electrons are being bound tighter.
  - Causes ionization to increases because electrons are being held on by protons.
- Distance of valence electrons from nucleus: As you go down the periodic table, the number of valence shells increases. This:
  - Causes the radius to get larger
  - Causes ionization energy to decrease because electrons are further from nucleus and are therefore not held on by nucleus as well.

If neither one of those two explanations work (rarely), then use your knowledge of electrons and electron configuration as best you can.
Cations are SMALLER than atoms, because when an atom loses an electron(s) there is less electron-electron repulsion or loss of an energy level.
Anions are LARGER than their atoms, because when atoms gain electrons this causes more electron-electron repulsion.

MASS SPECTROSCOPY: Shows you relative abundance of isotopes. Compare peak height for percent abundance. The isotope below would have an atomic mass slightly greater (but close to) 24. This is because the isotope with mass number 24 is the most abundance. The average of all the mass numbers and their relative abundance is the atomic mass for that element.



PES (PHOTOELECTRON SPECTROSCOPY

- Peak height= # of electrons in sublevel
- Peak location indicates sublevel (larger binding energy would indicate a sublevel closer to nucleus)

COMBUSTION ANALYSIS: This is just stoichiometry.

Generic Combustion reaction

$C_xH_y(O)_z + O_2 \rightarrow CO_2 + H_2O$

1. Find mass of carbon: All of the carbon in carbon dioxide cam from the compound burned
2. Find mass of hydrogen: All of the hydrogen in water came from the compound burned
3. Find mass of oxygen by subtraction (mass left over)
4. Calculate empirical formula

This method can be applied to other reactions if it makes sense.

DON'T FORGET:

- Density = mass/volume
- The % composition by mass for a pure compound does not change.
- 10^9 nanometers = 1 meter
- In electron configuration:
  - d sub level is one energy level less than the period.
  - Remove electrons from s sublevel before d sublevel for transition metals.
- Isotopes of an element have the same number of protons, but different numbers of neutrons.
- Metals are on the left side of the zig-zag line and nonmetals are on the right side of this line on the periodic table.

PERCENT COMPOSITION/EMPIRICAL AND MOLECULAR FORMULA

- The % composition by mass for a pure compound does not change.
- Empirical formula rhyme→ % to mass, mass to mole, divide by small, times until whole…Get the simplest whole # ratio of the moles (or atoms) in the compound.
- The molecular formula for a compound is a whole # multiple of the empirical formula ratio.

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Unit 2: MOLECULAR/IONIC STRUCTURE AND PROPERTIES

2.1 Types of chemical bonds **2.2** Intramolecular force and potential energy **2.3** Structure of ionic solids **2.4** Structure of metals and alloys **2.6** resonance and formal charge **2.7** VSEPR and Bond hybridization

VSEPR:
This is an easy point. Review your molecular geometries and bond angles!

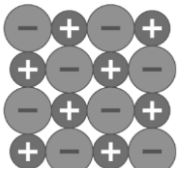
FORMAL CHARGE:
The molecule with the lowest formal charge is the most likely structure

Do not find unless prompted

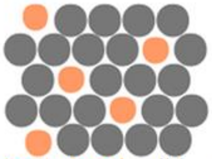
$$\left(\begin{array}{l}\text{Formal Charge on an atom}\\ \text{within a Lewis structure}\end{array}\right)=\left(\begin{array}{l}\text{The number of}\\ \text{valence electrons}\\ \text{around that atom}\\ \text{in the free atom}\end{array}\right)-\left(\begin{array}{l}\text{The number of}\\ \text{non bonding electrons}\\ \text{around that atom}\\ \text{in Lewis structure}\end{array}\right)-\frac{1}{2}\left(\begin{array}{l}\text{The number of}\\ \text{bonding electrons}\\ \text{around that atom}\\ \text{in Lewis structure}\end{array}\right)$$

STRUCTURE OF IONIC SOLIDS:
Strength of Ionic bond increases when:

- Ions are highly charged (dominate)
- Ions are small

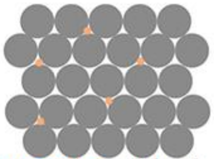


ALLOYS
- **Interstitial alloy:** when atoms with small enough radius sits in the "holes" of the metallic lattice
- **Substitutional alloy:** atom is similar in radius and replaces metal atom sin the metallic lattice



Substitutional solid soln.
(e.g., Cu in Ni)

OR



Interstitial solid soln.
(e.g., C in Fe)

METALLIC BONDING
- Electrons are mobile throughout the metallic cations. This allows metals to conduct electricity
- Metals also tend to be malleable, ductile, and lustrous

LEWIS DIAGRAM
Another easy point. Readers are very likely to give the point if:

- All atoms have OCTECTS (8 electrons). This does not include hydrogen, beryllium, boron
- The molecule has the correct number of total valence electrons

RESONANCE:
Occurs when more than one valid lewis structure can be drawn for a molecule.

