Chapter 14 - Things to Know

14.1   What factors can affect the rate of a reaction?

14.2   Rates of reaction: units used
        Average vs. instantaneous rate, how to calculate each using a graph of
        concentration vs. time.
        Relating the "overall" rate of the reaction to rates of change of reactants and
        products, using a balanced equation. Understand the meaning and be able to
        write the mathematical expressions. Given one rate, be able to calculate another
        rate.
        How does the rate change as time goes on? Why?

14.3   Rate law: form of rate law (Rate = $k[A]^x[B]^y$), order of reaction, rate constant,
        overall order.
        What does a rate law tell you?
        How can you determine the rate law experimentally? (know two ways)
        Is there any other way of determining a rate law?
        Method of initial rates: given a chart of data from different experiments,
        determine rate law, calculate k. What is the logic?

14.4   Concentration-time equations: zero, first, and second order. Know how to tell the
        equations apart, be able to do the algebra! (Given any 3 pieces of information,
        calculate the 4th)
        What are the units of k? (Depends on overall reaction order)
        Graphing: for each order (0, 1, or 2), what do you graph in order to get a straight
        line? How do you determine the rate constant from the graph?
        Half-life: what is it? Useful for first order reactions - why? How is it determined?
        How can you find the half-life from a concentration vs. time graph? How does it
        give you a shortcut in certain situations? Understand the meaning of $t_{1/2}$.

14.5   <u>Collision Theory</u> - what must happen for a reaction to occur?
        What is E_a? How does E_a correspond to the rate of a reaction? <u>Why</u>?
        Explain at the molecular level how changing concentrations or changing
        temperature or different activation energies affect the rate of reaction. How does
        the # molecules vs. kinetic energy diagram fit in?
        Be able to sketch the Boltzmann distribution and explain the meaning.
        <u>Transition State Theory</u> - what is a transition state? Understand potential energy
        diagrams, label/determine ΔH, E_a (forward) and E_a (reverse).
        Arrhenius equation: relates rate constants at different temperatures, and includes
        E_a.
        What is the "frequency factor" and what affects it? (The frequency factor is NOT
        the same as the frequency of collisions.)
        Know how to do calculations with the two-point form of the Arrhenius equation.
        (Solve for either E_a or k.)
        A graph of ln k vs. 1/T is linear (for <u>any</u> reaction order). How do you determine E_a
        from the graph? Be able to do this.

14.6 What is a mechanism?
What is an elementary reaction? Why can you write the rate law for an elementary reaction without any other information?
<u>Why can't you normally write the rate law from a balanced equation?</u>
Molecularity (know terms, classify reactions)
Rate-determining step (slowest)
Getting the rate law from a mechanism: two types we'll do.
1. Initial slow step (easy)
2. Initial fast, equilibrium step (can't include intermediates in the overall rate law, so you have to make a substitution)
Intermediate vs. catalyst – identify in a mechanism.
What if the mechanism doesn't match the rate law?

14.7 What does a catalyst do? How?
Explain **why** lowering the activation energy leads to a faster rate of reaction. (Use the Boltzmann distribution!)

Chapter 15 - Things to Know

15.1 What does it mean if a system is at equilibrium? What's going on? Anything?
What is "equal"? (NOT the concentrations!)

15.2, Writing K_c, K_p, K_{eq} expressions. Don't include liquids or solids in K expressions. Why?

15.3 What does K depend on?
Must use units of molarity in K_c expressions, and atmospheres in K_p expressions. What about in K_{eq} expressions?
The K's themselves don't have units, but the quantities you plug into the K expressions do have units.
$K_p = K_c(RT)^{\Delta n}$. What is Δn? Is K_p ever equal to K_c?
Know how to manipulate reactions and their K expressions:
•If you reverse a reaction, invert K   (take 1/K)
•If you multiply a reaction by a number N, raise K to the Nth power. (K^N)
•If you divide a reaction by a number N, take the Nth root of K. ($\sqrt[N]{K}$) (This is the same as raising K to the 1/N power. Example: $\sqrt[3]{K}$ is the same as $K^{\frac{1}{3}}$.)
•If you add two reactions, multiply their K's.

You can prove any of these rules to yourself by choosing an equation, manipulating it, writing a new K expression, and comparing it to the former one.

Understanding the meaning of the size of K:
K gives you an idea of the composition of the mixture at equilibrium (more reactants or more products, in general).

