CHM 152 Lab Final Study Guide

Review Lab:
- Concentrations of ions from salts: If a 0.10 M soluble salt is placed in water, the concentration of each ion depends on the ratio of ions in the salt. For example, a salt with the formula MX_2 dissociates in a 1:2 ratio: $MX_2 \rightarrow M^{2+}(aq) + 2X^-(aq)$. The cation will have the same concentration as the salt (1:1 ratio), but the anion's concentration will be double the salt concentration (2:1 ratio).
- Dilution: $M_1V_1 = M_2V_2$. Use this to calculate the diluted concentration of a substance after it is mixed with other solutions or diluted with water. Remember: V_2 = total volume of the entire solution!
- Solution Stoichiometry: If we know the concentration and volume for a solution, we can find moles: $M*V$ = moles of solute in known solution. Then the mol:mol ratio from the balanced equation can be used to find the moles of the unknown solution. Finally, the molarity formula, $M = \frac{moles\ of\ solute}{L\ of\ solution}$, is used to solve for either the concentration or volume for the unknown solution.

Kinetics:
- The main net ionic reaction is: $2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$ (reaction 1)
- The generic rate law is written as Rate = k $[I^-]^x$ $[S_2O_8^{2-}]^y$
- As soon as I_2 is produced in the main reaction, it immediately reacts with the thiosulfate ion in the clock reaction: $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$ (reaction 2). Once all the thiosulfate is consumed, the reaction mix turns blue as the I_2 that continues to accumulate in reaction 1 now reacts with starch. Since the same amount of thiosulfate is added to all runs, it reacts with a constant amount of I_2; thus the concentration of I_2 is constant for all runs. $[I_2] = 1/2\ [S_2O_3^{2-}]$
- The rate of the reaction can then be determined using Rate = $\Delta [I_2] / \Delta t = \Delta [S_2O_3^{2-}]/ 2\ \Delta t$
- $M_1V_1 = M_2V_2$ is used to determine the final concentrations for I^- and $S_2O_8^{2-}$ in the reaction mixtures.
- The values of x and y are determined from the initial rates method using a table of experimental data (Rate of Reaction, $[I^-]$ and $[S_2O_8^{2-}]$ for different runs)
- The rate constant, k, is determined from the experimental rate law: Rate = k $[I^-]^x$ $[S_2O_8^{2-}]^y$ where the known values for x, y, Rate, $[I^-]$ and $[S_2O_8^{2-}]$ are plugged in for each run.
- The average k for the 5 room temperature trials is calculated.
- The final experimental rate law is reported with the constants plugged in (x, y and the average k).
- The activation energy, E_a, is found from an Arrhenius plot of ln k versus 1/T, where the slope of the plot = -Ea/R.   The effect of temperature change on the reaction rate is examined.
- The effect of a catalyst on the reaction rate is examined.
- The effect of concentration changes (for the reactants I^- and $S_2O_8^{2-}$) on the reaction rate is also examined.

Le Chatelier's Principle:
- Equilibrium mixes contain a mixture of both reactants and products. If K is small there are more reactants present, and if K is large then more products are present.
- Addition of a reactant will shift the equilibrium position toward products.
- Addition of a product will shift the equilibrium position toward reactants.
- Removal of a reactant (by addition of a substance not in the original equation that causes a side reaction) will shift the equilibrium position toward reactants to replace its concentration.
- Removal of a product (by addition of a substance not in the original equation that causes a side reaction) will shift the equilibrium position toward products to replace its concentration.
- Adding /removing heat and interpreting directions of shift can help determine if a reaction is endothermic or exothermic.
  - Endothermic: heat acts as a reactant   Heat + Reactants $\leftrightarrows$ Products

- Adding heat will shift the equilibrium toward products.
- Removing heat will shift the equilibrium toward reactants.
  o Exothermic: heat acts as a product: Reactants ⇆ Products + Heat
- Adding heat will shift the equilibrium toward reactants.
- Removing heat will shift the equilibrium toward products.

Introduction to Strong and Weak Acids:

- pH values of acids are determined by the amount of H_3O^+ produced when they dissociate in water.
- pH = -log [H_3O^+] can be rearranged to [H_3O^+] = 10^{-pH}
- The % of dissociation/ionization is calculated from: % Ionization = $\frac{[H_3O^+]}{[HA]_{initial}}$ x 100 %
- Strong acids dissociate to a much larger extent than weak acids. Therefore, two acids with the same concentration (one strong and one weak) will have different pH values. The stronger acid will produce more hydronium in solution and have a lower pH.
- Diluting a weak acid will increase its percent ionization (Le Chatelier's principle). Diluting the acid does not change whether it's a strong or weak acid.
- A weak acid can be more acidic (have a lower pH) than a strong acid if the concentration of the weak acid is <u>much</u> larger thus producing more hydronium ions in solution.
- 2 monoprotic acid solutions with approximately the same concentration (and same volume) will require the same volume of strong base to reach the equivalence point. Its the moles of acid present (and number of protons) that determines the volume of base needed, not the strength of the acid!
- Use the balanced neutralization reaction and stoichiometry to solve for the concentration or volume of acid or base in an acid-base titration problem. (See solution stoichiometry calcs in the review lab.)