- The actual molecule has a bond length that is average of the bond lengths in the resonance structures.
- Do not draw unless prompted

HYBRIDIZATION
Electron domains

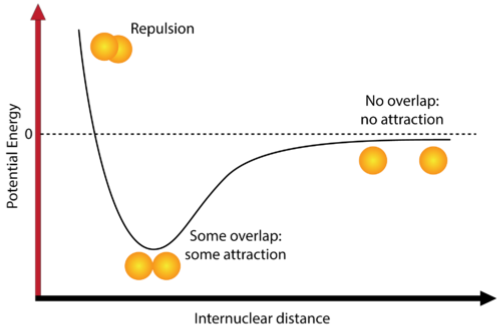
- Bonds (single, double, triple all are ONE domain)
- Lone pair of electron

sp: only two domains

sp^2: three domains

sp^3: four domains

INTRAMOLECULAR FORCE AND POTENTIAL ENERGY



The minimum potential energy represents the ideal bond length

DON'T FORGET:
- Covalent bonds are formed between two nonmetals sharing electrons.
- Ionic bonds are formed when a metal transfers electrons to a nonmetal and the opposite charges attract.
- The greater the electronegativity difference between 2 atoms, the more polar the bond becomes.
- $H_2O_2N_2Cl_2Br_2I_2F_2$ -- the diatomic elements.
- Asymmetrical molecules = dipoles <u>DO NOT</u> cancel = polar molecule;
  symmetrical = dipoles cancel = nonpolar molecule

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Unit 3:

INTERMOLECULAR FORCES AND PROPERTIES

3.1 Intermolecular Forces **3.2** properties of solids **3.3** solids, liquids and gases **3.4** ideal gas law **3.5** kinetic molecular theory **3.6** deviation from ideal gas law **3.7** solutions and mixtures **3.8** representations of solutions **3.9** separation of solutions and mixture chromatography **3.10** solubility **3.12** photoelectric effect **3.13** beer-lambert law

SOLUBILITY

Substances with similar IMF strengths will be miscible in one another.

If one substance has a much weaker IMF, it will not be able to overcome the IMF in the other substance and the two substances will then be immiscible.

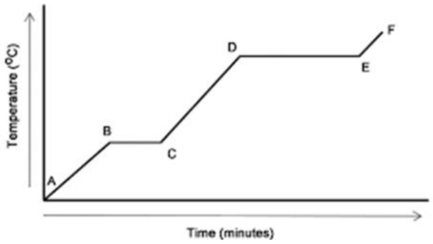
SOLUBILITY RULES

All sodium, potassium, ammonium and nitrate salts are soluble in water

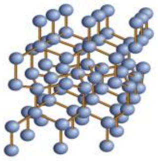
HEAT CURVE

Note the temperature does not change during phase changes. This is because the energy is being to overcome IMF. Bonds are NOT broken during phase changes!

- Use dimensional analysis during phase changes
- Use $q=cm\Delta T$ for all other points



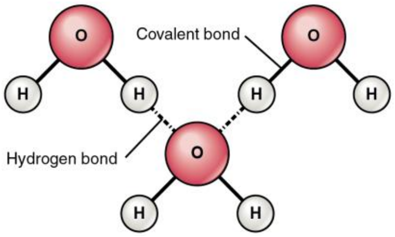
COVALENT NETWORK SOLIDS



- Common examples: Diamond, graphite, or binary compounds (like silicon dioxide or silicon carbide
- These will have **VERY** high melting points due to strong, repeated covalent interactions

INTERMOLECULAR FORCES

- London Dispersion force (LDF): All molecules experience some degree of LDF. In general, the larger the molecule, the more electrons that molecule has leading to stronger the LDFs.
- Dipole-dipole interaction: IMF between polar molecular. This force gets stronger as molecules get more polar
- Hydrogen bonding: generally the strongest IMF. Substances with hydrogen bonded to an **oxygen, nitrogen, or fluorine** (this is not the hydrogen bond! See picture below) can from hydrogen bonds with another electronegative atom. These are just a specific example of dipole-dipole interactions)
- Ion-dipole interaction: The IMF between an ion and polar molecular. See: "Dissolution process" box
- General strength from weakest to strongest: LDF, dipole-dipole, hydrogen bonding, ion-dipole
    - HOWEVER, do NOT assume this is always true! Look at what the data is telling you!
    - For example, sometimes a molecule is so large that the LDF experienced is greater than a polar molecule with dipole-dipole interactions.
- Physical properties tell you a lot about the strength of IMF. Stronger IMF generally leads to higher BP, lower vapor pressure, lower volatility, and higher viscosity in liquids.
- Always list all IMF's LDF ← dipole-dipole ←hydrogen bonding (IMF also includes what is to the left)



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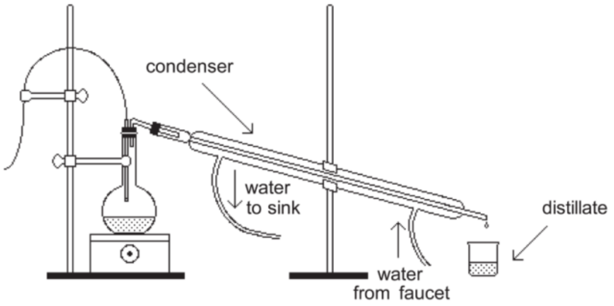
SEPARATION OF MIXTURES

Chromatography: Separates mixtures based on difference in polarity.

