Chapter 14:

This chapter really focuses on giving you a foundation in all things equilibrium so that you are ready for the coming application chapters. Here are the topics and some calculations that you must be able to do for the exam:

- ### The Equilibrium Constant:

You must be able to write an equilibrium constant (K) expression for ANY reaction you are given.

- Unlike kinetics, you WILL use stoichiometric coefficients, so make sure your equations are balanced.
- Do not include solid or liquid phase species.
- The concentrations you use must all be MOLARITIES, and must all be equilibrium concentrations.
- The constant itself will be unit-less.

Just for kicks, I am going to show you a new generic equation. This time with phases:

$$4A(s) + 2B(g) + C(aq) \leftrightarrow 3D(l) + 6E(aq)$$

$$K = \frac{[E]^6}{[B]^2[C]^1}$$

At this point, make sure you can use equilibrium concentrations to calculate the K. Make sure that you can write a K-expression for ANY reaction.

You should also be able to use a given equilibrium constant value and the reaction stoichiometry to calculate equilibrium concentrations given initial concentrations and one equilibrium concentration. I am not going to show you one here, but you saw the math in class.

- **The Equilibrium Constant using Pressures:**

When all of the reactants and products are in the gas phase, you may also see the equilibrium constant written as a K_P. This is done in the same way as a regular equilibrium constant expression, but you must use pressures in atmospheres instead of molarities. There is a quick calculation that gets you from a Kc to a Kp. The trick is making sure that you get the Δn correct. It is calculated by taking the number of moles of gas on the product side of the equation and subtracting the number of moles of gas on the reactant side of the equation. Note that it is only the gas phase molecules that count for this, and it is a total for each side.

$$K_P = K_c(RT)^{\Delta n}$$

Note that if the number of moles of gas is the same on the reactant and product sides of the equation, K_P is equal to K_C. If there are more moles of gas on the product side, Δn is positive and K_p is bigger than K_c. If there are fewer moles of gas on the product side, your K_P will be smaller than the K_c. *This will literally be the subject of a multiple choice question.*

At this point, make sure you can go between K_P and K_c correctly, and that you can calculate a K_P correctly.

- **Extent of Reaction:**

The value of K tells us about how far the reaction will go, meaning when you put the reactants together, do you expect to see mostly products, hardly any products, or somewhere in the middle.

- **If K is very large (Greater than 10^3) expect to see mainly products. We call it: "Very Product-Favored" *This doesn't mean that the reaction is fast!* It does mean that the reaction proceeds to near completion and you won't have many reactants left.**
- **If K is very small (Less than 0.001), expect to see very few products and mostly unreacted reactants at equilibrium. We call this "reactant favored". Again, equilibrium tells you NOTHING about the speed of the reaction!**
- **If K is in between these extremes, you will see reasonable amounts of both reactants and products at equilibrium.**

In order to know where you are in a reaction (the extent of reaction) you need to calculate a Q-value or a "Reaction Quotient". This is done the same way as you calculate an equilibrium constant, but you do not have to use equilibrium concentrations. After you calculate Q, you compare it to K to tell you whether the reaction is going towards products, towards reactants, or if the reaction is already at equilibrium.

- **If Q is larger than K: You have too many products to be at equilibrium, so the reaction will progress back toward the reactant side. You will see the product concentrations decreasing and the reactant concentrations increasing.**
- **If Q is smaller than K: You have too many reactants to be at equilibrium. The reaction is going to move toward the products meaning the product concentrations are going up, and the reactant concentrations are decreasing.**
- **If Q is equal to K, you are already at equilibrium and you will not see the reactant or product concentrations change for all eternity unless you mess it up by stressing it out (see Le Chat section!)**

At this point, make sure you can calculate Q and compare it to K. You should be able to predict the direction of a reaction and what is happening to each reactant and product.

- **Le Chatelier's Principle:**

If stress is applied to a reaction mixture that is at equilibrium, the mixture will react in the direction that relieves the added stress. We will say that the reaction will "shift to reactants" or "shift to products"

Stresses are:

1. Adding or removing a reactant or product.
    - Make sure that the reactant or product that you are adding is not a solid or liquid. These will have no effect on the reaction. (not in K or Q, so not able to stress the equilibrium)
    - The reaction will shift to CONSUME an added reactant or product.
    - The reaction will shift to REPLENISH a removed reactant or product.
2. Changing the pressure or volume of a reaction that contains gas phase species.
    - Adding an inert gas does not stress the system!
    - When the reaction container is compressed (increased P) the reaction shifts to the side with fewer moles of gas.
    - When the reaction container is stretched (decreased P) the reaction shifts to the side with more moles of gas.
3. Changing the temperature.
    - This causes a change in K, but the quick way to get to the correct shift is to consider heat a reactant if the reaction is endothermic, and heat a product if the reaction is exothermic.

At this point, make sure you can do the listed Le Chat problems from the book. Be able to tell me if the reaction will shift and which direction for any stress listed above. Use the shift to say "the concentration of ______ has gone up/down because of the stress." No numbers here.

- **Using a K value and initial concentrations to calculate all equilibrium concentrations:**

This is the algebra lesson! You will need to be able to construct an ICE chart, write a K-expression, do some stoichiometry, and solve for x.

- You do not keep track of solids and liquids here, they aren't in the K-expression.

Here is a list of steps to help you work the problems:

1. Write a balanced equation, and write your K-expression.
2. Below the balanced equation, construct your ICE chart and fill in all of the initial concentration values.
3. Determine which way the shift will occur (Q). Note that it will always shift towards a 0.
4. Fill in the C (change) line using x's and stoichiometry.
5. Sum the I and C lines to give you E (equilibrium) values for all of the species.
6. Plug in the equilibrium concentrations to the K-expression and solve for x.
   a) Use the quadratic formula here if needed (I will provide it).
   b) If you can approximate x, do that!
   c) Close your eyes and imagine you are in a math class. One equation, one unknown. You've got this!
7. Now use the x you found to calculate the equilibrium concentrations.

At this point, you must be able to write the K-expression, correctly construct an ICE table, and solve for x. You also have to know how to approximate x, and when you are allowed to do that.