Weak Acids, Weak Bases, and Salts:

- Salts are made up of cations and anions, and come from combining acids and bases together. The cation comes from a base, the anion comes from an acid. The relative strength of the acid and base will determine if the salt is acidic, basic, or neutral.
  o Acidic salts: weak base + strong acid; e.g. NH_4Cl: NH_4^+ is the conjugate acid of the weak base, NH_3. NH_4^+ is an acidic cation so it will hydrolyze to produce hydronium ions = a WA hydrolysis reaction. Cl^- is neutral because it comes from a strong acid and won't react with water.
  o Basic salts: strong base + weak acid; ex: KF: K^+ is neutral because it comes from a strong base and won't react with water. F^- is the conjugate base of the weak acid, HF. F^- is a basic anion so it will hydrolyze to produce hydroxide ions = a WB hydrolysis reaction.
  o Neutral salts: strong base + strong acid (ex: NaCl: both ions are neutral because they come from strong base and strong acid; neither one will react with water.) Neutral cations (group IA and IIA) and neutral anions (Cl^-, Br^-, I^-, NO_3^- and ClO_4^-) will NOT hydrolyze.
- Two chemical equations can be written for a salt solution: dissociation of the salt into its ions and the hydrolysis equation for the ion that is a conjugate of a weak acid or base.
  o Dissociation: salt dissociates into ions. Ex: NaF → Na^+(aq) + F^-(aq).
  o Hydrolysis: the ion in the salt from the weak acid or weak base will set up equilibrium in water. Ex: F^-(aq) + H_2O(l) ⇆ HF(aq) + OH^-(aq)
- K_a values can be calculated for weak acids, K_a = $\frac{[H_3O^+][A^-]}{[HA]}$
- K_b values can be calculated for weak bases, K_b = $\frac{[BH^+][OH^-]}{[B]}$
- After measuring pH values of acid, base, or salt solutions, the concentration of hydronium ([H_3O^+] = 10^{-pH}) or hydroxide ([OH^-] =10^{-pOH}) can be calculated. This calculated value represents the equilibrium [H_3O^+] (or [OH^-]); this is the equilibrium value (x) in an ICE table. The equilibrium constant (K_a or K_b) is then calculated by plugging in the equilibrium concentrations for all substances.

- Equilibrium constants can be calculated for ions depending on whether they produce hydronium (K_a) after hydrolysis or hydroxide (K_b) after hydrolysis.
- As acid strength increases, pH decreases, K_a increases and % ionization increases.
- As base strength increases, pH increases, K_b increases and % ionization increases.

Acid-Base Titrations:
- **Techniques for a titration include**
  - Conditioning and filling a pipet with an acid
  - Conditioning and filling a buret with a base
    - Be sure to fill the tip and record the volume to 2 decimal places.
    - Record the initial and final volumes for the titration
    - Note: we condition our glassware to ensure that the concentration of the solution being dispensed is accurate (i.e. not diluted with water)!

- Titration curves were obtained for a strong acid and a weak acid. Different regions of the curves were compared and the pK_a value was obtained for a weak acid.

- **When a strong acid is titrated by a strong base:**
  - The pH is initially low since the acid completely ionizes to form hydronium ions
  - Before the equivalence point the moles of acid are larger than the moles of base thus the pH depends on the concentration of the excess acid present in solution.
  - The pH at the equivalence pt is 7 because the acid and base have completely reacted and we are left with water and a neutral salt in solution.
  - After the equivalence point, the excess sodium hydroxide in solution causes the pH to be high. pH depends on the concentration of excess NaOH present in solution

- **When a weak acid is titrated by a strong base:**
  - The initial pH is a little higher than for the strong acid. The weak acid forms less hydronium ions since it doesn't ionize completely. (WA calc - use K_a and the [HA] to find pH)
  - Half way to the equivalence point, we have a buffer solution containing equal amounts of HA and A⁻ so the pH = pKa. (Buffer region – use change table to find moles of acid remaining and the moles of conj base formed then plug into HH to find the pH)
  - Estimating the pH at the half-eq pt on the WA plot gives us the pK_a, thus $K_a = 10^{-pKa}$
  - The pH at the equivalence pt is > 7 because after the acid and base are neutralized we are left with water and a basic salt in solution. (WB calc – use K_b and the [A⁻] to find pOH then convert it to pH)
  - The curve for the weak acid is the same as the strong acid after the equivalence point since excess strong base is present.