- Paper Chromatography: The component that is most similar to the polarity of "mobile phase" will move up more (greater R_f value)
    - Read carefully to determine polarity of mobile phase and stationary phase.
- Thin Layer Chromatography: Works similarly. The stationary phase is typically silica (polar)

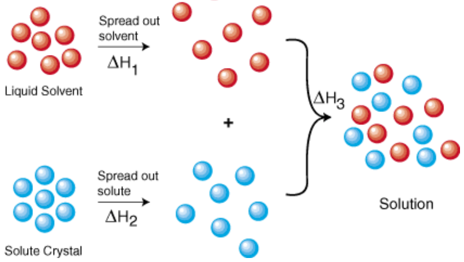
Distillation: Separates mixtures based on differences in boiling points.

- The substance with the lower boiling point will be separated out first.



DISSOLUTION PROCESS

Both bonds and IMF are both broken and formed in the process of dissolving salts in water. Be able to identify endothermic/exothermic processes happening (more in unit 6)



*from spark notes of all places

BEER-LAMBERT LAW

- Cannot use for colorless solutions
- The more a color solution absorbs light, the more concentrated that solution.
    - You can quantify this relationship.

$$A = \varepsilon bc$$

- If you plot Absorbance v.s concentration, the slope of the line is (molar absorptivity) x (pathlength)

GASES

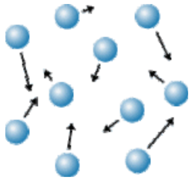
On multiple choice

- Round and estimate your answers
- Know the relationship between pressure, volume, temperature, and moles of a gas
- Use common sense and get rid of answers that do not make sense.

On Free response

- Use the equations given to you on your equation sheet! And watch your units.
- Use the correct r constant

- $Mw = dRT/P$ "dirty pee"
- Do NOT use 22.4 L = 1 mol unless at STP
    - Otherwise, use $PV=nRT$.
    - Use moles in stoichiometry. Seriously, this equation is you best friend.



Temperature is a measure of the **average** kinetic energy of particles in a gas, but this does not mean each particle has the same speed (as shown by vectors)

DON'T FORGET

- The more molar mass a gas has, the slower it moves at a given temperature.
- Temperature = Average Kinetic Energy (Gases at the same temperature have the same average kinetic energy.)
- When collecting a gas by water displacement: $P_{total} = P_{dry\ gas} + P_{water\ vapor}$
- Real gases behave most like an ideal gas at high temperature and at low pressure.
    - The more polar a gas is and the larger a gas is, the more it will **deviate** from ideal behavior.
    - Consequently, small, nonpolar gases are the most ideal.
- Molecular solids have low melting/boiling points, and they do not conduct electricity.
- Ionic solids have high melting/boiling points, and don't conduct electricity as a solid, but DO conduct as a liquid or (aq).

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Unit 4: CHEMICAL REACTIONS

4.1 Introduction for Reactions **4.2** Net Ionic Equations **4.3** Representations of reactions **4.4** Physical and Chemical Changes **4.5** Stoichiometry **4.6** Introduction to Titrations **4.7** Types of Chemical Reactions **4.8** Intro to acid-base Reactions **4.9** Redox Reactions

CHEMICAL REACTION

$aA + bB \rightarrow cC + dD$

where A and B are the reactants and C and D are the products. a, b, c, d isthe stoichiometry ratio in which reactants react and products are formed.

STOICHIOMETRY

1. Convert to moles
2. Mole ratio
3. Convert to the units you need

Remember ratio within ionic compound is important as well.

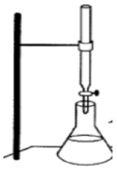
PARTICLE DIAGRAM TIPS

- Make sure charge is always balanced
- Stoichiometric ratio
- See if anything is in excess

TITRATIONS

Titrant: Solution of known concentration (in the buret)

Analyte: Solution being analyzed



At equivalence point,
MOLES OF TITRANT = MOLES OF ANALYTE

Choosing an indicator:

- For acid-base titrations, use an indicator that changes color at the pH of equivalence point
- For Redox titrations: $KMnO_4$ often is the titrant because it changes color near equivalence point (so indicator needed)

NET IONIC EQUATIONS

- Precipitation reactions:
  $A^{x+}(aq) + B^{y-}(aq) \rightarrow A_yB_{x(s)}$
- Acid base reactions:
  - Strong acid, use H^+
  - Strong base, use OH^-
  - Weak acid and weak base, write the entire formula.
- Solubility rules: Compounds containing NH_4^+, K^+, Na^+, and NO_3^- are soluble. These ions will be spectators and would not be included in any net ionic equation

TYPES OF REACTIONS

ACID BASE REACTIONS: involve the transfer of one ore more protons between chemical species

PRECIPITATION reactions: involves mixing solutions with soluble ions to produce an insoluble product

REDOX REACTIONS: involve the transfer of electrons.