The size of K, by itself, does **NOT** tell you which way the reaction will go to get to equilibrium! To answer this, you would also need to know what you have to start with. (What are the initial concentrations/pressures?) See section 15.6!

15.5   Calculating values of K:
1. Given all concentrations or pressures at equilibrium, calculate K_c or K_p (easy)
2. Given initial amounts and one equilibrium amount, determine all of the other equilibrium amounts and K:
•set up a chart of initial, change, and equilibrium amounts (can be in moles, M, atm - whatever is convenient for your problem. Has to be something that is proportional to moles. Can't use grams.)
•From the one given equilibrium amount, find the value of x and then the other eq. amounts. Plug into the K expression.
Variation: given initial amounts and some other way of finding how much reacted (such as the total pressure, the percent or fraction of the original that reacted, etc.), calculate K.

15.6   Reaction Quotient Q - the expression looks just like the K_c or K_p or K_{eq} expression, but the amounts used are the actual amounts rather than the equilibrium amounts. Calculating Q and then comparing it to K allows you to predict whether the reaction will go forward or backward to reach equilibrium. (Q must become equal to K)

What is the difference between the phrases "lies to the left" and "shifts to the left"?
"lies to the left" refers to the size of K: in this case, K<1 (mostly reactants at equilibrium)
"shifts to the left" refers to Q. In this case. Q>K and the reaction will proceed in the reverse direction until equilibrium is reached.
Understand the difference between these two phrases! (same idea for "lies to the right" vs. "shifts to the right")

15.5   Calculations involving K's:

1. Given K and all but one equilibrium concentration, find the missing concentration. (easy - just rearrange)

2. Given initial amounts and K, calculate all equilibrium amounts (concentrations or pressures).
•set up a chart (in units of molarity or pressures): initial, change, equilibrium amounts. (Eq. amounts will be in terms of x.) You will have to decide which way the reaction will go to reach equilibrium. This may involve calculating Q.
•plug the expressions into the K expression, and solve for x. This often involves using the quadratic equation. Watch out for the "perfect squares" shortcut. It's also possible that the expression might be too complicated for us to solve exactly (it might have an x^3 or x^4 term). If the value of K is very small, you may be able to neglect x in comparison to numbers you are adding it to or subtracting it from. This will allow you to simplify the equation and solve for x.

For reactions with very large or very small K values, there are four possible situations.
• K is very small and reaction is going forward: set up a chart and neglect x's since x's will be very small.
• K is very small and reaction is going backward: this means that it will go backward to completion until the limiting reactant is used up, and then forward a little to reach equilibrium. Set up two charts. For the first one, assume LR goes to zero. For the second one, assume the x's are very small so you can neglect them to simplify the equation.
• K is very large and reaction is going backward: it won't go back very much. Set up a chart and neglect x's since x's will be very small.
• K is very large and reaction is going forward: this means that it will go forward to completion until the limiting reactant is used up, and then backward a little to reach equilibrium. Set up two charts. For the first one, assume LR goes to zero. For the second one, assume the x's are very small so you can neglect them to simplify the equation.

15.7   Le Châtelier's Principle - how will the equilibrium shift (will it go forward or reverse to get to a new equilibrium) if you:
•Add or remove reactant or product?
•Add or remove a solid?
•Change volume or pressure? (look at the sign of Δn_{gas})
•Raise or lower the temperature? (look at the sign of ΔH)
•Add a catalyst?
•Add an inert gas?
•Add something that reacts with one of your reactants or products?
Also be able to answer how concentrations will change as the equilibrium shifts.

Choosing optimum conditions for a reaction (maximizing yield)
High or low P? (look at the sign of Δn_{gas})
High or low T? (look at the sign of ΔH)
Remove one or more products as they are formed
Change the proportions of reactants - use an excess of the cheaper one.

Chapter 16 - Things to Know

1.   Properties of acids and bases
2.   Arrhenius definition of acids and bases
3.   Be able to write the equation for the reaction between an Arrhenius acid and base.
4.   Definitions of Brønsted acids and bases.
5.   What is an amphoteric substance? How can you recognize one?
6.   Conjugate acid-base pair (Given one, be able to give the formula and charge of the other.)

7.   Proton-transfer reactions, labeling each reactant and product as a base or an acid.

8.   Strong vs. weak acids and bases

9.   For a proton-transfer reaction, the equilibrium lies toward the side with the weaker acid and base. Why? Weak acids have a high affinity for their protons and do not want to give them up. Stronger acids more readily donate their protons.