- Be able to write a balanced reaction for an acid-base neutralization reaction and use provided concentrations/volumes to obtain the equivalence point volume or M for one of the solutions.
- Be able to calculate the pH at any point for a SA-SB titration and a WA-SB titration.

Qualitative Analysis:
- Qualitative analysis is the process of finding out what ions or compounds are contained in a sample based on their chemical reactivity and physical properties such as solubility.
- In this lab, qualitative analysis methods are used to separate carbonate, sulfate, chloride, and iodide anions.
- The flow chart is a useful tool that can be used to visualize the stepwise addition of the reagents and the separation and identification of the ions/ precipitates as the scheme proceeds.

- Centrifuging a sample greatly accelerates the settling of a precipitate suspended in solution allowing the precipitate to be separated from the supernatant solution above it.
- Litmus paper can be used to test for acidity (blue paper turns red) and basicity (red paper turns blue).
- Carbon dioxide gas is produced when an acid, such as nitric acid, is added to a solution containing carbonate. Thus, acidification allows carbonate ions to be separated from the other anions.
- Barium ions (from barium nitrate) react with sulfate ions to form barium sulfate. The $BaSO_4$ precipitate should be separated from the supernatant solution above it (containing the halide ions).
- The chloride and iodide ions (in the supernatant solution) react with $AgNO_3$ to form AgCl (white) and AgI (yellow) precipitates.
- After 6 M NH_3 is added to the silver halide precipitates, the more soluble AgCl dissolves and forms a soluble complex ion, $Ag(NH_3)_2^+$ as well as chloride ions. The solid precipitate (AgI) is then separated from the supernatant solution (containing chloride and silver diamine complex ions).
- The basification step illustrated how the formation of a complex ion can cause an insoluble salt (AgCl) to dissolve.
- When nitric acid is added to the supernatant solution containing chloride and $Ag(NH_3)_2^+$ ions, the ammonia molecules are neutralized by the acid, thus freeing the silver ions. The Ag^+ and Cl^- ions now combine to reform the AgCl precipitate.
- No reaction occurs when 15 M NH_3 is added to AgI. The solid ppt (AgI) doesn't dissolve in NH_3.

Thermodynamics:
- The law of conservation of energy states that heat/energy is always conserved.
  - $q_{sys} = -q_{surr}$
  - $q_{sys} = -(mass)*(specific\ heat\ capacity)*(\Delta T)$
  - $\Delta H_{rxn} = q_{sys} / moles$
- ΔH_{rxn} - The change in enthalpy describes the heat of reaction. This is the heat gained or lost by the system during a reaction (@ constant P).
  - Exothermic (ΔH -): heat is released by the system.
  - Endothermic (ΔH +): heat is gained by the system.
  - Breaking bonds absorbs heat/energy while making bonds releases heat/energy.
  - If T decreases when a salt dissolves in water, then the salt is absorbing heat from the water causing the water T to decrease = endothermic dissolution of a salt ($-\Delta T$ but $+\Delta H$ due to negative sign in equation from heat transfer between the solution and the salt)
  - If T increases when a salt dissolves in water then the salt is releasing heat to the water causing the T to rise = exothermic dissolution of a salt ($+\Delta T$ but $-\Delta H$)
- Entropy describes the amount of randomness in a system. The universe tends to moves towards disorder.
  $\Delta S_{Total} = \Delta S_{System} + \Delta S_{Surroundings}$
  - $\Delta S_{Total} > 0$ (positive) moves towards disorder = spontaneous
  - $\Delta S_{Total} < 0$ (negative) moves towards order = nonspontaneous
- Gibbs free energy predicts whether a reaction is spontaneous at a specific temperature.
  $\Delta G = \Delta H - T\Delta S$
  - Spontaneous when $\Delta G < 0$ (negative)
  - Nonspontaneous when $\Delta G > 0$ (positive)
  - At equilibrium when $\Delta G = 0$
- Not all reactions are spontaneous at all temperatures. The combination of ΔH, ΔS, and T (in Kelvin) in the equation $\Delta G = \Delta H - T\Delta S$ and their magnitude determines the value of ΔG and therefore predicts spontaneity.