Ex) combustion reactions

ASSIGNING OXIDATION NUMBERS

1. The oxidation number of an uncombined element is always zero
2. A monatomic ion's oxidation number is equal to charge
3. When elements are not in their ground state, assign oxidation numbers **in this order.**
4. F = -1
   O= -2
   H= +1 (unless metal hydride; H=-1)
   group 1 and 2 are +1 and +2, respectively
5. The sum of oxidation numbers equals the charge of the compound.

Oxidation: Electrons are lost (oil)
Reduction: Electrons are gained (rig)

Redox reactions involve BOTH oxidation and reduction

PHYSICAL CHANGES

Involves only changes in intermolecular interactions

CHEMICAL CHANGES

Involves the breaking or forming of bonds

Signs of chemical reaction (1) color change (2) production of a gas (3) production of a precipitate (4) energy released in the form of heat or light (5) color change

THE GREAT DEBATE: IS THE DISSOLUTION OF SALT IN WATER PHYSICAL OR CHEMICAL?

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Unit 5: KINETICS

5.1 Reaction rates **5.2** Introduction to rate law **5.3** concentration changes over time **5.4** elementary reactions **5.5** collision model **5.6** reaction energy profile **5.7** introduction to reaction mechanisms **5.8** reaction mechanism and rate law **5.9** steady-state approximation **5.10** multistep reaction energy profile **5.11** catalysis

COLLISION MODEL

1. The reactants come into contact (the collide)
2. Collisions are met with a certain minimum energy, known as **activation energy, E_a**
3. A collision has a correct molecular orientation.

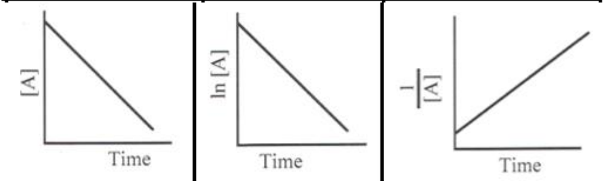
RATE CONSTANT, K

The units for the rate constant is determined by the overall order of the reaction.

$$\boxed{\frac{\text{liters}^{(\text{overall order} - 1)}}{\text{moles}^{(\text{overall order} - 1)} \times (\text{the unit for time})}}$$

INTEGRATED RATE LAWS

Zero Order	First Order	Second Order
$[A] = -kt + [Ao]$	$\ln[A] = -kt + \ln[Ao]$	$\frac{1}{[A]} = kt + \frac{1}{[Ao]}$



- The graph that yields the straight line determines the order of the reactant.
- The slope of the straight line is the rate constant, k.
- For first order reactions, if you plot [A] v.s time you get a half-life

$$t_{1/2} = \frac{0.693}{k}$$

DON'T FORGET

1. Ways to speed up a reaction: (1) Add a catalyst. (2) Increase reactant concentration. (3) Increase surface area. (4) Increase pressure of gases. (5) increase temperature.
2. The taller the "hill" (or activation energy) the slower the reaction.
3. In reaction mechanisms:
   - Intermediates are produced in one step and used up in a later step.
   - Catalysts are used up in one step, and produced in a later step.

DETERMINING RATE LAW

Rate = k $[A]^x[B]^y$

- k is the specific rate constant. The faster a reaction, the larger the k value. Rate constant units will change, see "rate constant" box
- [A] and [B] represent the concentrations of reactants A and B in mol/L
- x and y can **only be determined by analyzing experimental data**.
  - Exponents are usually positive integers. Rarely are fractional or negative integers
- **First Order:** If doubling the initial [concentration] of a reactant causes the initial rate to double.
- **Second Order:** if doubling the initial [concentration] of a reactant causes initial rate to quadruple
- **Third order:** If doubling the initial [concentration] of a reactant causes the initial rate to increase 8 times **uncommon**
- **Zero order:** If doubling the initial [concentration] of a reactant does not change the initial rate
- **Best way of determining order:** $Z^n = Y$
  - Where Z is how you manipulate the concentration and Y is how the rate is affected. The rate order will be n.
  - For example, if you triple concentration and rate increases by 9 times, then n has to be 2. So the reaction is second order.

    $3^n = 9$, n is 2.

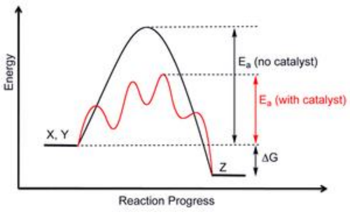
RATE LAW FROM MECHANISMS

- Mechanisms can be shown for reactions that do not happen in a single step.
- Rate law can be determined (from coefficients) for the slow step
  - If the slow step contains an intermediate, you must use **steady state approximation**

$$\begin{array}{lll}
\text{Step 1:} & NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) & \text{(slow)} \\
\text{Step 2:} & NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) & \text{(fast)} \\
\hline
\text{Overall:} & NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) &
\end{array}$$

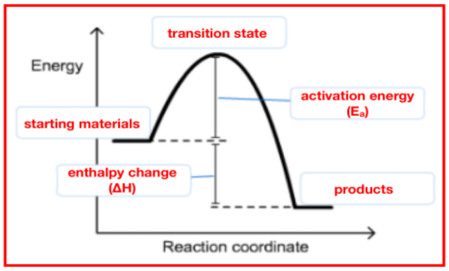
Catalysis

- Catalysts increase the rate of reaction by providing a new mechanism.
- The new mechanism will have a
  - lower overall activation energy and/or
  - Higher frequency of collisions