10.   Be able to write the reaction for the autoionization of water.

11. $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$ at 25°C

Know how to calculate $[H_3O^+]$, $[OH^-]$, pH, or pOH. Is the solution acidic, basic, or neutral? (What do we assume in all of these calculations? What would happen if at a temperature different from 25°C?)

12.   Strong acids and bases ionize completely (memorize them). Weak acids and bases ionize slightly. Be able to calculate the pH of any strong acid or strong base solution.

13.   Weak acids and bases have a range of strengths, but strong acids and bases all have the same strength in water ("leveling effect" of solvent).

14.   The stronger the acid, the weaker its conjugate base. But see # 15 below. A weak acid does NOT have a strong conjugate base!

15.   If an acid is weak, its conjugate base is also weak.

If an acid is strong, its conjugate base is <u>so weak</u> that it has <u>no</u> basic properties in water. Consider it neutral.

If a base is strong, its conjugate acid is <u>so weak</u> that it has <u>no</u> acidic properties in water. Consider it neutral.

16.   Be able to write the K_a reaction and expression for any weak acid.

17.   Weak acid calculations:

1. Given [HA] and pH, calculate K_a: the pH gives the equilibrium $[H_3O^+]$ and therefore x. Set up a chart, determine all eq. concentrations, and calculate K_a. Note: no need to neglect x, since you won't have a quadratic equation to solve.

2. Given initial [HA] and K_a, find $[H_3O^+]$, $[A^-]$, and/or pH: Set up a chart. Plug into K_a expression and solve for x. Often, you may neglect x to simplify the expression (this is OK to do if [HA]/K_a >1000). If it's not OK to neglect x, use the method of successive approximations. Do not use the quadratic equation. (If you insist on using the quadratic equation, make sure to check your answer to see if it's reasonable!)

18.   Be able to calculate percent ionization.

19.   Polyprotic acids: be able to write all reactions: K_{a1}, K_{a2}, (K_{a3})

The <u>first</u> ionization determines the pH of the solution. In calculations, make simplifying assumptions. Also be able to calculate the concentration of each ion in the solution.

20.   Weak bases: be able to write the K_b reaction and expression for any weak base. Calculations: similar to the calculations for weak acids.

1. Given [B] and pH, calculate K_b: the pH gives the equilibrium $[H_3O^+]$, so you can find $[OH^-]$ and therefore x. Set up a chart, determine all eq. concentrations, and calculate K_b. Note: no need to neglect x, since you won't have a quadratic equation to solve.

2. Given initial [B] and K_b, find pH: Set up a chart. Plug into K_b expression and solve for x. Here, x = [OH$^-$], so you have an extra step in order to find pH. Neglect x or use successive approximations. (If [B]/K_b >1000, it's OK to neglect x.)

21. K_a of acid × K_b of conjugate base = K_w

22. Be able to recognize weak acids, weak bases, and neutral species. Many ions are acidic or basic.

Acids: Uncharged molecules whose formulas start with H (HCN, HF)
Organic compounds whose formulas end in COOH (CH_3COOH)
Positively charged nitrogen containing ions (NH_4^+, $CH_3NH_3^+$)
Metal cations except those in groups I and II   (Al^{3+}, Fe^{3+})

Bases: Uncharged molecules containing nitrogen (NH_3, CH_3NH_2)
Anions which are conjugates of weak acids (CN$^-$, F$^-$, PO_4^{3-})

Amphiprotic species: Anions with an ionizable hydrogen (HCO_3^-, $H_2PO_4^-$)
Compare K_a and K_b of **this ion** to see if it will be acidic or basic.

Neutral species: Group IA and IIA ions (Na$^+$, Ba^{2+}, etc.)
Anions of strong acids (Cl$^-$, NO_3^-, etc.)

To decide whether a solution of an ionic compound is acidic, basic, or neutral, look at each of the ions it contains.

23. Comparing strengths of acids based on their structure
a. binary acids in same column (larger size, stronger acid)
b. binary acids in the same period (more electronegative, stronger acid)
c. oxyacids with the same structure but a different central atom (more electronegative central atom, stronger acid)
d. oxyacids with a different number of oxygens (more O, stronger acid)
Be able to explain <u>why</u> in each case above!

24. Definitions of Lewis acids and bases. Be able to recognize a Lewis acid-base reaction and identify the acid and base.