Electrochemistry:

- Oxidation is the process of losing electrons/losing hydrogens/gaining oxygens
- Reduction is the process of gaining electrons/gaining hydrogens/losing oxygens
- An oxidizing agent oxidizes another species while it is reduced.
- A reducing agent reduces another species while it is oxidized.
- Reactions between solid metals and metal solutions can be used to place metals in order of activity. The activity series is based on how easily a metal will be oxidized to a cation.
- The more active metal will be oxidized = anode.
- Voltages of Galvanic Cells can be measured by setting up two compartments and connecting a wire to the two metals. Key components of the Galvanic Cell include:
  - Each metal is placed in a 1.0 M solution of the metal nitrate.
  - A salt bridge is made by soaking a piece of string in a soluble ionic compound (i.e., $NaNO_3$).
  - Leads are connected to each metal piece. Electrons flow from the anode to the cathode in the wire connecting the electrodes. A voltmeter is connected to the wire and leads to read voltage.
  - If the battery is connected properly the cell potential is positive.
- Reduction (or oxidation) potentials of metals can be determined after the overall cell potential (E^o_{cell}) is measured and a standard reduction potential is known. For example, in the Electrochemistry lab, the zinc reduction half-reaction was used as the standard. If zinc was oxidized, the sign of its reduction potential was changed to represent the oxidation potential and half-reaction is also reversed.
- $E^o_{cell} = E^o_{ox} + E^o_{red}$. This equation can be used to find the unknown metal's half-reaction potential.
- From the E^o_{cell} value, ΔG^o can be determined: $\Delta G^o = -nFE^o_{cell}$.
- The equilibrium constant can then be calculated using $E^o_{cell} = (RT/nF) \ln K$
  - In both equations, F is Faraday's constant: 96,500 J/V· mol e$^-$
  - n = moles electrons (number of electrons transferred when the half-reactions are balanced)
  - R = 8.314 J/mol·K
  - T = temperature in Kelvins
- Solid metals can not be reduced, they can only be oxidized. Metals are good reducing agents.
- Metal cations in solution are reduced. They make good oxidizing agents.
- A spontaneous reaction has a positive cell potential (E^o_{cell}). It will have a negative value of ΔG^o as well as a large equilibrium constant, K > 1.
- As the cell potential increases, ΔG^o decreases and K increases.

Nuclear:

- Nuclear reactions produce entirely different substances as products, unlike chemical reactions in which particles are conserved.
  - Notations for nuclear particles are written with mass numbers as a superscript to the left of the element symbol. Atomic numbers (number of protons) may be written as a subscript to the left of the element symbol. (Atomic numbers are often omitted since the number of protons for an element is always the same and can be found on the periodic table.)

$$\begin{matrix} \text{mass number} = A \\ \text{atomic number} = Z \end{matrix} E = \text{Element symbol}$$

  - Isotopes are substances that differ in the number of neutrons. Ex: ^{14}C vs ^{12}C.
- Nuclear particles include:
  - Alpha: ^4_2He ($^4_2\alpha$)
  - Beta: $^0_{-1}e$ ($^0_{-1}\beta$)
  - Gamma: $^0_0\gamma$
- 3 of the main types of nuclear decay are:

alpha (α) emission (or decay): a helium nucleus, $_2^4\alpha$ or $_2^4$He , is emitted. For alpha decay, the mass number of the daughter decreases by 4 and the atomic number decreases by 2

beta (β) emission (or decay): an electron, $_{-1}^0\beta$ or $_{-1}^0$e, is emitted when a neutron inside an atom decays to produce a proton and an electron. For beta decay, the mass is the same but the atomic number of the daughter increases by 1.

gamma (γ) emission (or decay): high energy photons or gamma rays, $_0^0\gamma$, are emitted. This generally accompanies the emission of other particles (e.g. alpha, beta, etc.)

- Nuclear equations are balanced by equalizing the mass numbers and atomic numbers of all reactants and products. A coefficient will count for both the mass number and atomic number.

    o Ex: $_{92}^{238}$U $\rightarrow$ 6 $_{-1}^0$e + 8 $_2^4\alpha$ + _____
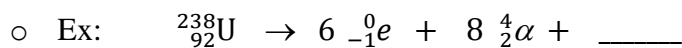
    o The unknown product can be predicted by balancing the mass and atomic numbers. It has an atomic number of 82 and a mass number of 206. Thus, the particle is $_{82}^{206}Pb$.

- Radioactive decay reactions all follow first order kinetics:

$$t_{1/2} = \frac{0.693}{k} \qquad \ln\left(\frac{A_t}{A_0}\right) = -kt$$

where A_t represents the amount of substance left after time t, k is the rate constant, t is the time that has passed, and A_o is the initial mass or amount of substance.

- If the half-life ($t_{1/2}$) of a particle is known, the rate constant (k) can be calculated. Since radioactive decay is always first order, the units of k will always be time^{-1} (ex: s^{-1}, min^{-1}, yr^{-1}, etc.).

- The first order integrated rate law (shown above on the right) can be used to calculate the amount (or percent) of the substance remaining or the amount of time that the sample has decayed.

- Another useful equation for first order decay is $A_t = (1/2)^n A_0$ where n = # of half lives (n = t / $t_{1/2}$). Note: The amount of sample gets cut in half each time a half-live is passed.