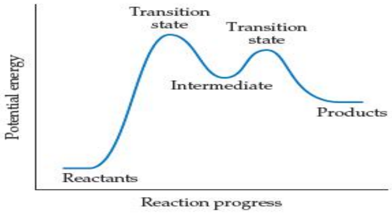


ENERGY PROFILES

Single Step



Multi-step



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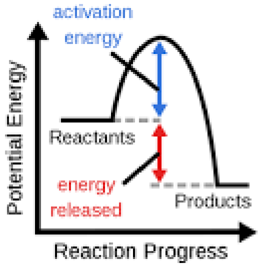
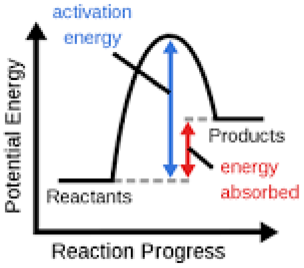
Unit 6: THERMOCHEMISTRY

6.1 endothermic and exothermic processes **6.2** energy diagrams **6.3** heat transfer and thermal equilibrium **6.4** heat capacity and calorimetry **6.5** energy of phase changes **6.6** introduction enthalpy of reaction **6.7** bond enthalpies **6.8** enthalpy of formations **6.9** hess's Law

ENERGY DIAGRAMS



Exothermic reaction



Endothermic reaction

HEAT CAPACITY

- $q = cm\Delta T$, units for heat (q) are usually in joules
- The higher a substance's heat capacity, the less the temperature will change
- For solutions:
    - make sure to plug the mass of the entire solution
    - often times, you will be told to assume the specific heat of the solution is just that of water

ENTHALPIES, ΔH^o

- Units are typically kJ/mol_{rxn}
    - mol_{rxn} is very important! You need to be mindful of coefficients
- Know your enthalpy definitions: heat of formation, heat of combustion, heat of vaporization, heat of fusion
- $\Delta H = q/mol_{rxn}$ * be sure to be mindful of units

CALORIMETRY

- The measure of heat transfer
- $cm\Delta T = cm\Delta T$
- metal and water
    - heat lost by the metal is gained by the water!
- Make a solution
    - if the temperature of the water increases, this means the dissolution process is EXOTHERMIC
    - if the temperature of the water decreases, the dissolution process is ENDOTHERMIC

HEAT CURVE

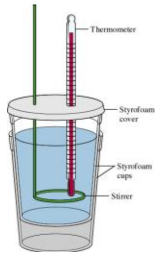
*look at "heat curve" box from unit 3. Also applicable here 😊

HEAT OF FORMATION

- If heats of formations are given to you, use the equation below to find heat of reaction

$$\Delta H^o_{rxn} = \sum \Delta H_f{}^o{}_{products} - \Delta H_f{}^o{}_{reactants}$$

COFFEE-CUP CALORIMETER



BOND ENTHALPIES

- BREAKING BONDS/FORCES **ALWAYS** REQUIRE ENERGY (Endothermic) (+)
- BONDS/FORCES FORMED **ALWAYS** RELEASE ENERGY (exothermic) (-)
- When determining what the overall process is assign the positive (endo) and negative (exo) values accordingly, the sum of the bond enthalpies
    - Overall process is **endothermic** if the sum of bonds/forces broken > sum of the bonds/forces formed
    - Overall process is **exothermic** if the sum of the bond/forces broken < sum of the bond/forces formed

DON'T FORGET

- Exothermic reactions: (–) ΔH; feels hot; heat is a product; temperature goes up…(endothermic is the opposite.)
- Hess's Law: Doubling a reaction? ΔH will double. Reversing a reaction? The sign for ΔH changes. Adding reactions? Add the ΔH's.

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Unit 7: EQUILIBRIUM

7.1 Introduction to equilibrium **7.2** Direction of reversible reactions **7.3** Reaction Quotient and equilibrium constant **7.4** Calculating the equilibrium constant **7.5** Magnitude of the Equilibrium constant **7.6** Properties of the equilibrium constant **7.7** Calculating Equilibrium concentrations **8.8** Representations of Equilibrium **7.9** Introduction to le chatlier's principle **7.10** Reaction Quotient and le chateler's principle **7.11** Introduction to solubility equilibria **7.12** Common-ion Effect **7.13** pH and Solubility **7.14** Free Energy of dissolution

ICE TABLES

- When figuring out concentrations at equilibrium, ICE tables are most useful.
- Two types of equilibrium problems
  - You are given k value
    - Do not forget to write what "x" is equal to
  - You are asked to find k value
    - Given methods to help you find out entire ICE table: percent ionization, pH, total pressure at equilibrium, given an equilibrium value; given in a graphical representation

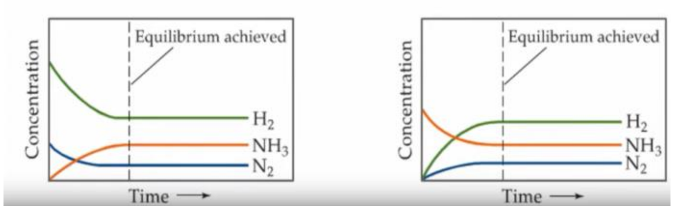
EQUILIBRIUM EXPRESSION

$$aA + bB \rightleftharpoons cC + dD$$

$$\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} = K$$

- $K = K_c, K_{sp}, K_p, K_a, K_b$
- Unlike rate constant, k, equilibrium constant is **unitless**

GRAPHICAL REPRESENTATION



REACTION QUOTIENT, Q

- You cannot assume you are at equilibrium! If you are given amount for species, determine Q to predict how reaction will proceed.
- Q expression is set up the same as equilibrium expression
  - Q> K; too many products; equilibrium will shift backwards.
  - Q<K; too many reactants; equilibrium will shift forwards
  - Q= K equilibrium has been established; no changes

LE CHATELIER

- Changes to concentration and pressure
  - These are really just Q v.s. K problems…see "Reaction Quotient" box
- Changes to temperature causes K to change
  - If temperature is increased, the endothermic direction is favored
  - If temperature is decreased, the exothermic direction is favored

SOLUBILITY EQUILIBRIA, K_{sp}

$$AB_{(s)} \rightleftharpoons aA^+_{(aq)} + bB^-_{(aq)}$$

$$K_{sp} = [A^+]^a\,[B^-]^b$$

- Insoluble salts still dissolve to some degree so have a measurable Ksp value

Ion ratio	Ksp espression
1:1	$Ksp = x^2$
1:2	$Ksp = 4x^3$
1:3	$Ksp = 27x^4$
2:3	$Ksp = 108\,x^5$

- when in doubt, just set up an ICE table
- X= molar solubility, the higher the molar solubility, the more soluble the salt.

DON'T FORGET

- Magnitude of k
  - K>>1, mostly products are present at equilibrium
  - K<<1, mostly reactants are present at equilibrium
  - K= 1 same amount of reactants and products present at equilibrium.
- Use [ ] for concentration and ( ) for pressure
- Manipulating K: Reversing a reaction? $1/K_{eq}$ Doubling a reaction? $(K_{eq})^2$ Adding reactions? Multiply the K's together
- Catalysts and inert gases DO NOT shift an equilibrium.
- Changes in pressure (caused by changing the volume of a container) can shift an equilibrium ONLY IF the # of gas particles are different on each side

PREDICTING A PRECIPITATE

- Q>Ksp; a precipitate will form
- Q<Ksp; no precipitate will form; ions stay in solution
- Q=Ksp; system at equilibrium

COMMON ION EFFECT

- A solid is less soluble in a solution that contains a common ion.
  - Just set up an ICE table, instead of starting with an initial concentration of 0 for both ions, you will have an initial concentration of the common ion (because it was already there in solution). Solve for x as you normally would.

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Unit 8: ACIDS AND BASES

8.1 Introduction to acids and bases **8.2** pH and pOH of strong acids and bases **8.3** weak acid and base equilibria **8.4** Acid-base reactions and buffers **8.5** acid-base titrations **8.6** molecular structure of acids and bases **8.7** pH and pka **8.8** Properties of buffers **8.9** Henderson-hasselbalch equation **8.10** buffer capacity

STRONG ACIDS AND BASES

- Completely ionize in solution
    - **Strong acids:** HNO_3, HCl, HBr, HI, H_2SO_4, $HClO_4$
    - **Strong bases:** alkali metal hydroxides and heavier alkaline-earth metal hydroxides.
- [H+] and [OH-] is going to equal the concentration of the acid and base, respectfully. Keep in mind the ratio of H+/OH- in the formula

WEAK ACIDS AND BASES

- Only partially ionize, so exist in equilibrium (Ka, Kb)
- Set up an ice table. If finding [H+] or [OH-], make sure to identify what x is when solving ICE table
- The smaller the Ka/Kb value is, the weaker the species (percent ionization is smaller)
    - % dissociation =

$$\frac{[H+]or\ [OH-]}{initial\ concentration\ of\ species}$$

BUFFERS

- Contains a weak acid/weak base and it's conjugate.
- If Buffer solution is HA/A-
    - With addition of a strong acid
        - $H^+ + A^- \rightarrow HA$
    - With addition of a strong base
        - $OH^- + HA \rightarrow H_2O + A^-$
- You can ONLY use Henderson-Hasselbalch Equation for a buffer solution

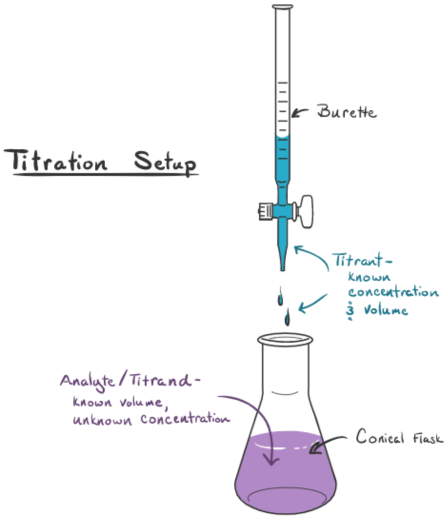
$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

RELATIVE STRENGTH OF ACIDS

- Length of bond length; longer bond length can lead to substance being more acidic (Think HF v.s HI)
- More oxygens/ more electronegative atoms on an anion makes it more acidic since the proton is "more ionizable".

TITRATION

- **Equivalence point:** When moles of analyte= moles titrant
    - Can use $M_1V_1 = M_2V_2$ **ONLY** when ratio is 1:1
    - Otherwise use stoichiometry
- **End point:** When the solution color changes. This is not necessarily the same as equivalence point, but the goal is to get these points close to each other.
    - pKa of indicator should be equal to pH at equivalence point



DON'T FORGET

- The stronger the acid, the weaker its conjugate base.
- Acid-Base reactions favor the direction of the "strong side" to the "weak side"…If K>1, then the reactants are stronger.
- Group I cations, NH_4^+, and NO_3^- salts are always soluble in water. These are usually the spectator ions in a chemical reaction.
- $pH = -\log[H^+]$ $[H^+] = 10^{-pH}$
- When you take the -log [OH-], this gives you pOH. Subtract from 14 to get pH

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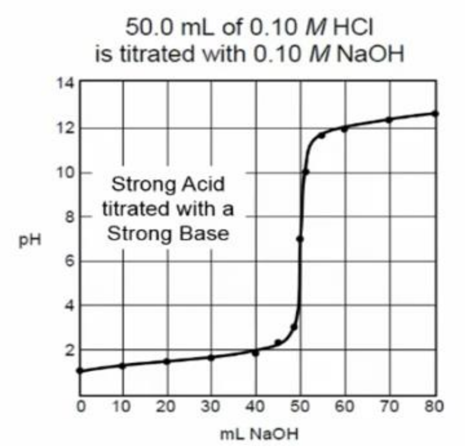
ACID BASE TITRATION

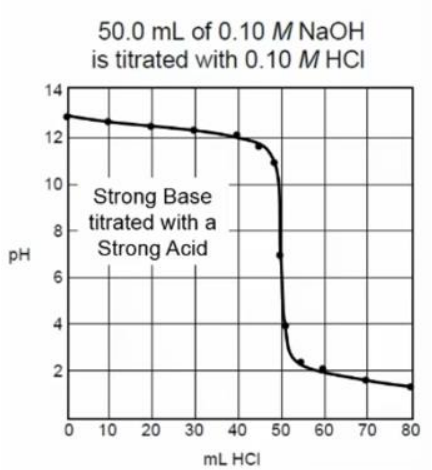
STRONG ACID WITH STRONG BASE TITRATION

- Equivalence point pH=7
- Strong acid in excess: Find moles of H+ in excess over total volume
- Strong base in excess: Find moles OH- in excess over total volume

$$SA(aq) + SB(aq) \rightarrow \text{neutral salt } (aq) + H_2O(l)$$

Net ionic: $H^+ + OH^- \rightarrow H_2O$

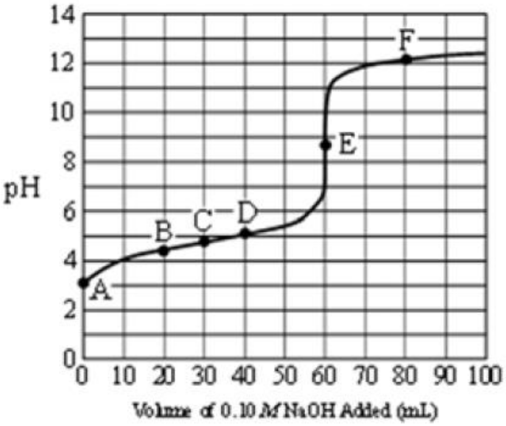




WEAK ACID WITH STRONG BASE TITRATION

$$HA + OH \rightleftharpoons A^- + H_2O$$

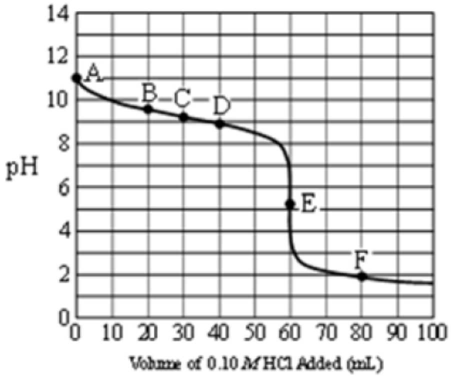
- Weak acid is excess then a buffer solution (HA/A-) is formed, use H-H equation
- Point C is very important. It is the half-equivalence point and it is where [HA]=[A-] so pH = pKa
- Equivalence point is going to have a pH higher than 7 because the salt present at this point is slightly basic.
- If strong base is in excess, find pH by excess [OH^-]



WEAK BASE WITH STRONG ACID TITRATION

$$B + H_3O^+ \rightleftharpoons HB^+ + H_2O$$

- Weak base in excess the a buffer solution (B/HB^+) is formed, used HH equation
- Point C is half equivalence point, pH=pKa
- Equivalence point is going to have a pH slightly lower than 7 because the salt present at this point is slightly acidic.
- If strong acid is excess, find pH by the [H_3O^+]



Unit 9: APPLICATIONS OF THERMODYNAMICS

9.1 Introduction of Entropy **9.2** Absolute entropy and entropy change **9.3** Gibbs free energy and thermodynamic favorability **9.4** thermodynamic and kinetic control **9.5** Free energy and equilibrium **9.6** couple reactions **9.7** Galvanic (voltaic) and electrolytic cell **9.8** cell potential and free energy **9.9** cell potential under nonstandard conditions **9.10** electrolysis and faraday's law

ENTROPY, S

- Measures the degree of disorder or dispersal of energy. When matter is dispersed, ΔS is positive.
- Entropy increases when:
    - Increase in # of moles of gas
    - Solid to liquid to gas
    - Solid to aqueous
    - Decrease in pressure (gas) or increase in volume
    - Increase in temperature

GIBBS FREE ENERGY

- $\Delta^oG < 0$ (negative): Process is thermodynamically favored
- $\Delta^oG > 0$ (positive): Process is thermodynamically **un**favored
- $\Delta^oG = 0$, the system is at equilibrium

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -RT\ln K \\ &= -nFE^\circ\end{aligned}$$

FREE ENERGY AND EQUILIBRIUM

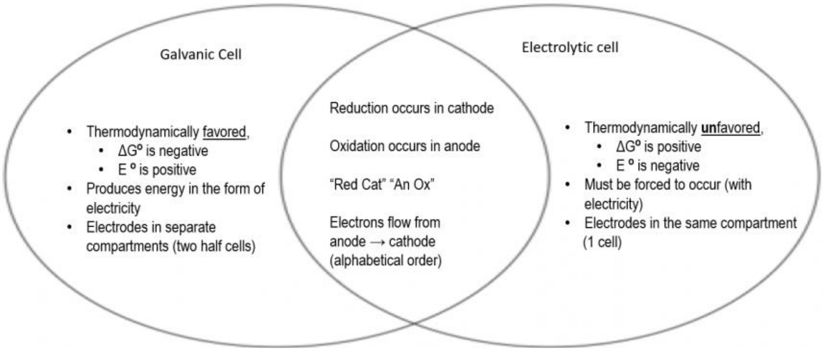
$\Delta G^o = -RT \ln K$

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

At non standard conditions:

$\Delta G = \Delta G^o + RT \ln Q$, understand this qualitatively

ELECTROCHEMICAL CELLS



Galvanic Cell:

- Thermodynamically favored,
    - ΔG^o is negative
    - E^o is positive
- Produces energy in the form of electricity
- Electrodes in separate compartments (two half cells)

Reduction occurs in cathode

Oxidation occurs in anode

"Red Cat" "An Ox"

Electrons flow from anode → cathode (alphabetical order)

Electrolytic cell:

- Thermodynamically **un**favored,
    - ΔG^o is positive
    - E^o is negative
- Must be forced to occur (with electricity)
- Electrodes in the same compartment (1 cell)

COMPARING ENTHALPY AND ENTROPY TO DETERMINE GIBBS

ΔH^o	ΔS^o	ΔG^o is negative (favorability) at:
Negative	Positive	All temperatures
Positive	Negative	No temperatures
Negative	Negative	Low temperatures
Positive	Positive	High temperatures

STANDARD REDUCTION POTENTIALS (SRP):

- Cell potentials, E^o are embedded in problems.
    - Flip the SRP that is at the anode. This would make it an oxidation equation
        - For galvanic cells, this will always be the more negative SRP
        - For electrolytic cells, the anode or cathode will often be identified in some way.

NONSTANDARD CONDITIONS, NERST EQUATION

$$E_{cell} = E^o - \frac{RT}{nF}\ln Q$$

Value of Q	Sign of ln Q	Initial Voltage
Q = 1	0	Stays the same
Q < 1	Negative	increases
Q>1	Positive	decreases

A change in the concentration of the solution results in the change of initial voltage.

Change in mass of electrode would have no effect on voltage.

DON'T FORGET

- ΔH and ΔS are usually NOT given in the same units!! When using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, make sure they match units.
- When using $\Delta G^\circ = -RT \ln K$, the value for R is 8.314 J/mol K so the answer for ΔG will be in the units of Joules.
- "kinetic control." High activation energy is a common reason for a process to be under kinetic control.
- LEO says GER … Oxidation always occurs at the anode in both a battery and an electrolytic cell.
- Salt bridge: Cations flow to the cathode, and the anions flow to the anode.
- While a battery is discharged, the cathode gains mass and the anode loses mass.
- If you reverse a reaction, the sign of E°_{cell} changes, but if you double a reaction, E°_{cell} DOES NOT change!!
- When adding the two half reactions together, the electrons MUST cancel out.
- Electroplating/Electrolysis Calculation: grams = (Molar Mass of the metal)(amps)(seconds)/(n)(F) or g=(MM)(I)(t)/nF

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